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IL PROCESSO CICLI ALTERNATI – MBR PER IL TRATTAMENTO AVANZATO DELLE ACQUE REFLUE *(ADVANCED WASTEWATER TREATMENT BY MEMBRANE BIOREACTORS OPERATING THE ALTERNATE CYCLES PROCESS)*

S.S.D. ING-IND25/ Impianti Chimici

Coordinatore: Prof. Hugo Luis Monaco
Firma ____________

Tutor: Prof. Franco Cecchi
Firma ____________

Dottorando: Ing. Francesco Fatone
Firma ____________

To My Aunt

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Parts of this thesis have been published or submitted for publication. Below the list of the reference papers is reported:

Fatone, F., Bolzonella, D., Battistoni, P., Cecchi, F., (2005), Removal of nutrients and micropollutants treating low loaded wastewaters in a membrane bioreactor operating the automatic alternate-cycles process, *Desalination*, 183, 395-405 - Elsevier Science Ltd, Oxford, ISSN: 0011-9164

Fatone, F., Battistoni, P., Pavan, P., Cecchi, F., (2006), Application of a membrane bioreactor for the treatment of low loaded domestic wastewater for water re-use, *Water Science and Technology* 53 (9), 111-121 - IWA Publishing, London, ISSN 0273-1223

Battistoni, P., Fatone, F., Bolzonella, D., Pavan, P., (2006), Full scale application of the coupled alternate cycles-membrane bioreactor (AC-MBR) process for wastewater reclamation and reuse, *Water Practice and Technology* 1 (4) - IWA Publishing, London ISSN Online: 1751-231X

Fatone, F., Battistoni, P., Pavan, P., Cecchi, F., (2007), Operation and maintenance of full scale MBRs for municipal wastewater treatment and reuse: a detailed overview on a case study, *Industrial and Engineering Chemistry Research*, Submitted

Fatone, F., Battistoni, P., Bolzonella, D., Pavan, P., Cecchi, F., (2007), Long term experience with an automatic process control for nitrogen removal in membrane bioreactors, *Desalination*, Submitted

Battistoni, P., Cola, E., Fatone, F., Bolzonella, D., Eusebi, A.L., (2007), Micropollutants removals and operating strategies in ultrafiltration membrane systems for municipal wastewater treatment: preliminary results. *Industrial and Engineering Chemistry Research,* Submitted

Battistoni, P., Fatone, F., Cola, E., Pavan, P., (2007), A methodology to upgrade municipal wastewater treatment plant by the alternate cycles process. *Industrial and Engineering Chemistry Research*, Submitted

Furthermore, two papers under preparation are going to be submitted for publication by the end of 2007 and have been omitted from the list above.

Abstract

Today membrane bioreactors (MBRs) can no longer be considered a novel technology for wastewater treatment. However, the most appropriate practice to design and operate these systems is not consolidated. The major aim of this three-year research activity was to develop a biotechnological system which could be sustainable and ready for the widespread application for advanced municipal wastewater treatment. The basic technological idea was to couple a MBR with the intermittent aeration of the bioreactor and the process control automation. Therefore, the alternate cycles process, which operates the automatic control of the intermittent aeration in the biological reactor on the basis of the on-line signals of dissolved oxygen and redox potential, was applied to a membrane bioreactor in the so-called AC-MBR system. The experimental activity has been carried out, always treating real municipal sewage, on three different scale-levels: the big pilot membrane plant, the demonstration and the full scale MBRs. All the experimental facilities were equipped with submerged modules of hollow fibre ultrafiltration membranes (filtration area respectively of 21,6; 69,9 and 12.130 m^2). In particular, the pilot plant was used to assess (a) the impact of biomass bulk parameters on the membrane fouling and (b) the role of fouling/cake layer for metals removal. The demonstration MBR was used to investigate the nutrients and micropollutants removals and reliability of control algorithm. Finally, the full scale validation of the technology was possible by supervising the real AC-MBR system. The demonstration study was carried out over about 500 days. The plant was fed with real wastewater, where salts of nitrogen and phosphorus and external carbon source were dosed in certain runs to increase the influent loadings. Nine steady state experimental runs were carried out increasing the nitrogen loading rate (NLR), run by run, from 0,05 up to 0,25 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$, while the C/N ratio was always $\leq$ 8÷9. NLRs around 0,16÷0,17 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$ were considered the maximal treatment capacity of the AC-MBR system in terms of influent nitrogen. Under the maximal treatment capacity, the carbon and nitrogen removal were excellent: the ammonia nitrification was almost complete (nitrification efficiencies >90%), while the denitrification was the rate limiting step for the alternating system. According to the mass balances, the biological process removed 0,1 kgN per $kgCOD_{removed}$, notwithstanding the over-aeration phenomena were often observed in night-times. The autotrophic nitrification seemed not very sensitive to the sludge age within the range experimented (20÷50 days). On the other hand, the automatic control system played a key role to optimize the nitrogen removal. In fact, it was able to manage the alternation of the anoxic and aerobic phases consistently with the influent loadings. This flexibility was lost for C/N<5÷6, that may be considered a border line for the good efficiency of the dynamic system. The phosphorus was basically removed only for biomass assimilation. However, the P biological removal was enhanced when external acetate was included in the carbon source, and the resulting removal rates were around 60%.

Occurrence of micro-pollutants in municipal wastewater systems was firstly screened analysing five full scale treatment plants. Among the huge number of hazardous substances potentially transported in municipal sewers system, the screening action allowed to select the target compounds and their real abundances. As for the metals, As, Hg, Pb, Cd are present in the raw municipal wastewaters in a range of 0,1÷10 μg/L, while Cu, Ni, Cr are in the range 10÷70 μg/L. Many metals are partially associated to the suspended particulate matter and are removed already in the conventional physical head-works of the treatment facility. Basically, the MBRs were more effective than conventional systems for the removal of metals notwithstanding the low influent abundances. Enhanced performance of the MBRs were quantifiable in 7÷17% and major effects were exerted in the sequence Cd>Cu>Pb>Cr>Ni>Hg. On the other side, the As was removed in the range 30÷60%, according very fluctuating performances. The better removal performances of the MBRs were attributed partially to the sieving effect of the membrane, but also the fouling/cake layer seemed to

play an important role. In fact, the direct filtration of the activated sludge was more effective than the tertiary filtration. Moreover, the layer effect was not the same for all the metals. For instance, it was permanent and stable for Cd and temporary for Ni. On the other hand, no significant role was played by the sludge age within the range experimented. As for the organic xenobiotics, the abundance of Polynuclear Aromatic Hydrocarbons (PAHs) was lower than 2 μg L^{-1} also when petrochemical industries were present in the catchments area. These compounds were mostly associated to the suspended particulate and were removed already in conventional physical headworks (20÷40%). Then, the biological secondary conventional treatments exerted a further removal in the range 20÷50% and total PAHs effluent from conventional systems were in the range 0,1÷0,14 μg L^{-1}. The effect of the membrane systems was valuable only as sieving effect, but did not involve significant improvement of the effluent quality. The occurrence of VOCs was mainly due to organic solvents such as benzene, toluene and xylenes (BTEX) and trimetylbenzene. The influent abundances were in the range 3÷10 μg L^{-1} for the BTEX, mainly toluene, and 0,1÷1 μg L^{-1} for the trimetylbenzene. The stripping of these compounds was remarkable (40÷60%) already in the initial physical headworks, moreover the biological conventional processes were effective so far to involve further 10÷50% removal. The effect of the membrane system was not valuable because of the very low influent concentrations.

The impact on the biomass bulk parameters on membrane fouling was rather significant operating super-critical permeate fluxes. In particular, a variation from2 to 5 gMLSS L^{-1} caused a significant impact in terms of fouling rate increase. Otherwise, the permeability decline was almost insensitive to variations of mixed liquor concentration from 5 to 10 gMLSS L^{-1}.

Finally, the long term operation of the full scale AC-MBR represented a successful validation of the technology. As for the operating strategy, the biomass concentration was decided on the basis of the nitrification potential and the biomass was maintained as low as necessary for complete ammonia nitrification. This choice allowed to optimize both the removal performances and the oxygen transfer to the biomass. Following this strategy, the plant was operated with MLSS concentration in the range 6÷8 g L^{-1} and sludge age in the range 14÷21 days. The macropollutants removal were in the range 94÷96%, 89÷91% and 58÷67% respectively for COD, total nitrogen and total phosphorus. The alternating process lost the flexibility for NLRs in the range 0,14÷0,16 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$, that practically confirmed the demonstration results. The ultrafiltration process was managed according to the hydrodynamic environment characterized by (a) net permeate flux of 26 LMH, (b) Specific Aeration for Membrane Scouring (SAD_m) in the range 0.12÷0.19 $Nm^3 h^{-1} m_{membrane}^{-2}$, (c) Return Activated Sludge ratio in the range 1,5÷2,5, (d) filtration cycle of permeation (600 sec)/relaxation (60 sec). Moreover the routine cleaning protocol includes one maintenance cleaning in place (mCIP) per week using hypochlorite (400÷600 mgCl L^{-1}). Within these boundary conditions, the long-term membrane permeability was in the range 230÷240 LMH bar^{-1}. The increase of SAD_m from 0,12 to 0,19 Nm^3 h^{-1} m^{-2} did not involve a permeability gain that could balance the increased power requirements, probably because the major role in fouling amelioration was played by the chemical cleanings. Even with concern to fouling phenomena, the MLSS concentration played a minor role within the range 8÷11 g L^{-1}. Long term fouling phenomena during the routinely operation of the plant were sustainable and the seasonal fluctuations of inloading were well faced by the membrane system. Major fouling rose in case of short term (intended as 15÷30 days) singular events like the failure of the equipment for the chemical dosage or random discharge of landfill leachate into the sewers system, which change the nature of the feed. As a result, the UF system showed to be severely influenced from very unsteady conditions and short term variations of the feed nature. From the industrial sustainability standpoint, the appropriate management of the aeration was fundamental to achieve specific power requirements for the whole treatment in the range 0,44÷0,57 kWh/unit permeate also treating medium-high strength municipal wastewater. The operation and maintenance costs about power consumptions and chemical purchase were in the range 0.06÷0.08 €/unit permeate.

Riassunto

I bioreattori a membrana non possono più essere considerati una tecnologia di nuova generazione. Tuttavia, le metodologie per progettare e gestire questi sistemi sono tutt'altro che consolidate. Lo scopo principale dell'attività di dottorato è consistito nello sviluppare una biotecnologia che possa essere sostenibile e pronta per la sua applicazione industriale su vasta scala nel trattamento avanzato delle acque reflue civili. L'idea tecnologica di fondo è stata di accoppiare la tecnologia del bireattore a membrana con processi ad aerazione alternata del reattore biologico e automazione di controllo del processo. Dunque, il processo a cicli alternati, che controlla automaticamente l'aerazione intermittente del reattore biologico sulla base dei segnali on-line di ossigeno disciolto e potenziale di ossido riduzione, è stato applicato in un bioreattore a membrana nel risultante sistema MBR-Cicli Alternati. La sperimentazione è stata condotta sempre su liquami civili reali e su tre differenti livelli impiantistici: la scala pilota di grossa taglia, i bioreattori a membrana dimostrativo e in piena scala. Tutte le installazioni sperimentali hanno operato con membrane da ultrafiltrazione, sommerse e a fibre cave (area di filtrazione rispettivamente 21,6; 69,9 and 12.130 m^2). In particolare, l'impianto pilota è stato usato per studiare (a) l'impatto sul fouling dei parametri di bulk del fango attivo e (b) il ruolo del fouling/cake layer sulla rimozione dei metalli. L'impianto MBR dimostrativo è stato utilizzato per studiare la rimozione di nutrienti e microinquinanti, e l'affidabilità dell'algoritmo per il controllo automatico di processo. Infine, la validazione della tecnologia in piena scala è stata possibile grazie alla supervisione di un reale bireattore a membrana operante il processo a cicli alternati in reattore unico. Lo studio a scala dimostrativa è durato circa 500 giorni. L'impianto è stato alimentato con acque reflue civili reali, anche addizionate di sali di azoto e fosforo e di carbonio esterno per incrementare i carichi influenti. La sperimentazione si è sviluppata in nove periodi sperimentali in stato stazionario al variare del carico specifico di azoto che è variato, periodo per periodo, da 0,05 a 0,25 $kgN \cdot m_{reattore}^{-3} \cdot d^{-1}$, mentre il rapporto carbonio/azoto è stato sempre $\leq$ 8÷9. La massima capacità di trattamento del sistema in termini di carico di azoto influente è stata valutato attorno a 0,16÷0,17 $kgN \cdot m_{reattore}^{-3} \cdot d^{-1}$. Sotto tale valore si sono osservate ottime rimozioni di carbonio e azoto: la nitrificazione dell'ammoniaca è stata sempre quasi completa (efficienza di nitrificazione > 90%), mentre la denitrificazione è stato la fase limitante per l'intero processo alternato. I bilanci di materia mostrano come il processo biologico sia stato capace di rimuovere 0,1 kgN per $kgCOD_{rimosso}$, nonostante fenomeni di sovraerazione fossero particolarmente frequenti nei periodi notturni. La nitrificazione dell'ammoniaca non è stata influenzata significativamente dall'età del fango nel range sperimentato (20÷50 giorni). D'altra parte, il sistema di controllo automatico ha avuto un ruolo chiave per la rimozione dell'azoto. Infatti, tale sistema è stato capace di gestire l'alternanza delle fasi anossiche e aerobiche in funzione dei carichi influenti. Questa flessibilità è stata persa dal sistema per C/N<5÷6, che può essere anche considerato un valore sotto il quale la flessibilità di un sistema dinamico a cicli alternati è compromessa. Il fosforo è stato sostanzialmente rimosso per sintesi di nuova biomassa. Tuttavia, fenomeni di intensificazione di rimozione biologica del fosforo sono stati osservati quando carbonio esterno in forma di acido acetico è stato dosato nell'influente. In questo caso la rimozione del fosforo ha raggiunto valori di circa 60%.

Riguardo ai microinquinanti, la reale presenza di alcuni composti pericolosi e tossico-nocivi nei sistemi di trattamento delle acque reflue è stata preliminarmente verificata tramite campagne di campionamento/analisi su cinque impianti italiani di trattamento in piena scala. Questa attività preliminare ha permesso di selezionare, tra le centinaia di composti pericolosi potenzialmente presenti nelle acque di scarico in fognatura civile, i composti su cui focalizzare l'attenzione a causa del loro reale contenuto nelle acque reflue influenti agli impianti di depurazione civili. Per quanto riguarda i metalli, As, Hg, Pb, Cd sono stati rilevati nelle acque di scarico grezze nel range di 0,1÷10 $\mu g\ L^{-1}$, mentre Cu, Ni, e Cr erano nel range 10÷70 µg/L. Molti metalli influenti agli impianti

di trattamento sono risultati parzialmente associati ai solidi sospesi e rimossi già nei pre-trattamenti fisici convenzionali. Generalmente i bioreattori a membrana si sono dimostrati più efficaci dei sistemi convenzionali per la rimozione dei metalli nonostante le basse concentrazioni in gioco. Le migliori prestazioni degli MBR sono state quantificate in +7÷17%, e i metalli maggiormente rimossi nei sistemi a membrana possono essere ordinati secondo la sequenza Cd>Cu>Pb>Cr>Ni>Hg. D'altra parte, nei sistemi a membrana l'arsenico è stato rimosso nella misura del 30÷60%, ma con prestazioni molto fluttuanti. Le migliori prestazioni degli MBR sembrano dovute non solo alle capacità di ritenzione della membrana, ma anche il fouling/cake layer potrebbe avere un ruolo importante. Infatti, la filtrazione diretta del fango attivo è stata più efficace della filtrazione terziaria dell'effluente secondario. Inoltre, l'effetto layer non sembra essere uguale per tutti i metalli. Per esempio, è stato osservato quanto questo meccanismo sia alquanto stabile e permanente per il Cd, e temporaneo per il Ni. Quanto ai parametri operativi del processo biologico, l'età del fango non sembra avere giocato un ruolo primario all'interno del range sperimentato (20÷50 giorni). Passando alle sostanze organiche xenobiotiche analizzate, le concentrazioni di Idrocarburi Policiclici Aromatici (IPA) sono state sempre inferiore ai 2 µg L^{-1}, anche nel caso di un impianto civile posizionato in un area industriale petrolchimica. Gli IPA sono stati riscontrati sostanzialmente in associazione alla sostanza particolata sospesa e importanti rimozioni si sono osservate già nei pre-trattamenti fisici degli impianti convenzionali (20÷40 %). Quindi, si è osservato come i trattamenti biologici convenzionali operano una rimozione ulteriore del 20÷50% e la concentrazione globale di IPA nell'effluente secondario è quantificabile in 0,1÷0,14 µg L^{-1}. L'effetto dei sistemi a membrana sulla leggera migliore rimozione di IPA è sostanzialmente imputato alla ritenzione di fango attivo e macromolecole, ma non ha comportato miglioramenti significativi della qualità dell'effluente finale. Riguardo ai composti organici volatili, la loro presenza nelle fognature civili si è attribuita sostanzialmente a residui di solventi organici come benzene, toluene e xilene (BTEX) e trimetilbenzene. Le concentrazioni rilevate nelle acque reflue grezze sono state nel range 3÷10 µg L^{-1} per i BTEX e 0,1÷1 µg L^{-1} per il trimetilbenzene. La volatilizzazione di queste sostanze negli impianti convenzionali è sostanziale (40÷60%) già nei pre-trattamenti fisici iniziali, inoltre i processi biologici secondari sono capaci di rimuovere ulteriormente composti organici volatili nella misura del 10÷50%. L'effetto aggiuntivo dei sistemi a membrana per la rimozione di queste sostanze non è sembrato significativo, tuttavia dettagliate valutazioni sono state difficili a causa delle concentrazioni in gioco nell'ordine di grandezza di 10^{-1}÷10^{-3} µg L^{-1}.

L'impatto dei parametri di bulk del fango attivo sul fouling delle membrane è stato significativo in condizioni supercritiche di flusso di permeato. In particolare, variazioni di solidi sospesi nel mixed liquor (MLSS) da 2 a 5 g L^{-1} hanno comportato impatti significativi in termini di incrementi del *fouling rate* per le membrane di ultrafilrazione. D'altra parte, i fenomeni di fouling sono sembrati sostanzialmente insensibili a variazioni di MLSS da 5 a 10 g L^{-1}.

Infine, l'esercizio nel lungo periodo del bioreattore a membrana a cicli alternati in piena scala ha rappresentato la piena validazione del sistema proposto e precedentemente sperimentato su scala dimostrativa. Riguardo alla strategia operativa, la concentrazione di biomassa nel reattore è stata decisa sulla base del potenziale di nitrificazione ed è stata mantenuta tanto bassa quanto necessario per la pressoché completa nitrificazione dell'ammoniaca. Questa scelta ha permesso di ottimizzare sia le prestazioni del processo biologico che il trasferimento di ossigeno alla biomassa, così da minimizzare le richieste energetiche per l'aerazione de sistema. In base a questa strategia, l'impianto MBR ha operato con concentrazione di MLSS nel range 6÷8 g L^{-1} ed età del fango nel range 14÷21 giorni. Le rimozioni di macroinqunanti sono state nel range 94÷96%, 89÷91%, 58÷67% rispettivamente per COD, azoto totale e fosforo totale. Il processo a cicli alternati ha perso la sua flessibilità per carichi specifici di azoto di 0,14÷0,16 $kgN \cdot m_{reattore}^{-3} \cdot d^{-1}$, sostanzialmente confermando i risultati della sperimentazione dimostrativa. Il processo di ultrafiltrazione è stato gestito secondo un'idrodinamica del reattore caratterizzata da (a) flusso di permeato netto di 26 LMH; (b) aerazione specifica per il membrane scouring di 0,12÷0,19 $Nm^3 h^{-1} m_{membrana}^{-2}$, (c) rapporto di ricircolo totale nel range 1,5÷2,5; (d) ciclo di filtrazione secondo permazione (600 sec)/relaxation (60 sec). Inoltre, il protocollo operativo prevedeva un lavaggio di mantenimento per settimana con concentrazione di ipoclorito a 300 mgCl L^{-1}. Con queste condizioni a contorno, la permeabilità di lungo termine delle membrane di ultrafiltrazione è stata di 230÷240 LMH bar^{-1}. L'incremento di aerazione specifica da 0,12 a 0,19 $Nm^3h^{-1}m^{-2}_{membrana}$ non ha portato guadagni in termini di permeabilità tali da giustificare l'incremento di consumi energetici, probabilmente perché il maggiore effetto nella riduzione dei fenomeni di fouling è dovuto al lavaggio chimico di mentenimento delle membrane. Sempre con riferimento ai fenomeni di fouling delle membrane, la concentrazione di MLSS non è sembrata avere un impatto negativo significativamente elevato nel passaggio da 8 a 11 g L^{-1} nel reattore di ultrafiltrazione, a conferma di quanto osservato in scala pilota. I fenomeni di fouling nel lungo termine e in condizione operative ordinarie sono risultate sostenibili e il sistema è stato in grado di far fronte alle fluttuazioni stagionali di carico. Più evidenti fenomeni di fouling delle membrane sono stati osservati in caso di esercizio fortemente non stazionario dell'impianto, come nel caso della manutenzione straordinaria dell'impianto per il dosaggio di chemicals durante i lavaggi di mantenimento o l'irregolarità delle caratteristiche dell'influente dovuta a scarichi di percolato di discarica in rete fognaria. Dunque il sistema di ultrafiltrazione si è mostrato molto sensibile alle variazioni di carico e di natura dell'influente del breve periodo. Riguardo alla sostenibilità industriale del trattamento, l'appropriata gestione dell'aerazione è risultata fondamentale per raggiungere consumi specifici, riferiti all'intero trattamento, di 0,44÷0,57 $kWh/m^{-3}_{permeato}$, pur trattando acque reflue con concentrazioni di macroinquinanti medio-alte. I costi di gestion relativi ai consumi energetici e all'acquisto di chemicals per i lavaggi di mantenimento ammontano a circa 0.06÷0.08 €/$m^{-3}_{permeato}$.

Introduction

The Membrane BioReactor process (MBR) for wastewater treatment is an effective combination of the well known and widely applied activated sludge process with the membrane separation process. The development of this technology over the last years has been rapid and let suppose the widespread application also for municipal wastewater treatment. The drivers for MBR technology implementation are, in fact, so many: the stricter legislations, the water scarcity and the need for reclamation and reuse, the decreasing investment costs of the membranes, the stronger real scale experience with MBRs which support greater confidence in this technology. However, MBRs are experiencing a strange period, when the market is growing rapidly side by side to the number of research papers published on this topic. This lets understand how the MBRs design and operation practice is not consolidated and still needs investigations.

The potential of MBRs for much more performing treatment of municipal wastewater has been widely stated. The non-potable reuse purpose has often been achieved directly, without further treatment step after the final filtration of the activated sludge. However, the high power requirements and the costs for membrane purchase and replacements represent the bottleneck for the widespread application of MBRs in municipal wastewater systems, both small and decentralized and large for highly urbanized cities.

General objective and structure of this thesis

This thesis deals with the problems that arise from the analyses of the real existing scenario concerning wastewater treatment, and has the final objective to define the potential of the technology for ready application in full scale systems. Much research, in fact, is based on a purely scientific approach, often on lab scale, with synthetic wastewater. Although this is necessary to develop sound theory and fundamental knowledge, it is very difficult to translate the excellent results obtained in full-scale installations. To overcome this drawback, the approach of this research was to increase the size of the installations and to deal with the problems at different levels: pilot, demonstration and full scale. As expected, this methodological choice introduces many unknowns, but reflects better the reality and gave more objective results, although the precision of the final remarks is almost given in terms of ranges.

As a matter of fact, this thesis deals mainly with the membrane bioreactors operating the automatic control of the intermittent aeration for the biological process, but includes also side aspects that are necessary to understand the reasons of investigations and the importance of the conclusions.

Therefore, the topic is dealt with concern to the design aspects, the carbon and nutrients removal performances, the micropollutants occurrence and removal if operating in municipal systems, the fouling phenomena of the filtration module and, finally, the full scale validation of the process. So many experimental results are presented, but the main conclusions are reduced to key numbers which really describe the know-how and of the technology studied.

For a general understanding of the MBR technology and its present development, the *Chapter I* deals with the fundamentals of the activated sludge processes and membrane filtration, outlining also the present state of the full scale MBR application. *Chapter II* describes the experimental installations used for the research, while the analytical plans are described chapter by chapter just before the results. *Chapter III* deals with the design methodology for the alternating activated sludge systems on the basis of an empirical approach. *Chapter IV* examines the experimentations on demonstration MBRs focusing on the removal performances for carbon and nutrients. *Chapter V and VI* deal respectively with metals and organic persistent compounds in municipal wastewater systems. These two chapters have similar structures: firstly the occurrence of the pollutants is presented, so to identify the target compounds and quantify the size of the problems, then the removal in conventional full scale systems is briefly presented, so to understand the present risk for the environment; finally the possible effect of the membrane technology is illustrated, so to evaluate the real benefits achievable and how much the performances can be improved using industrially sustainable technologies. *Chapter VII* treats the membrane fouling, and in particular the impact of biomass bulk parameters on the performances of an industrial hollow fiber submerged module. Finally, *Chapter VIII* reports a detailed overview on a case study where the technology previously investigated at demonstration scale has been applied and validated on a full scale municipal wastewater treatment plant. *Chapter IX* reports a general evaluation of the main findings, together with the addresses for possible further research.

Chapter I. Fundamentals

This chapter provides the background information for this thesis. It is divided in three main parts: the first is dedicated to the activated sludge process; the second describes the principles of membrane filtration with emphasis on application for wastewater treatment; finally, the combination of both processes is concisely discussed outlining the main features of the membrane bioreactors (MBRs). For the compilation of the first part the 4th edition of the handbook on "Wastewater Engineering; Treatment and Reuse" (Metcalf & Eddy; 2003) is used. For the third part, the books "Membrane Bioreactors in wastewater treatment" by Stephenson et al (2000) and "The MBR book" by Judd (2006) are mainly used. Among the other sources, the PhD thesis "Filtration characteristics in membrane bioreactors" of H. Evenblij (2006) has been used.

1. Activated sludge process – description and definitions

Since its first application in 1913 by Ardern and Lockett (1914) in Manchester, England, the activated sludge process has found wide application all over the world. The concept is founded on the observation that the biomass present in the wastewater could be 'activated' by intensive aeration, stirring and recirculation. Once this biomass was activated it could be used to treat a wastewater. 'For reference purposes and failing a better term, the deposited solids resulting from the complete oxidation of sewage have been designated "activated sludge".'(Ardern and Lockett, 1914). The same paper reports questions and remarks following the presentation of the work by Ardern and Lockett, e.g. Mr. O'Shaughnessy regarded 'the paper as an epoch-making one, provided that the process experimentally established by the authors could ultimately be applied on the large scale at reasonable cost'. Eighty years later, the same remarks were heard when MBR was introduced as an option for large scale municipal wastewater treatment… One of the major features of the activated-sludge process is the formation of floc particles, ranging from 50-200 µm. These floc particles contain bacteria that are held together by extracellular polymeric substances (EPS) (Flemming and Wingender, 2000), and can be removed by gravity settling. What remains is a relatively clear liquid that can be discharged, and sludge that can be returned to the aeration tank to continue biodegradation. The activated sludge flocs contain a wide range of species of bacteria and protozoa. These organisms are responsible for the conversion of organic material and nutrients. Depending on the type of organism and boundary conditions, different types of conversions can take place. Most important type of conversion is aerobic oxidation, in which oxygen is the electron acceptor and organic compounds act as the electron donor. Two other reaction types are nitrification and denitrification, processes in which ammonia is converted to nitrite and nitrate (nitrification), which is further converted to nitrogen gas (denitrification). The reactions are all performed as part of the life cycle of the respective bacteria. For each reaction type the bacteria require a carbon source, an electron donor and an electron acceptor, which together yield an end product. The aerobic oxidation is a relatively easy to achieve reaction, since it requires only oxygen, organic compounds and a solids retention time of a few days. The first treatment plants that were built were designed mainly to perform this type of reaction, which required only aeration and mixing. In the past two decades also nutrient removal was incorporated in almost all biological treatment systems (Van der Graaf, 1995). This requires more complicated measures to provide conditions in which the desired bacteria can grow in sufficient numbers. Nitrifying bacteria for example require a solids retention time of 10 to 20 days, to properly perform nitrification (Metcalf&Eddy, 2003).

Type of bacteria	Reaction name	Carbon source	Electron donor	Electron acceptor	Products
Aerobic heterotrophic	Aerobic oxidation	Organic compounds	Organic compounds	O_2	CO_2, H_2O
Aerobic autotrophic	Nitrification	CO_2	NH_3, NO_2	O_2	NO_2, NO_3
Facultative heterotrophic	Anoxic denitrification	Organic compounds	Organic compounds	NO_2, NO_3	N_2,CO_2,H_2O

Nowadays, the purification mechanisms that take place in activated sludge have been widely studied and reliable predictive models (Activated Sludge Model 1,2,3) are commonly used. Following there is a summary of the main fundamentals about the removal mechanisms for carbon, nitrogen and phosphorus in activated sludge systems.

1.1 Carbon substrate utilisation

Carbon, as COD, in municipal wastewater is mainly present as a particulate form and can be removed both by physical and biological methods. Part of the particulate organic matter could be removed by sedimentation (if present) whereas the rest is removed by biological processes. Clearly, the soluble fraction is more readily biodegradable, while the particulate matter needs to be hydrolysed before consuming. Biological carbon removal in wastewater treatment processes is mainly due to respiration, that is CO_2 evolution, both in aerobic and anoxic conditions, and then to biomass growth. The generic equation for aerobic oxidation of organic matter in wastewater (formula COHNS) is the following:

$$\mathrm{COHNS} + \mathrm{O_2} + \text{Nutrients} \xrightarrow{\textit{bacteria}} \mathrm{C_5H_7NO_2} + \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{H_2O} + \text{Other end products}$$

The rate at which new biomass is formed, r_X, can be represented as:

$$r_X = \mu \cdot X$$

where r_X is the volumetric rate of biomass production [g $_{\text{biomass}}$/L·h], μ the maximum specific growth rate [h^{-1}] and X the biomass concentration [g $_{\text{biomass}}$/L].

Experimentally, Monod found that the growth rate depends on the substrate availability according to the following equation:

$$\mu = \mu_{\max} \frac{S}{k_S + S}$$

where μ is the specific growth rate [h^{-1}], μ_{max} the maximum specific growth rate [h^{-1}], k_S the half-velocity constant [g $_{\text{substrate}}$/L] and S the substrate concentration [g $_{\text{substrate}}$/L].

Therefore, the resulting expression for the growth rate is:

$$r_X = X \cdot \mu_{\max} \cdot \frac{S}{k_S + S}$$

The rate of biomass growth and the rate of pollutants use, the so called substrate, r_S, are related by means of a yield coefficient through the following general equation:

$$r_X = Y \cdot r_S$$

where r_X is the volumetric rate of biomass production [g $_{\text{biomass}}$/L·h], Y the real biomass yield [g $_{\text{biomass}}$/g $_{\text{substrate}}$] and r_S the volumetric rate of substrate uptake [g $_{\text{substrate}}$/L·h].

The rate of organic compounds (that is the substrate) utilisation is generally represented by means of a Monod-type equation and can be defined as follows:

$$r_S = -X \frac{\mu_{\max}}{Y} \frac{S}{k_S + S}$$

where r_S is the volumetric rate of substrate uptake [g $_{\text{substrate}}$/L·h], X the biomass concentration [g $_{\text{biomass}}$/L], μ_{max} the maximum specific growth rate [h^{-1}], Y the true biomass yield [g $_{\text{biomass}}$/g $_{\text{substrate}}$], k_S the half-velocity constant [g $_{\text{substrate}}$/l] and S the substrate concentration [g $_{\text{substrate}}$/l].

The term μ/Y is often replaced by the term K, defined as the maximum rate of substrate utilization per unit of biomass. Therefore, the equation will be redefined as follows:

$$r_S = -X \cdot K \cdot \frac{S}{k_S + S}$$

If one considers also the endogenous decay, can write: $r_d = -k_d X$ where r_d id the rate of biomass decay [g $_{\text{biomass}}$/L·h], K the maximum rate of substrate utilization per unit of biomass [g $_{\text{substrate}}$/g $_{\text{biomass}}$·h], k_d the endogenous decay coefficient [h^{-1}] and X the biomass concentration [g $_{\text{biomass}}$/L].
So the net growth rate is:

$$r'_X = X \cdot \mu_{\max} \cdot \frac{S}{k_S + S} - k_d X$$

The observed biomass yield will be defined as follows

$$Y_{obs} = -\frac{r'_X}{r_S}$$

1.2 Nitrogen biological removal

Biological nitrogen removal requires a two-step process. In the first step ammonia is oxidized to nitrate (nitrification) and various process configurations are then employed to provide the nitrate as an electron acceptor for biological respiration so that it can be reduced to molecular nitrogen (denitrification). Furthermore, the assimilation of nitrogen as cell constituent is to be taken into account.

1.2.1 Assimilation of nitrogen

Since N constitutes an essential nutrient for activated sludge microorganisms, a part of the influent S_{NH} will be assimilated for the synthesis of cellular material. If S_{NH} is limiting, S_{NO3} or S_{NO2} can be used for the assimilative requirement, after being reduced to S_{NH} (Metcalf & Eddy, 2003). Assimilatory N-removal occurs under aerobic, anoxic and anaerobic conditions.
The overall removal of N via assimilation depends on the daily sludge production, which on itself is generally proportional to the organic sludge loading rate and inversely proportional to the activated sludge retention time (SRT). In high loaded systems, the nitrogen assimilation may attain a significant rate, especially when treating concentrated wastewater in terms of COD and N. In the treatment of municipal wastewater the percentage of N removal via assimilation may range from 8 to 30% (Kujawa-Roeleweld K., 2000). However, if the treatment plant involves sludge handling processes, a portion of the assimilated N will return in the form of S_{NH} to the activated sludge tank via reject waters. For design purposes, the N-load from reject waters has to be included in the total N-load.

1.2.2 Nitrification

The nitrification process is a prerequisite for a dissimilatory N-removal. The S_{NH} form the influent and formed by hydrolysis and ammonification of biodegradable N_{org}, is oxidised in a two-step reaction to S_{NO3} by many species of autotrophic nitrifying bacteria which derive energy from inorganic compounds. The oxidation of S_{NH} is generally attributed to *Nitrosomonas europaea* and the oxidation of S_{NO2} to *Nitrobacter agilis*. The energy-yielding two-step oxidation of ammonia to nitrate is generally accepted to be as follows:

$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O + 352$ kJ/mol (*Nitrosomonas)*

$NO_2^- + 0.5O_2 \rightarrow NO_3^- + 73$ kJ/mol	(*Nitrobacter*)
$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O + 425$ kJ/mol	(Total reaction)

There is no organism described which is able to perform the overall nitrification process. Due to a low yield and substrate (S_{NH}) level, compared with COD, nitrifiers constitute only 2-5% of the total activated sludge population (Kujawa-Roeleweld K., 2000). The autotrophic nitrifiers are considered to be more susceptible to pH, temperature and toxic chemicals than heterotrophs.

Based on the above reactions, the oxygen required for complete oxidation of ammonia is 4.57 $g/gN_{oxidized}$ with 3.43 g/g used for nitrite production and 1.14 g/g used for nitrate production.

During ammonia oxidation to nitrite a significant amount of alkalinity is destroyed (approximately 7.14 mg as $CaCO_3$ per $mgNH_4$-N oxidized).

The portion of nitrifiers in the mixed liquor of an activated sludge tank treating municipal wastewater is typically in the 2-5% range due to the low yield and substrate level associated with ammonia oxidation compared to BOD removal. Thus a proper sludge retention time must be chosen in order to preserve the nitrifying fraction from washing out. The required SRT is equal to the reciprocal of the net specific growth of the nitrifying organisms:

$$SRT = \frac{1}{\mu_n - K_{nd}}$$

where μ_n is the nitrifying bacteria specific growth rate (g new cells/ g cell d) and K_{nd} is the endogenous decay rate of the nitrifying bacteria (g cells decayed/g cells d).

1.2.3 Denitrification

In the dissimilatory N-removal, denitrification is the reduction of S_{NO3} or S_{NO2} via a chain of intermediates to the end product nitrogen gas (N_2), as a consequence of redox reactions to obtain energy from organic material. The pathway of denitrification consists of a number of steps by which electrons are passed form the electron transport pathway to one of the N-oxides to produce a more reduced N-oxide. The generally accepted entire denitrification pathway can be described as:

$$NO_3^-{}_{(aq)}^{(+5)} \rightarrow NO_2^-{}_{(aq)}^{(+3)} \rightarrow NO_{(g)}^{(+2)} \rightarrow N_2O_{(g)}^{(+1)} \rightarrow N_{2(g)}$$

Each N-oxide (NO_3^-, NO_2^-, NO and N_2O) can serve thus as electron acceptor.

To characterise the denitrifying sludge activity, the specific denitrification rate (k_D) can be used. Most commonly, k_D is defined as a mass of S_{NO3} removed per time unit (t) per mass of volatile suspended solids (MLVSS, X_V):

$$k_D = -\frac{dS_{NO3}}{dt} \cdot \frac{1}{X_V} \ [\text{mgN gVSS}^{-1}\ \text{h}^{-1}]$$

The denitrification potential (DP, mgN/l) is the maximal mass of nitrate that can be denitrified in the anoxic volumes of a considered system per unit of influent flow. The DP depends on the concentration of biodegradable COD in the influent and the sludge activity.

The denitrification capacity (DC, mgN/l) is related to the DP and to the system configuration. It is the concentration of nitrate per influent flow that is denitrified in the system. In the most beneficial conditions the DC is equal to the DP. When, for instance, DO is present in the recycle streams entering the anoxic reactor the availability of biodegradable COD for denitrification is increased and the DC is lower than the DP. Anoxic volumes determine how much of biodegradable COD is utilised for the denitrification process and this affects the denitrification capacity. The DC is also affected by environmental factors such as temperature, pH and toxic components.

Another indication of denitrification performance is the denitrification efficiency that can be defined as the reduction rate of denitrifiable N, the amount of S_{NO3} that can be denitrified in a given system. This can be assessed for a N-balance that can attain different rates of complexity concerning the number of defined N.-fractions and the number of involved N-conversions.

1.2.3.1 Conditions for denitrification

In order to perform a satisfactory denitrification, a number of conditions is necessary to be accomplished:

- presence of N-oxides;
- presence of facultative heterotrophic biomass;
- absence or low level of dissolved oxygen;
- presence of a suitable electron donor.

Presence of N-oxides

To assure the nitrate and/or nitrite level, denitrification has to be proceeded (in time or place) by nitrification or N-oxides have to be available in the wastewater.

Presence of facultative heterotrophic biomass

In the respiratory metabolism of heterotrophic organisms, organic substrate is oxidised to the end products CO_2 and H_2O. during oxidation, organisms are able to capture energy for substrate utilization, maintenance and growth. The energy becomes available via a series of internally mediated redox reactions, involving electron and proton transport from an electron donor (organic substrate) to the final electron acceptor (oxygen or N-oxides) through a number of intermediate enzyme complexes. A large fraction of heterotrophic organisms – facultative heterotrophs – in biological treatment plants is capable for dissimilative denitrification. When dissolved oxygen (DO) becomes limiting, they can metabolise organic substrate with nitrate and/or nitrite as terminal electron acceptor.

Not the entire active biomass fraction that respires aerobically, is expected to use N-oxides as terminal electron acceptor (Orhon et al., 1996). Also not all denitrifying organisms can execute the entire pathway of denitrification but only part of it, i.e. from one ionic N-compound (NO_3^- or NO_2^-) to one of the gaseous N compounds (NO, N_2O or N_2). Such organisms are referred as partial denitrifiers. Other organisms reduce nitrate only to nitrite and they are called nitrate reducers. The electron transport pathways for aerobic and anoxic respiration have common enzyme complexes for a substantial part, which are utilised under both conditions. Other enzyme complexes are specific to only aerobic or anoxic respiration. Reduction of each N-oxide is catalysed by the corresponding N-oxide reductase.

Absence or low level of dissolved oxygen

When oxygen is absent or present at very low concentrations, nitrate/nitrite will act as electron acceptor (anoxic conditions).

The synthesis of N-oxide reductases can be executed in absence or at low levels of DO and the presence of the specific N-oxide, the reactant for a reductase. When the environment for facultative organisms is changed from aerobic to anoxic conditions, the synthesis of some oxidases – enzymes specific for aerobic respiration – is inhibited and the synthesis of reductases is initiated. When the facultative organisms are transferred to aerobic conditions the formation of reductases is inhibited (Wild et al., 1994).

Different electron transport pathways have a significant influence on the energy conservation. It can be deduced or proved experimentally that free energy released in presence of organic material and oxygen is higher than in the presence of N-oxides. It means, that if both are present, the more energy yielding process will take pace preferentially. An example of the oxidation-reduction reaction with glucose and nitrate or oxygen shows this difference:

$5C_6H_{12}O_6 + 24NO_3^- \rightarrow 30CO_2 + 18H_2O + 24OH^- + 12N_2 + 2394$ kJ/mol

$C_6H_{12}O_6 + 6NO_2 \rightarrow 6CO_2 + 6H_2O + 2881$ kJ/mol

The inhibitory effect of DO on denitrification has been extensively reported in literature and a high variety in reported DO levels can be found. The high variety in reported DO levels can be explained by the existence of a DO gradient in bacterial flocs, where, despite of aerobic conditions in the environment outside the floc, anoxic conditions prevail in its centre (Krul, 1976). The structure of activated sludge flocs, their size as well as mixing conditions may play an important role in the process performance and different results can be found on the limiting DO level.

Presence of a suitable electron donor

The oxidation of biodegradable organic compounds provides energy for facultative heterotrophs for the synthesis of new biomass and endogenous respiration. The energy for denitrification from organic compounds can be categorised as follows:

- internal, present in the influent wastewater;
- self-generated, in the system from decay and lysis of biomass;
- external carbon source as e.g. methanol, ethanol, acetic acid, starch, etc.

The composition and concentration of organic compounds determine the denitrification rate. When wastewater forms the only source of organic substrate the availability of biodegradable COD can be a shortcoming.

When nitrate serves as electron acceptor, the stoichiometrically equivalent mass of oxygen is used: 1 mgN-NO_3 (S_{NO3}) $\equiv$ 2.86 mgO_2 (S_{O2}) (Van Haandel et al., 1981). COD is required for two purposes during denitrification. One portion (1-Y_{HD}) is oxidised by denitrifying heterotrophs to CO_2 and H_2O, form which process energy is released and this energy is utilised for the assimilation of a second portion of COD (Y_{HD}). The anoxic heterotrophic yield (Y_{HD}) is equal to the efficiency of the cell to convert organic substrate into biomass (Copp & Dold, 1998). The total COD consumption to reduce 1 mgS_{NO3} will be 2.86/(1-Y_{HD}). When assuming, according to ASM1 (Henze et al., 1987), Y_{HD} = 0.67, a theoretical demand of organic biodegradable substrate of 8.67 mgCOD is required to reduce 1 mgS_{NO3}. In practice, the theoretical COD requirement for heterotrophic denitrification will be determined by the net biomass yield of activated sludge (including biomass decay).

The amount of COD for biomass synthesis will depend on the chemical structure of the COD compounds in the influent and within one group of organic compounds on the number of C-atoms.

1.2.4 Non-conventional N-conversions

For the removal of nitrogen from wastewater, the conventional N-conversion through nitrification and denitrification (via nitrate) is a wide implemented technology. Nevertheless, several authors (e.g. Patureau et al., 1997) reported new microbial nitrogen conversions that will be referred here as non conventional N-conversions.

Heterotrophic nitrification and aerobic denitrification

Aerobic denitrification is carried out by bacteria that can co-respire nitrate and oxygen, like *Thiosphaera pantotropha*, *Alcaligenes faecalis* and *Comamonas Sp. Strain SGLY2*. The same microorganisms were found to be capable of heterotrophic nitrification. Conflictive opinions categorise the rate of these processes as negligible or substantial (Münch et al., 1996). In most cases it has been recognised that only at high wastewater COD/N ratio (i.e.>10) a portion of N can be denitrified aerobically but it should be kept in mind that often aerobic denitrification can be confused with conventional denitrification in aerobic reactors subjected to oxygen diffusion limitation and with the formation of anoxic zones inside flocs or biofilms.

Autotrophic denitrification

Autotrophic nitrifiers (e.g. *Nitrosomonas europaea*) were observed to be responsible for a substantial production of N-gases (N_2O, NO or N_2) that may indicate that they can carry denitrification of nitrite with ammonium or hydrogen as electron donor (in Kujawa-Roeleweld, 2000). The conversion rates are however an order of magnitude slower than these for conventional nitrification and denitrification reactions.

Anaerobic ammonia oxidation (Anammox)

The Anammox process is based on the hypothesis of microbial catalysis of two autotrophic conversions: anaerobic oxidation of ammonia to N-gas and anaerobic oxidation of nitrite to nitrate. This process, once established, may be characterised by high conversion rates.

1.3 Phosphorus biological removal

At present there are two main mechanistic/biochemical models describing the phenomenon of biological excess phosphorus removal (BEPR): the Comeau/Wentzel (Comeau *et al.*, 1986) and Mino (Henze *et al.*, 1995) models respectively. The two models recognize the following:

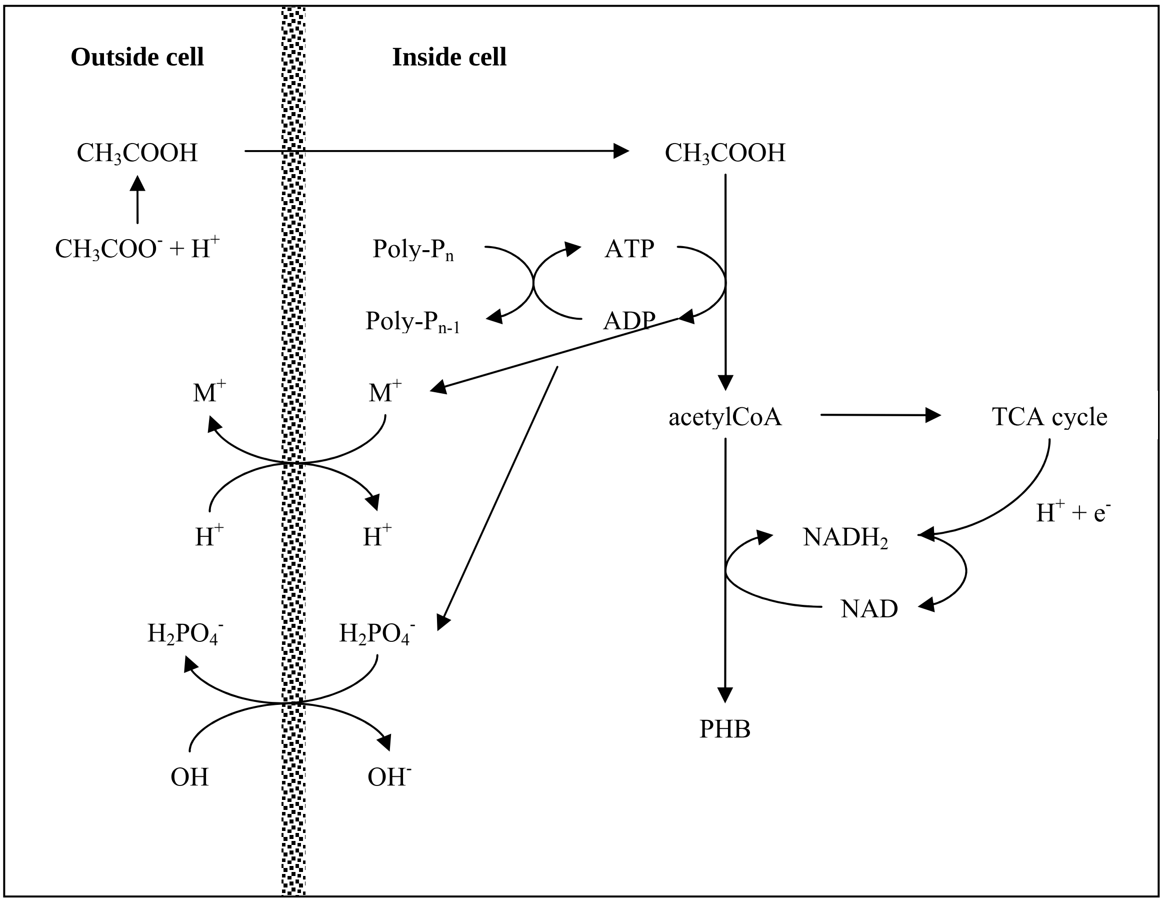
- Stimulation of BEPR processes requires anaerobic/aerobic sequencing;
- Short chain fatty acids (SCFA), e.g. acetate, play a central role in the anaerobic phase.

1.3.1 The Comeau/Wentzel model

The Comeau/Wentzel model recognizes that a number of organism types have been implicated in mediating BEPR, these organisms being called collectively Bio-P or poly-P organisms. However, taking note of the experimental evidence that implicates the genus *Acinetobacter* in BEPR, the model accepts this genus as typical of the poly-P/Bio-P group. On this basis Comeau/Wentzel considered carbon and phosphorus biochemical specific to *Acinetobacter* spp. Reported in literature, together with pathways accepted as operating generally in microorganisms. From these they identified two key parameters that appear to regulate these pathways, namely the ATP/ADP and NADH/NAD ratios.

Under anaerobic conditions. A schematic diagram setting out the proposed behaviour under anaerobic conditions is given in Fig.1.1.

Figure 1.1. Schematic diagram fro the behaviour proposed by the Comeau/Wentzel model under anaerobic conditions.



This can be summarized as follows:

(i) the high extracellular acetate concentration allows passive diffusion of acetate into the cell;

(ii) the intracellular acetate is activated to acetyl-CoA by coupled ATP hydrolysis. Hydrolysis of ATP releases cations M^+ (usually K^+ or Mg^{2+}) and the anion $H_2PO_4^-$;

(iii) the cations are released to the bulk solution via a proton mediated antiport protein carrier, and the phosphorus released via a hydroxyl mediated antiport protein carrier;

(iv) the ATP is regenerated from ADP by transfer of an energy-rich phosphoryl group from polyphosphate (poly-P) to the ADP. Originally this transfer was proposed to be direct, catalyzed by the enzyme ATP:polyphosphate phosphotransferase according to the following reaction:

$$(\mathrm{PolyP})_n + \mathrm{ADP} \leftrightarrow (\mathrm{PolyP})_{n-1} + \mathrm{ATP}$$

However, there is evidence to suggest that there is an intermediate step in the ATP generation mediated by the combined action of the enzymes AMP:polyphosphate phosphotransferase and adenylate kinase according to the following reactions:

$$(\mathrm{PolyP})_n + \mathrm{AMP} \leftrightarrow (\mathrm{PolyP})_{n-1} + \mathrm{ADP}$$

$$\mathrm{ADP} + \mathrm{ADP} \leftrightarrow \mathrm{ATP} + \mathrm{AMP}$$

Whichever pathway is operative, the net result is a decrease in the stored poly-P concentration and a generation of ATP.

(v) Two acetyl-CoA molecules condense to form acetoacetyl-CoA;

(vi) Acetoacetyl-CoA is reduced by NAD(P)H_2 to form hydroxybutyryl-CoA, which then is polymerized to form poly-β-hydroxybutyrate (PHB);

(vii) To supply the reducing equivalents (NAD(P)H_2) needed to convert acetoacetyl-CoA to hydroxybutyryl-CoA, some acetate is metabolized via the tricarboxylic acid (TCA) cycle. Division of acetate between the formation of PHB and the TCA cycle is illustrated in Fig.1.2.

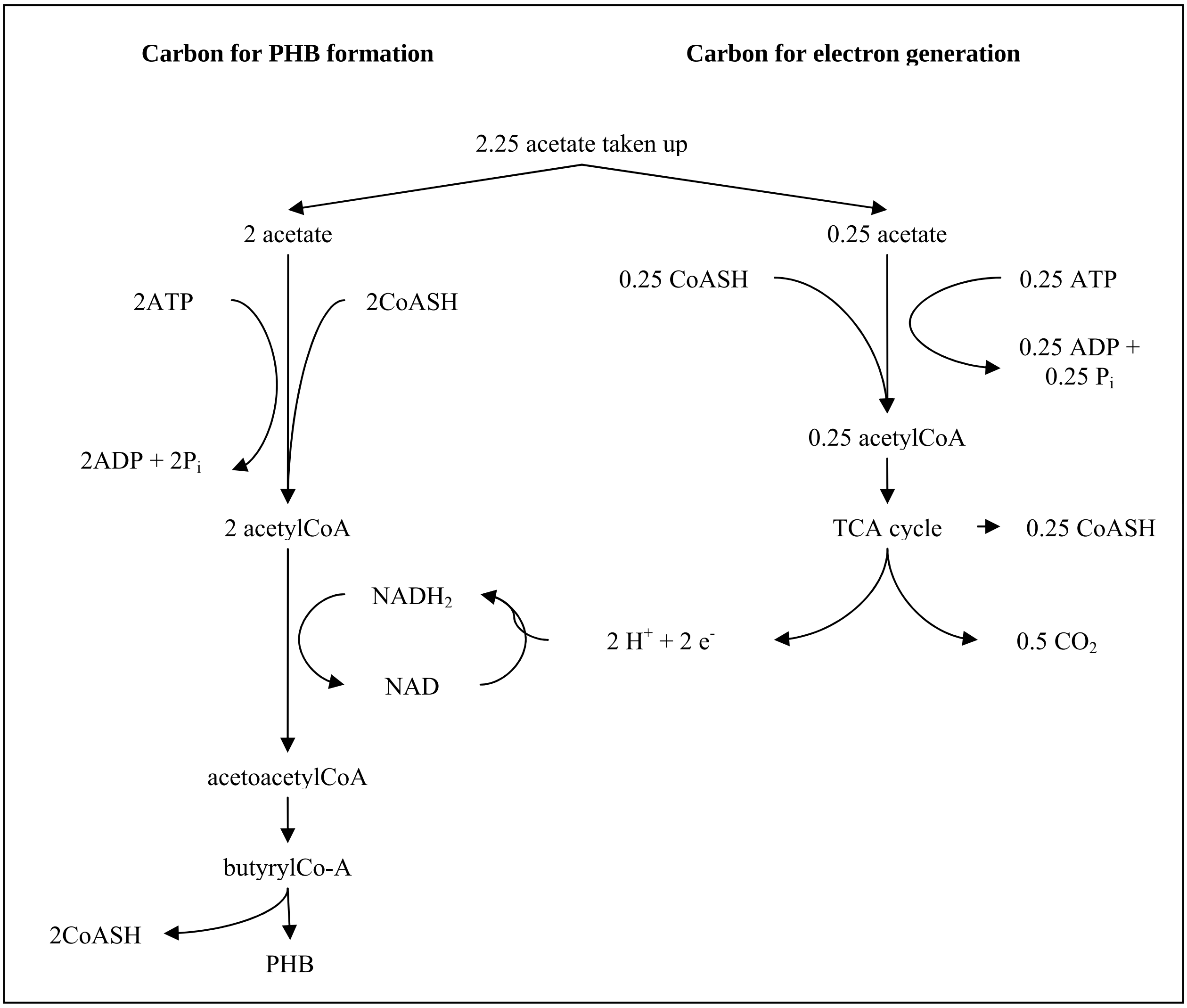


Figure 1.2. Stoichiometry proposed in the Comeau/Wentzel model for acetate utilization in PHB formation under anaerobic conditions.

(viii) Conversion of intracellular acetate to PHB maintains a favourable concentration gradient for further diffusion of acetate into the cell.

Conversion of acetate (Ac) to PHB $(C_4H_6O_2)_n$ can be summarized in the following equation:

$$2nAc + 2nATP + nNADH_2 + CoASH \rightarrow (C_4H_6O_2)_nCoA + nNAD + 2nADP + 2nP_i$$

Metabolism of acetate via the TCA cycle can be summarized as follows:

$$nAc + nATP + 4nNAD \rightarrow 4nNADH_2 + nADP + nP_i + 2nCO_2$$

The net result of these processes can be obtained y combining Eqns (5.3) and (5.4) in a stoichiometric ratio that maintains a balance of reducing equivalents (Eq.5.5):

$$9nAc + 9nATP + CoASH \rightarrow (C_4H_6O_2)_{4n}CoA + 9nADP + 9nP_i + 2nCO_2$$

Under aerobic conditions. The Comeau/Wentzel model for behaviour under aerobic conditions is set out in Fig.1.3 and can be summarized as follows:

(i) PHB is broken down and can be used for either anabolic or catabolic metabolism.
(ii) In anabolism carbon skeletons generated from PHB (directly or indirectly) are incorporated into cell mass.
(iii) In catabolism the PHB is broken down to acetyl-CoA, which enters the TCA cycle. Reducing equivalents ($NADH_2$) generated are subsequently oxidized via the electron transfer pathway; simultaneous oxidative phosphorylation generates ATP.
(iv) The ATP generated is used for cell energy requirements (e.g. synthesis) and resynthesis of poly-P.
(v) Phosphate uptake for poly-P synthesis occurs via the hydroxyl mediated antiport and cation uptake via the proton mediated antiport.

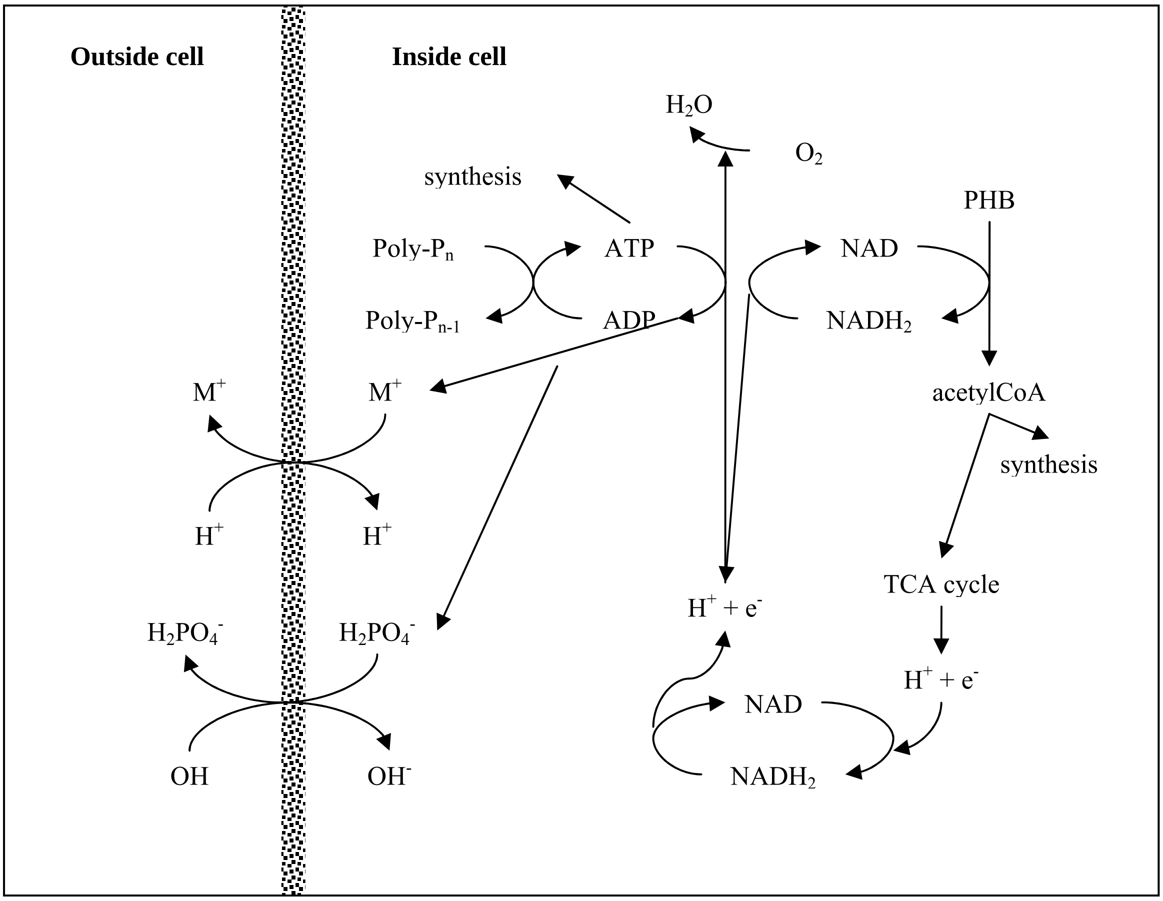


Figure 1.3. Schematic diagram for the behaviour proposed by the Comeau/Wentzel model under aerobic conditions.

1.3.2 The Mino model

The Mino model was developed to explain observations on a laboratory scale anaerobic/aerobic receiving an artificial substrate of acetate, propionate, glucose and peptone and to explain observations on batch tests conducted using sludge for the laboratory-scale system.

Under anaerobic conditions. A schematic diagram of the Mino model is given in Fig.1.4.

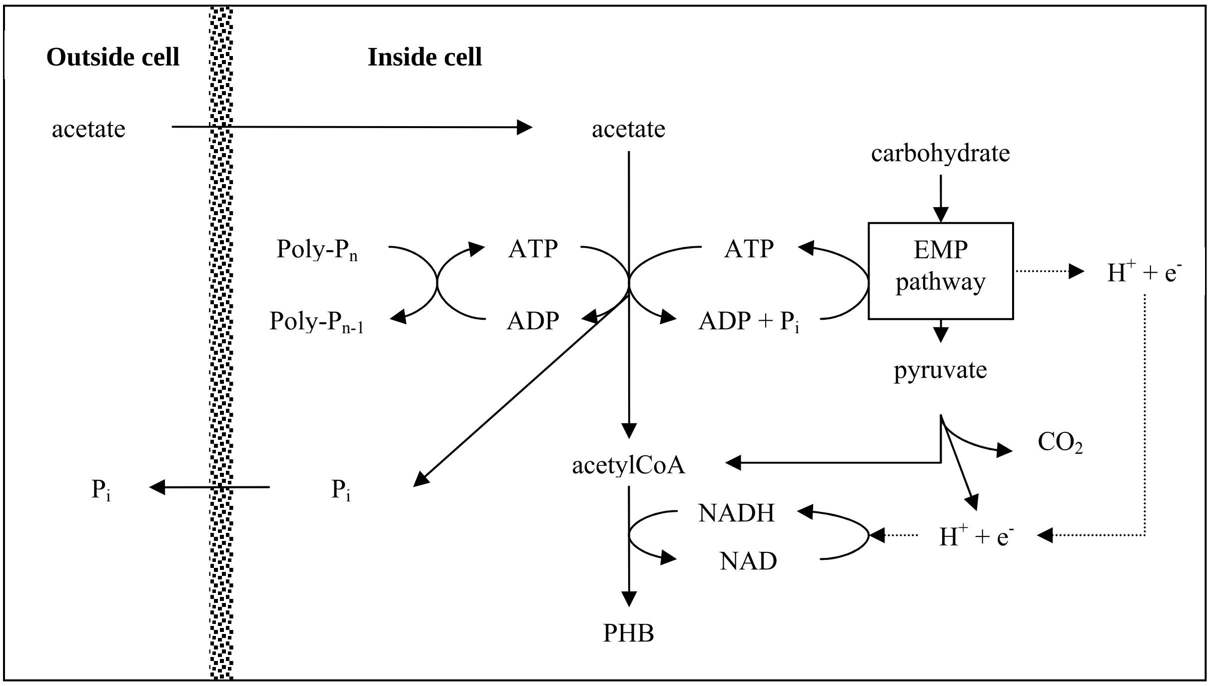


Figure 1.6. Schematic diagram for the behaviour proposed by the Mino model under anaerobic conditions.

The proposed behaviour can be summarized as follows:

(i) acetate is taken up by the organism.
(ii) Intracellular acetate is activated to acetyl-CoA by coupled hydrolysis of ATP, P being released to the bulk solution.
(iii) The ATP requirements in (ii) above are supplied by the accumulated poly-P.
(iv) PHB is synthesized from acetyl-CoA (AcCoA) according to the following reaction:

$$2nAcCoA + nNADH_2 \rightarrow (C_4H_6O_2)_n + nNAD + 2nCoASH$$

(v) The reducing equivalents ($NADH_2$) in (iv) are supplied as follows. Under the anaerobic conditions, carbohydrate $(C_6H_{10}O_5)_n$ is converted to pyruvic acid via the Embden-Meyerhof-Panas (EMP) pathway with the production of reducing equivalents ($NADH_2$). The pyruvic acid then is converted to acetyl-CoA with production of CO_2. The overall reaction for breakdown of carbohydrate to acetyl-CoA can be expressed as follows [Eq.5.7]:

$$(C_6H_{10}O_5)_n + 3ADP + 3nP_i + 4nNAD + 2nCoASH \rightarrow 2nAcCoA + 4nNADH_2 + 3nATP + 2nCO_2$$

Thus the reducing equivalents required in the reduction of acetate to PHB are supplied by the consumption of carbohydrate via the EMP pathway.

(vi) Combining the reaction for the consumption of glycogen with that for the activation and conversion of acetate to PHB the following net reaction for changes in intracellular carbon can be obtained:

$$(C_6H_{10}O_5)_n + 6nAc + 3nATP \rightarrow (C_4H_6O_2)_n + 3nADP + 3nP_i + 2nCO_2$$

Under aerobic conditions. A schematic diagram is shown in Fig.1.7.

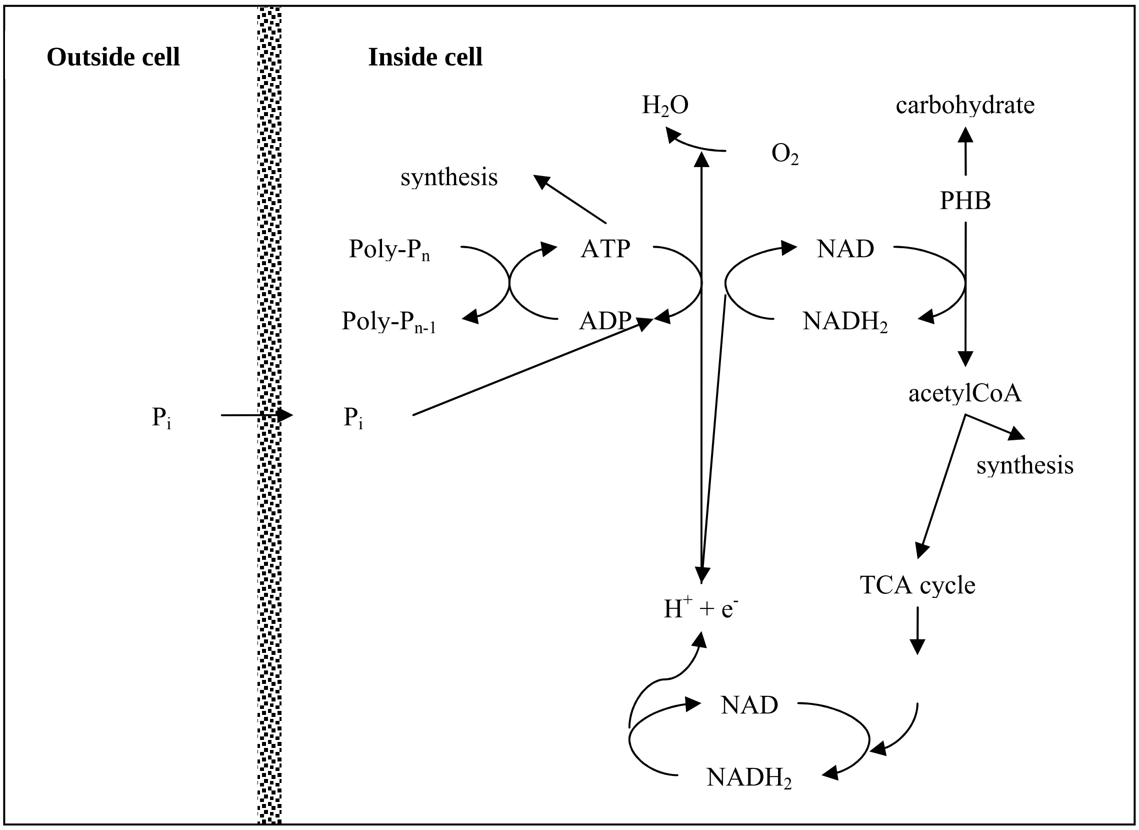


Figure 1.7. Schematic diagram for the behaviour proposed by the Mino model under aerobic conditions.

This can be summarized as follows:

(i) PHB is broken down and used for anabolism, catabolism and for synthesis of carbohydrate.
(ii) In anabolism the PHB is used as a carbon source for cell synthesis.
(iii) In catabolism the PHB is consumed for oxidative phosphorylation (ATP generation).
(iv) The ATPO generated is used for the cell energy requirements and to resynthesize poly-P.
(v) The PHB also is used for carbohydrate synthesis under the aerobic conditions. This process is essential to maintain the require level of carbohydrate for the consumption during the subsequent anaerobic phase.

The description above was restricted to situations where acetate (or an equivalent short chain fatty acid) served as the sole external substrate in the anaerobic phase. However, normal domestic sewages may contain no or very low concentrations of acetate or other SCFAs. With domestic sewage, P release (and P removal) has been linked to a fraction of the biodegradable COD termed readily biodegradable COD (RBCOD) which consists of substrates that can be rapidly metabolized by microorganisms and very likely consists of material like simple carbohydrates and peptones.

2. The membrane filtration

Membrane filtration denotes the separation process in which a membrane acts as a barrier between two phases. In water treatment the membrane consists of a finely porous medium facilitating the transport of water and solutes through the membrane.

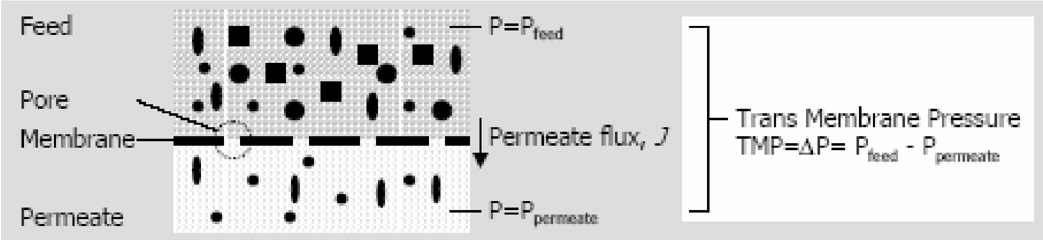


Figure 1.8 Schematic representation of membrane filtration (adapted from Hevenblij, 2006)

The membrane separates on the basis of molecular (or particle) size; it retains constituents bigger than the pore size. According to the pore size of the membrane, the filtration process can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO), see also Figure 1.9. In micro- and ultrafiltration the chemistry of the membrane does not play a major role in the separation process itself (Lonsdale, 1981). It should be noticed however that the chemistry plays an important role in the process performance, mainly in the interaction of feed water constituents with the membrane, which
may cause a resistance increase.

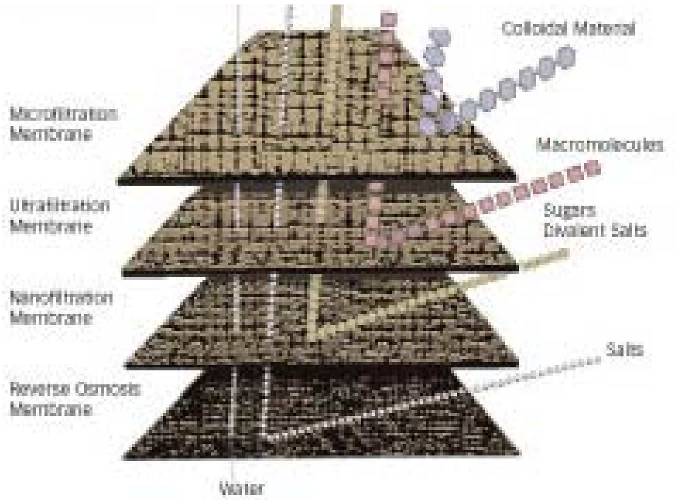


Figure 1.9 Membrane separation spectrum

2.1 TMP – viscosity - flux

The driving force for permeation is a trans membrane pressure (TMP) in most water treatment membrane filtration applications. The rate of permeate flux (J) for a pure solvent feed flowing under laminar conditions in tortuous membrane pores may be described by Darcy's law (Lojkine et al., 1992)

$$J = \frac{\Delta P}{\eta_p R_t}$$

where: J = permeation flux [L/m2Ph], or [m/s]
ΔP = trans membrane pressure [Pa], or [bar]
η_p= permeate dynamic viscosity [Pa·s]
R_t= total filtration resistance [m^{-1}]

In the presence of foulants, the total filtration resistance (R_t) is the sum of the clean membrane resistance (R_m) and a fouling resistance (R_f)

$$R_t = R_m + R_f$$

Remark the inverse proportionality of permeate flux to permeate viscosity. The permeate viscosity is often close to that of pure water (Manem and Sanderson, 1996). For the calculation of the permeate viscosity, the formula given by Huisman is widely used (Huisman, 1996):

$$\eta_p = \frac{479 \cdot 10^{-3}}{(T + 42.5)^{1.5}}$$

where: η_p= permeate dynamic viscosity [Pa·s]
T=temperature [°C]

2.2 Selectivity

The pore size of the membrane defines its selectivity. Selectivity is sometimes indicated by the molecular weight cut off (MWCO), which is the molecular weight of a solute corresponding to a 90% rejection factor for a given membrane; where the rejection factor (R), is (Koros et al., 1996):

$$R = 1 - \frac{c_{i,permeate}}{c_{i,feed}}$$

where R = rejection factor [-]
$c_{i,\text{ permeate}}$ = concentration of component i in permeate [mg/L]
$c_{i,\text{ feed}}$ = concentration of component i in feed [mg/L]

MWCO is used for membranes where particle size is not the determining factor, but difference in diffusivity result in selectivity of the membrane.

The driving force causing a trans membrane flux can be a temperature gradient, a concentration gradient, electrical potential difference or a hydraulic pressure gradient. The driving force in water treatment membrane processes is usually a hydraulic trans membrane pressure (TMP) (Mulder, 1996). With decreasing pore size the operating trans membrane pressure increases (Mulder, 1996), because the hydraulic resistance of the membrane increases; see also Table 1.1.

Table 1.1 Operating TMP for different membrane separation process

Membrane process	Pressure	Pore size
	bar	nm
Microfiltration (MF)	0.1÷2	100÷1000
Ultrafiltration (UF)	0.1÷2	10÷100
Nanofiltration (NF)	4÷20	1÷10
Reverse Osmosis (RO)	10÷30	0.1÷1

2.3 Permeability

A commonly used parameter to represent membrane performance in MBRs is the permeability. Permeability can be calculated as the ratio between the flux and the TMP:

$$Permeability, P = \frac{J}{TMP} \; [\mathrm{L/m^2 \cdot h \cdot bar}]$$

It can be observed that the permeability multiplied by the permeate viscosity equals the reciprocal of the filtration resistance.

The parameter permeability should be used with care, because it is a useless parameter when presented without more data. It can be useful when for example the clean water membrane permeability is known, as well as the mode of operation and which parameter is kept constant, flux or TMP. Temperature impact on membrane filtration through its influence on the permeate fluid viscosity must be considered. The common approach to comparing hydraulic performance obtained at different temperatures is to normalize the operating flux at a reference temperature (generally 20°C). This could be done by applying a temperature correction factor (Mulder, 2000). To avoid the interference of the temperature effect on MBR fouling, non-linear regression between critical flux and temperature was obtained (Judd, 2006):

$$P_T = P_{20} \cdot 1.025^{T-20}$$

2.4 Membrane material and configuration

2.4.1 Membrane material

Membranes can be manufactured from different materials, such as ceramics, organics and metals (Baker, 2000). Most commonly applied in water treatment are organic membranes, with a wide variety of membrane materials, pore sizes, pore size distributions, membrane configurations and production processes. The main reason to apply organic membranes is connected with the manufacturing costs. Ceramic membranes are about 10 times more expensive than organic membranes (Owen et al., 1995). Other differences can be found in resistivity for cleaning agents, hydrophobicity/hydrophilicity, mechanical strength etc. Ceramic membranes for example can resist extremely high trans membrane pressure and temperatures. Organic membranes, like cellulose acetate membranes, are usually sensitive for oxidising agents or biological activity of the medium.

The membrane structure can be isotropic or anisotropic. Isotropic membranes have a uniform composition and structure throughout. Anisotropic membranes (or asymmetric) membranes consist of a number of layers, each with different structures and permeability (Baker, 2000).

Table 1.2 Membrane materials

Organic membranes		*Ceramic membranes*	
Cellulose acetate	CA	TiO_2	ZrO_2
Polyetherimide	Ultem	Zircon Oxide	
Polyacrylonitrile	PAN		
Polyethersulphone	PES	*Metal membranes*	
Teflon		Aluminiumoxide	y-Al_2O_3
Polyvinylidenefluoride	PVDF		
Polyethylene	PE		

2.4.2 Membrane configuration

Membranes can be configured into membrane modules in different ways. Depending on the production process the membrane can be in the form of sheets, hollow fibres and tubes (Mulder, 1996). Flat sheet membranes are used to construct spiral wound modules or they can be mounted on a frame, resulting in the plate and frame modules, see Figure 1.10.

Tubular membranes are usually anisotropic membranes with the separating layer at the inside. Hollow fibre membranes are often isotropic membranes that can be operated inside out or outside in. Submerged hollow fibres can be oriented horizontally or vertically; for application in MBR where air scouring is applied, vertical orientation seems favourable (Chang and Fane, 2000).

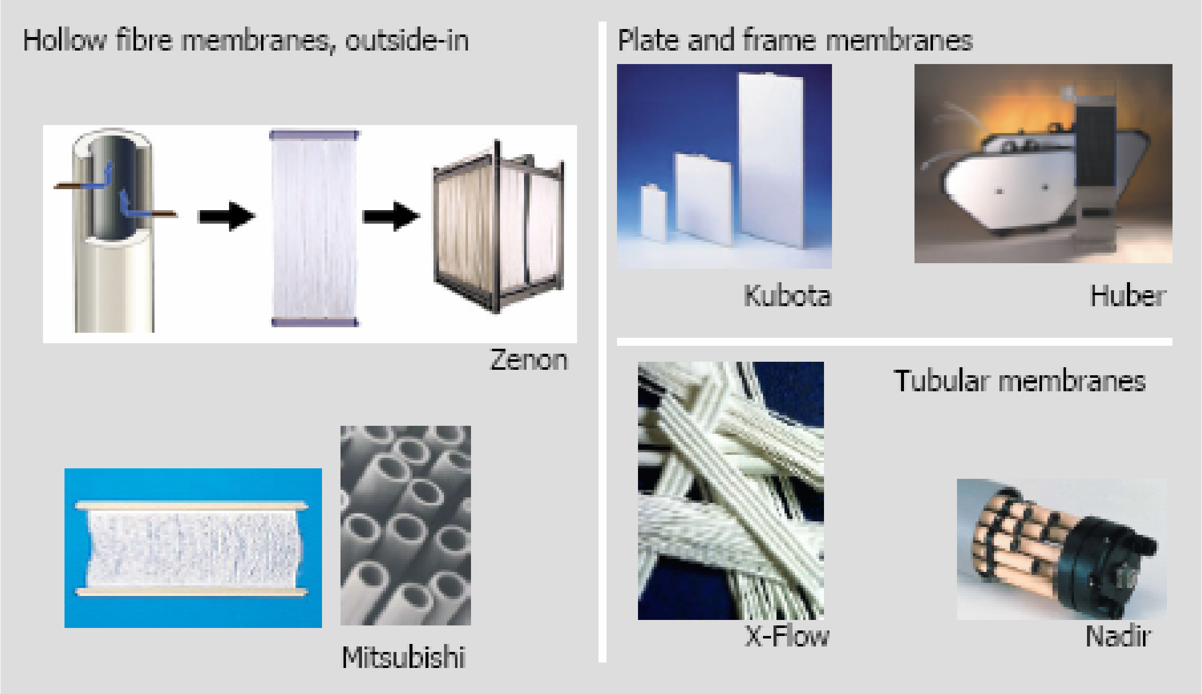


Figure 1.10 Examples of commercially available membranes, applied in cross flow filtration

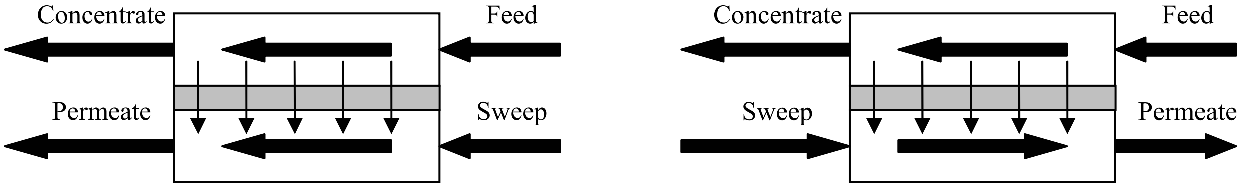
For the treatment of suspensions flat sheet, tubular and capillary membranes (hollow fibres) are preferred, see also Table 1.3. In recent years, membrane processes have found wide application and nowadays membrane processes exist for most of the fluid separations encountered in industry. (Bowen and Jenner, 1995).

Table 1.3 Membrane configurations and application in different separation processes

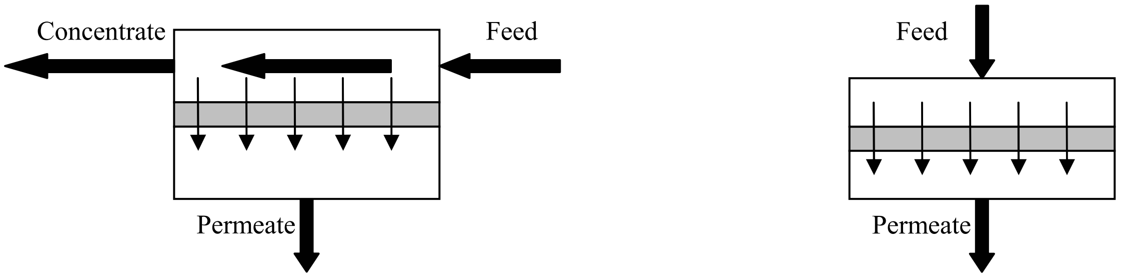
Membrane configuration		Applied in:			
		RO	NF	UF	MF
Spiral wound	SW	X	X	X	
Tubular	T		X	X	X
Hollow fibre inside-out	HF-IO	X	X	X	X
Hollow fibre outside-in	HF-OI			X	X
Plate and frame	PF			X	X

2.4.3 Types of filtration

Figure 1.11 presents schematic of the various types of ideal continuous-flow membrane separation process.



(a) Co-current flow **(b) Counter-current flow**



(c) Cross flow **(d) Dead-end flow**

Figure 1.11. Types of ideal continuous flows used in membrane separation processes.

Co-current flow (a) is the flow pattern in a membrane module in which the fluids on the upstream and downstream sides of the membrane move parallel to the membrane surface and in the same direction. Co-current flow is used in certain dialysis units.

Counter-current flow (b) is the flow pattern in a membrane module in which the fluids on the upstream and downstream sides of the membrane move parallel to the membrane surface but in opposite directions. Counter-current flow is also used in certain dialysis units.

Cross-flow or tangential flow (c) is the flow pattern in a membrane module in which the fluid on the upstream side of the membrane moves parallel to the membrane surface and the fluid on the downstream side of the membrane moves away from the membrane surface in a direction perpendicular to the surface.

Dead-end flow (d) is the flow pattern in a membrane module in which the only outlet for the upstream fluid is through the membrane.

However, really membrane filtration can be operated basically in dead-end and cross flow. In dead-end mode, all solutes, suspended and dissolved, are transported towards the membrane by the permeate flux. This leads to an increased concentration of retained material at the membrane and membrane fouling may occur. It was noted very soon that moving the feed flow tangential to the membrane surface results in much higher permeation fluxes ((Bechold, 1907) cited in (Ripperger and Altmann, 2002)). Another approach to avoid excessive accumulation of material at the membrane is the application of air scouring. In this way the fouling is intermittently removed, as further discussed in the last chapter of this thesis.

2.4.4 Fouling

Permeate flux decline is influenced by a number of factors relating to the feed water (composition), the membrane (element geometry/configuration, area and material composition), and operation (hydrodynamics). It is critically determined by the tendency of the membrane to be fouled by feed water components owing to their accumulation on the internal and external structures of the membrane. This increases the overall resistance to filtration, thereby commensurately increasing the energy demand.

Fouling is the general term given to the process by which a variety of species present in the water increase the membrane resistance, by adsorbing or depositing onto its surface, adsorption onto the pore surfaces within the bulk membrane material (pore restriction) or by complete pore-blocking. Fouling most commonly takes place external to the membrane, forming a dynamic layer at the membrane surface. As most membrane processes operate in the crossflow mode, fouling through the formation of such a dynamic layer might be expected to reach equilibrium once the adhesive forces between the layer and the membrane substrate are balanced by the shear forces at the layer-solution interface. In practice, equilibrium is not always attained, indicating some component of the overall hydraulic resistance to be time dependent.

The flux decline rate generally decreases with time but increases with increasing operating flux or pressure (Table 1.4).

Table 1.4. Specific flux decline rate for selected MBRs (from Gander et al., 2000)

Membrane configuration	Flux change (m^3/m^2d)	Pressure change (bar)	Time (days)	Specific flux decline rate (m/d bar)
Submerged, P+F, PS 0.4 µm	0.5	0.06	0.04	208
Submerged, P+F, PS 0.4 µm	0.1	0.7	0.2	0.79
Side-stream, T, C 0.1 µm	2.9	1.8	22	0.73
Submerged, P+F, PS 0.4 µm	0.9	0.06	39	0.38
Submerged, HF, PE 0.1 µm	0.2	0.7	70	0.004

P + F = plate & frame; PS = polysulfone; T = tubular; C = ceramic; HF = hollow fibre; PE = polyethylene.

Membrane fouling is caused by deposition and accumulation of feed components on the membrane surface and/or within the membrane pores. Three accepted mechanisms resulting in resistance to flow due to fouling of the membrane are (Fig.1.12):

- *gel/cake formation* caused by concentration polarization: this is an extreme case of concentration polarization where a large amount of matter has accumulated on the membrane surface due to size exclusion from pores.
- *pore plugging*: it occurs when particles become struck within the pores of the membrane.
- *pore narrowing*: it consists of solid material attaching to the interior surface of the pores.

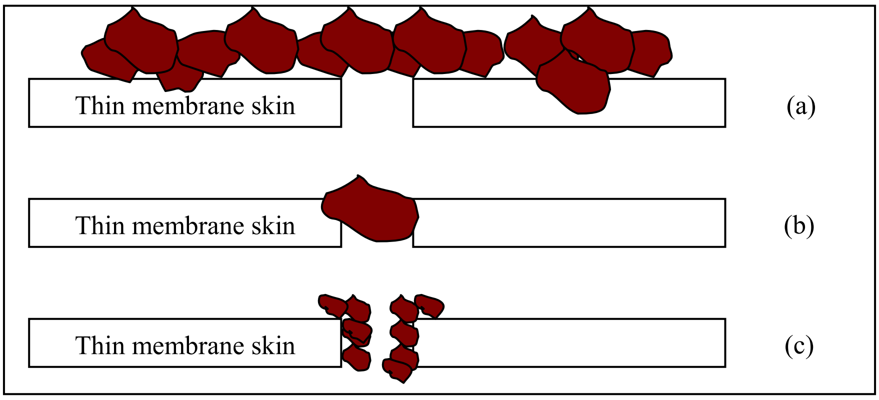


Figure 1.12. Mechanisms of membrane fouling: (a) gel/cake formation; (b) pore plugging and (c) pore narrowing.

Membrane fouling occurs through one or more of the following mechanisms:

- Accumulation of solute and gradual irreversible changes to the polarised layer (such as cake formation)
- Surface adsorption/deposition of solutes
- Adsorption/deposition of solute within the membrane.

There are many factors contributing to fouling including surface properties (chemistry, morphology, etc.), fluid dynamics conditions, ionic strength and solute concentration.

Fouling by individual components tend to be specific to the membrane material and application, but in general physico-chemical fouling, i.e. fouling unrelated to biological growth, can be attributed to two key components in the feed: proteins and colloidal/particulate materials.

Proteins can cause severe fouling of a many different MF membrane materials, in particular hydrophobic polymers such as polypropylene, causing flux declines of an order of magnitude or more (Judd & Till, 2000) ultimately due to irreversible deposition onto and penetration into the bulk membrane material. UF membranes, on the other hand, are somewhat less prone to fouling by macromolecules because the smaller pores are more impenetrable. For both UF and MF surface chemistry, specifically hydrophilicity and surface charge, plays an important part in determining the extent of fouling: hydrophobic materials are more prone to protein deposition leading to irreversible fouling.

Colloidal and particulate materials are similarly affected by physical changes in structure as a result of permeation. In this case, it is the aggregation rate which is affected by the physicochemical conditions via hydrodynamic and surface force effects.

With specific regard to filtration of activated sludge, it is widely recognised that the main foulants are the extracellular polymeric substances (EPS) excreted from cells (Judd, 2006; Le-Clech *et al.*, 2006).

2.4.5 The concentration boundary layer

During ultrafiltration and microfiltration, i.e. when the wall is porous, solids in the feed are brought to the membrane surface by convective transport and a portion of the solvents is removed from the fluid. This results in a higher local concentration of the rejected solute at the membrane surface as compared to the bulk, regardless of whether the solutes are partially or completely rejected by the membrane (Fig.1.13).

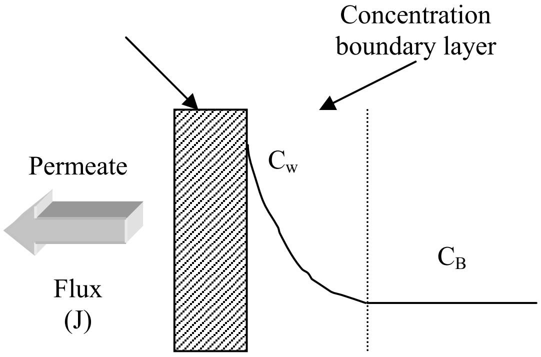


Figure 1.13. Concentration profile during membrane processing of partially or completely rejected solutes.

This solute build-up is known as *concentration polarization* and is chiefly responsible for the marked deviation in flux compared to pure water flux. Analogous to the velocity boundary layer, there will also be a concentration boundary layer that separates the region of higher concentration near the wall (i.e. near the membrane surface) from the lower, more uniform concentration in the bulk of the liquid this concentration boundary layer will be thinner than the corresponding velocity boundary layer since mass transfer by molecular diffusion is generally a much slower process than momentum transfer. In addition. The length over which the concentration boundary layer develops will be much longer. The length of the concentration profile entrance region (L_c) can be calculated from Eq.5:

$$L_c = \frac{0.1\gamma_w d_h^3}{D} \qquad (5)$$

where γ_w is the shear rate at the wall and D is the diffusion coefficient. The concentration gradient across the boundary layer is much steeper than the velocity gradient. Thus, it is generally assumed that in the bulk solution outside the boundary layer, the concentration profile is essentially uniform in the direction perpendicular to the membrane surface. The flow of fluid in the bulk stream influences the back transfer of accumulated solute into the bulk, thus keeping this boundary layer thin. This forms the basis of the film theory.

2.4.6 Concentration polarization

Concentration polarization is a complication that arises when hydrocolloids, macromolecules (such as proteins) and other relatively large solutes or particles are filtered. These compounds, being largely rejected by the membrane, tend to form a layer on the surface of the membrane. Depending on the type of solid, this layer could be fairly viscous and gelatinous. Thus a further resistance to the flow of permeate is encountered, in addition to those of the membrane and the boundary layer. The additional layer of solute is known by various terms such as the gel layer, CP layer, cake or polarization layer.

3. Membrane bioreactors (MBRs)

Membrane bioreactors (MBR) combines the biological degradation process by activated sludge with a direct solid/liquid separation by membrane filtration. By using micro or ultrafiltration membrane technology (with pore size ranging from 0.05 to 0.4 μm), MBR systems allow the complete physical retention on bacterial flocs and virtually all suspended solids within the bioreactor. As a result, the MBR has many advantages over conventional wastewater treatment processes. These include small footprint and reactor requirements, high effluent quality, good disinfection capability, higher volumetric loading and less sludge production (Stephenson *et al*., 2000; Judd, 2006). As a result, the MBR process has now become an attractive option for the treatment and reuse of industrial and municipal wastewaters, as evidenced by their constantly rising numbers and capacity.

3.1 MBR configuration

The membranes can be incorporated in the process in two ways:

- *Internal* The membranes are submerged in an aerated tank and permeation takes place under a vacuum, to the inside of the membrane (see Figure 1.13 a-b). Commonly used membrane configurations are hollow-fibre and plate and frame modules.
- *External* (*Side stream*) The membranes are placed external to the reactor and sludge is recirculated through the (tubular) membrane elements, where permeation takes place insideout (figure 1.13 c)

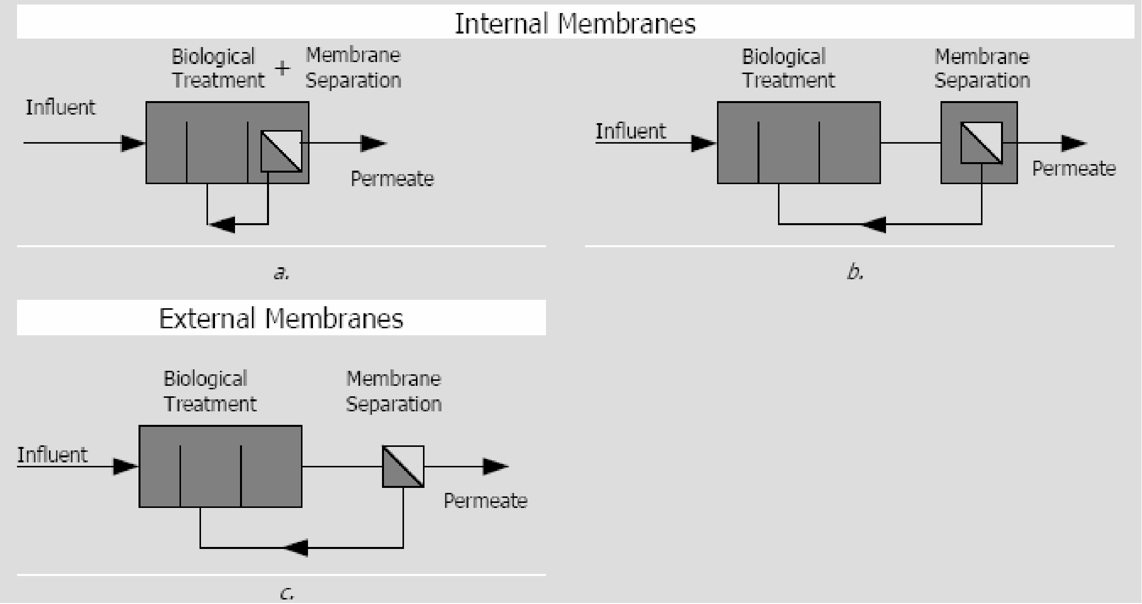


Figure 1.13 a-b-c. Different configurations of the MBR process: internal and external

The strict distinction between internal and external MBR is not maintained in practice, because in many applications there is a separate membrane compartment, with its own aeration and a circulation flow, as illustrated in Figure 1.13b (van der Roest et al., 2002; Meraviglia et al, 2003). A circulation through the membrane compartment, together with aeration is more effective for filtration performance than aeration alone (Chang and Fane, 2000).

However, membranes can also be coupled with bioprocesses for wastewater treatment in two other ways. Firstly, they can be used for the mass transfer of gases (such systems are not to be confused with so-called “membrane aerators” which is a term used for some fine bubble diffusers), usually oxygen for aerobic processes. Secondly, membranes can be used for the controlled transfer of nutrients into a bioreactor of the extraction of pollutants from wastewaters which are untreatable by conventional biological processes. The target pollutants are then removed in a reactor with the correct environmental conditions for biological treatment.

3.2 Advantages and disadvantages of membrane separation bioreactors

It is clear that the combining of membrane process with biological wastewater treatment processes result in advantages that were once exclusive to the former. In particular:

- Small footprint
- Complete solids removal from effluent. This perfect retention of the biomass enables to control SRT absolutely, which is a distinct advantage for bacteria having low growth rates, such as nitrifiers. Furthermore sludge bulking is not a problem.
- Effluent quality and disinfection. Complete mineralization of influent organic matter is facilitated by maintaining a high biomass concentration and the retention of high molecular-weight compounds by the membranes. As a result of membrane separation, SRT is independent of HRT. Membrane separation in bioreactors is most attractive for situations where long SRTs are necessary to achieve the removal of pollutants.
- No need for post treatment.
- Control and compactness of the whole system. Complete nitrification in a MBR was observed with a HRT as low as 7.5 hours.

- Sludge low/zero production rate. Conventional (activated sludge) processes for wastewater treatment transform organic pollutants into gas (CO_2 or CH_4), water and biomass. The cost of excess sludge treatment and disposal can represent up to 60% of the total operating cost (Canales et al., 1994). Therefore, the AS process transfers a water pollution control problem into a solid waste disposal problem. MBRs can work with high biomass concentration, decreasing the ratio of the food/microorganisms concentrations and amplifying the maintenance phenomena.
- High loading rate capability
- Rapid start-up
- Modular in design and retrofit of existing plants

- Some drawbacks to the process can be represented by:

- Aeration limitations. Owing to high biomass concentrations with a high specific activity in membrane bioreactors, there is a high consumption of oxygen due to oxidation processes and a high minimum maintenance energy is needed. The high oxygen consumption makes and advanced oxygen supply system necessary to keep the bioreactor compact.
- Membrane fouling. While the membrane-coupled activated sludge process has many advantages over the conventional activated sludge system, its practical application has been restricted due to the inherent membrane fouling problem, which leads to frequent membrane replacements and cleaning procedures. In this system membrane fouling is a result of the interaction between the membrane material and the components in activated sludge bulk, including feed components, cells, microbial metabolites, such as extracellular polymeric substances (EPS), etc.
- Membrane costs.

3.3 State of the art

There is regained interest at present in membrane bioreactors, initially developed in the 1970s, for the treatment of domestic and industrial wastewater. In particular, over the past 10 years, the use of membrane technologies has expanded significantly as a result of increasingly stringent discharge standards, increased use of reverse osmosis (RO) requiring pre-treatment processes and the decreased costs associated with membrane technologies. Designing the activated sludge unit with microfiltration (MF) or ultrafiltration (UF) modules in place of the secondary settler leads to the production of treated water of very low turbidity (< 0.5 NTU) and free of bacteria. Furthermore, this coupling extends the range of operation of the treatment plant previously limited by the settleability of the sludge, it is now possible to simultaneously obtain a low F/M ratio (< 0.2 kgCOD/kgMLSSd), small residence time (compact equipment) and high values of sludge age with the beneficial consequence of high efficiency of organic matter biodegradation and of nitrification. Uses of UF have included coupling UF with a membrane bioreactor to replace secondary clarification and filtration, as an advanced tertiary treatment process and as a pre-treatment for RO.

3.3.1 Drivers for MBR technology implementation

Of the many factors influencing the MBR market, those which are generally acknowledged to be the main influences today comprise:

- new, more stringent legislation affecting both sewage treatment and industrial effluent discharge (EC Bathing Water Directive (1976); Urban Wastewater Treatment Directive (1995); the Water Act (OFWAT, 2003); Integrated Pollution Prevention and Control (IPPC) Directive (1996); EU Landfill Directive (1999); EC Water Framework Directive (2000)
- local water scarcity;
- the introduction of state incentives to encourage improvements in wastewater technology and particularly recycling;

- decreasing investment costs (see figure 1.14);

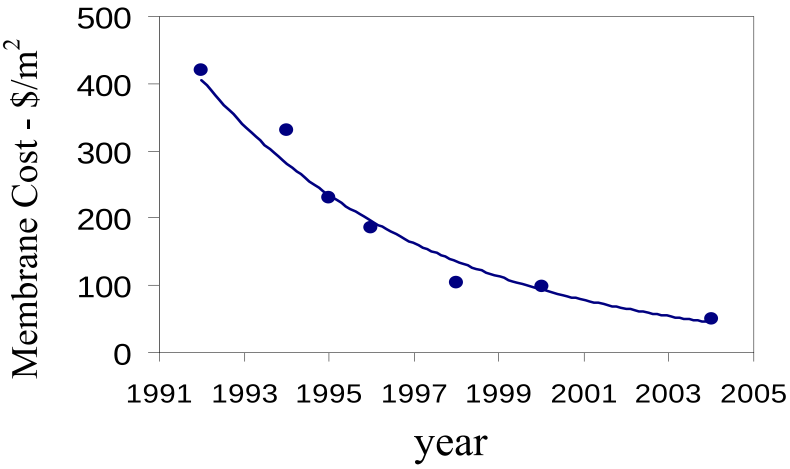


Figure 1.14. Capital cost of the MF membrane (adapted from Yoon et al. (2004))

- increasing confidence in and acceptance of MBR technology.

3.3.2 Early development of membrane bioreactors for wastewater treatment

Ultrafiltration as a replacement for sedimentation in the activated sludge process was first described by Smith et al. (1969).

In the 1970s the technology first entered the Japanese market through a license agreement between Dorr-Oliver and Sanki Engineering Co. Ltd. By 1993, 39 of these external membrane bioreactor systems had been reported for use in sanitary and industrial applications (Aya, 1994). Around the same time Thetford Systems, now part of Zenon Environmental, launched their version of an external membrane biomass separation system, the “Cycle-Let” process, for the aerobic treatment of domestic wastewater. In the late 1980s to early 1990s Zenon Environmental continued the early development of Dorr-Oliver in developing systems for industrial wastewater treatment, resulting in two successful patent applications. Zenon’s commercial system, ZenoGem®, was subsequently introduced in 1982. In 1989 the Japanese Government joined with many of the large companies to invest in the development of a low footprint, high product quality process that would be suitable for water recycling. This was in part demonstrated through the Aqua Renaissance programme ’90 (Kimura, 1991). One of the participant companies was Kubota, and they developed a flat plate immersed MBR. In 1982, Dorr-Oliver introduced the Membrane Anaerobic Reactor System (MARS) for the treatment of high strength food industry. Around the same time in the early 1980s two systems were being developed in the UK with either ultrafiltration or microfiltration membranes. This concept has been further developed in South Africa in the Anaerobic Digester Ultra Filtration process (ADUF).

While biomass separation MBRs have been extensively applied at full-scale, membrane aeration bioreactors (MABRs) and extractive membrane bioreactors (EMBRs) have only been operated at up to pilot-scale.

3.3.3 Current market of membrane bioreactors for wastewater treatment and present needs for research

Market analyst reports indicate that the MBR is currently experiencing accelerated growth, and that this growth is expected to be sustained over the next decade. The global market doubled over a 5-year period from 2000 to reach a market value of $ 217 million in 2005, this from a value of around $ 10 million in 1995. It is expected to reach $ 360 million in 2010 (Hanft, 2006). In Europe the total MBR market for industrial and municipal users was estimated to have been worth € 25.3 million in 1999 and €

32.8 million in 2002 (Frost and Sullivan, 2003). In 2004, the European MBR market was valued at € 57 million (Frost and Sullivan, 2005). Market projections for the future indicate that the 2004 figure is expected to rise annually by 6.7%; the European MBR market is set to more than double its size over the next 7 years (Frost and Sullivan, 2005), and is currently roughly evenly split between UK/Ireland (19%), Iberia (19%), Germany (18%), Italy (16%), Benelux (16%), France (12%). As far as the number of installations operating in Europe, by 2006 around 100 municipal full scale plants with a capacity > 500 PE were in operation in Europe, and around 250 large industrial plants with a capacity > 20 m^3/d (figure 1.15)

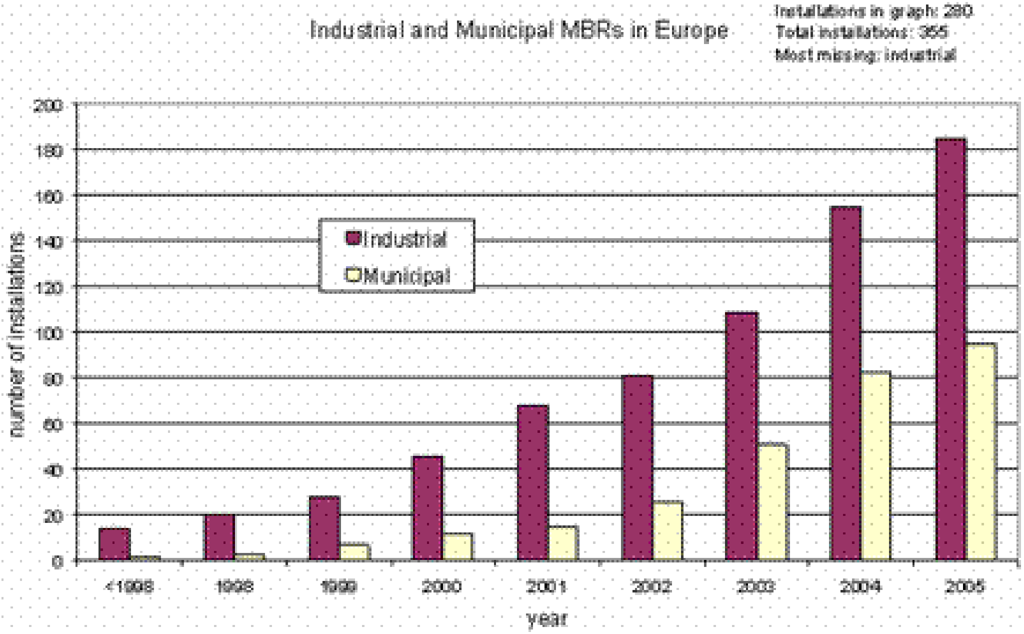


Figure 1.15. Industrial and municipal MBRs operating in Europe (adapted from www.mbr-network.eu)

Also the size of installations has grown from few thousands to hundreds of thousands population equivalent in only a few years. The first pilot-scale European submerged MBR plant for municipal wastewater was built in 1996 (in Kingston Seymour, UK), soon followed by the construction of the full scale Porlock WWTP (UK, commissioned in1998, 3800 PE), Buchel and Rodingen WWTPs (Germany, 1999, respectively 1000 and 3000 PE), and Perthes-en-Gatines WWTP (France, 1999, 4500 PE). A few years later only, in 2004 the largest MBR plant worldwide was commissioned to serve a population of 80000 PE (in Kaarst, Germany).

The future for the MBR market is thus generally perceived to be optimistic with, it is argued, substantial potential for growth. This level of optimism is reinforced by an understanding of the key influences driving the MBR market today and those which are expected to exert an even greater influence in the future. These key market drivers include greater legislative requirements regarding water quality, increased funding and incentives allied with decreasing costs and a growing confidence in the performance of the technology.

In the light of the before outlined scenario, the membrane bioreactors can no longer be considered as a novel process. This reliable and efficient technology has become a legitimate alternative to conventional activated sludge processes and an option of choice for many domestic and industrial applications (Le-Clech *et al.*, 2006). This firm belief supports the interest of the researchers who are investigating on this topic in order to have a better understanding of the mechanism of purifications in MBRs, the best plant configurations and operating practice that can optimize the removal performances and the capital and operation and maintenance costs, the solutions to reduce fouling phenomena and extend the membrane life. As a matter of fact the number of papers focused on MBR technology has had a rapid growth over the last years (figure 1.2).

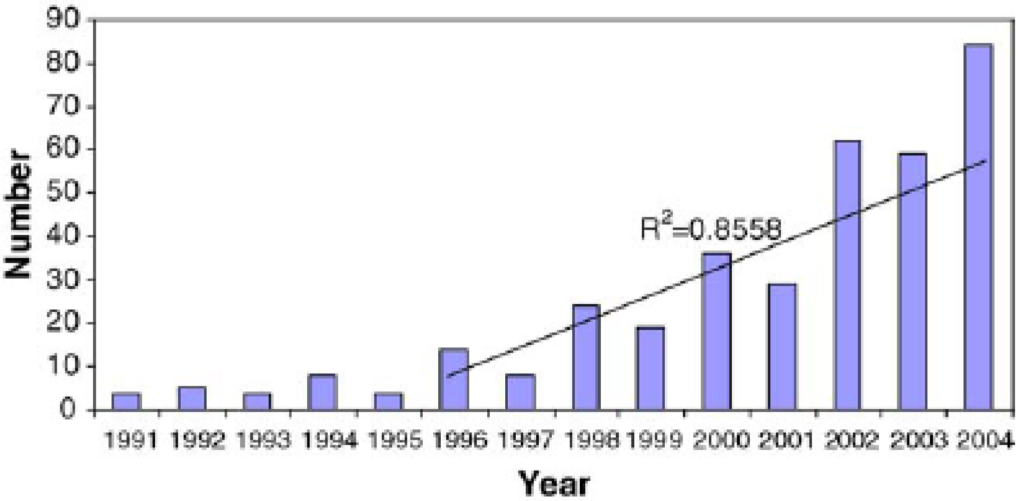


Figure 1.16. Scientific papers focused on MBR technology published worldwide on international journals (adapted from Yang *et al.*, 2006)

Furthermore, also the policy-makers confide in the widespread application of the MBR technology. Within the 6th FP the European Commission has decided to promote the development of the MBR technology while funding four projects entirely dedicated to research, development, capacity building and technological transfer in regards to this promising wastewater treatment process. These research projects will be implemented in parallel from October 2005 up to December 2009. Important technological breakthroughs, process improvement, knowledge and capacity transfer and building are expected, which will lead to better acceptance, competitiveness and broader implementation of the technology in both municipal.

3.3.4 Application of membranes as primary treatment of wastewaters

It has been commonly acknowledged that raw water quality impacts membrane fouling and performance.

Oh *et al.* (2000) employed three types of membranes, hollow fibre (MWCO 30000, PS), tubular (MWCO 100000, PVDF) and spiral wound (MWCO 50000, PS) to reuse the primarily treated sewage coming from the sewage treatment plant of Ulsan (Korea). Sewage taken from the primary treatment unit was fed into a 25 μm pre-filter and then supplied to the three membrane units. Each unit was composed of measuring devices for pressure and flowrates, a pre-filter with 5 μm pore size and a membrane module. The initial permeate flux of sewage was remarkably declined than that of pure water for each membrane, due to the increase of permeation resistance and fouling caused by impurities. The decline was most severe for the hollow-fibre module due to blocking and narrowing of flow passage by particles that could pass through a 5 μm pre-filter. The declines could be recovered by surface washing for the three modules and mainly by back-washing for hollow fibre module. Quality of permeates was not different one from the other in spite of the difference in MWCO since the portion of soluble substances, which could pass through he membrane, was considerable. The soluble TOC could be significantly reduced by activated carbon columns, nearly down to 30%. In consequence, the combination of membrane processes as the main separation unit and activated carbon columns as the post-treatment unit was found to be a successful system for the reuse of primarily treated sewage for industrial water.

Bourgeous *et al.* (2001) investigated the effects of wastewater particle size and concentration, mode of operation and backwash effectiveness on UF performance. The crossflow UF system consisted of 4 polysulfone hollow fibre membrane cartridges (HF 85-30-PM100, Koch Fluid Systems Inc.) each containing 3240 asymmetric membrane fibres with 7.9 m^2 filtering surface area. The fibres had an interior diameter of 0.672 mm, a nominal pore size of approximately 0.01 μm and a MWCO 0f

100,000 Daltons. Three methods were found to mitigate rapid fouling of UF membranes: (1) remove problematic particles prior to UF (e.g. employing pre-membrane granular filtration); (2) apply a more aggressive backwash period and/or (3) increase the shear rate in the fibre lumens by increasing water velocity (i.e. by recirculation). The processing of filtered primary effluent (30 mg/L TSS, 74 mg/L BOD_5) indicated that only 51% of the BOD_5 was removed leaving simple organic molecules that may be amenable to treatment via an attached growth process.

3.3.5 Application of membranes as secondary treatment of wastewater

One modification of conventional biological treatment processes is the replacement of the secondary sedimentation tank by membrane units: using this system, a higher degree of wastewater treatment can be obtained. By substituting the final clarifier in the conventional activated sludge process, a membrane device acts as a screen for the interception of suspended solids and microorganisms. In addition, various soluble organic substances, which might be either undecomposed organic substances contained in raw wastewater or microbial metabolic products produced during biological reactions.

Side-stream processes

Magara & Itoh (1991) first described the effects of factors as water temperature, suspended solids concentration, driving pressure and water velocity in a ultrafiltration unit external to a bioreactor for human excreta treatment, which is a typical application in Japan.

Defrance and Jaffrin (1999) investigated the critical flux concept as a means for achieving the operation of the bioreactor for long periods without chemical cleaning. Experiments were conducted on a membrane bioreactor containing 600 l of activated sludge, equipped with a 0.25 m^2 ceramic membrane. HRT was set at 24 h and SRT at 60 d, so that suspended solids concentration stabilized at 10 g/l. Two series of tests were conducted: at fixed TMP and at fixed permeate flux, set by a volumetric pump on the permeate. The critical flux was found to increase approximately linearly with velocity, reaching about 115 LMH at 4 m/s. Comparison of constant pressure and constant flux tests under same conditions showed that the critical flux was almost identical to the limiting or pressure-independent flux obtained at constant pressure.

Immersed membrane activated sludge processes

Several immersed membrane activated sludge systems based on the principle illustrated in Fig.1.17 have been described in the literature.

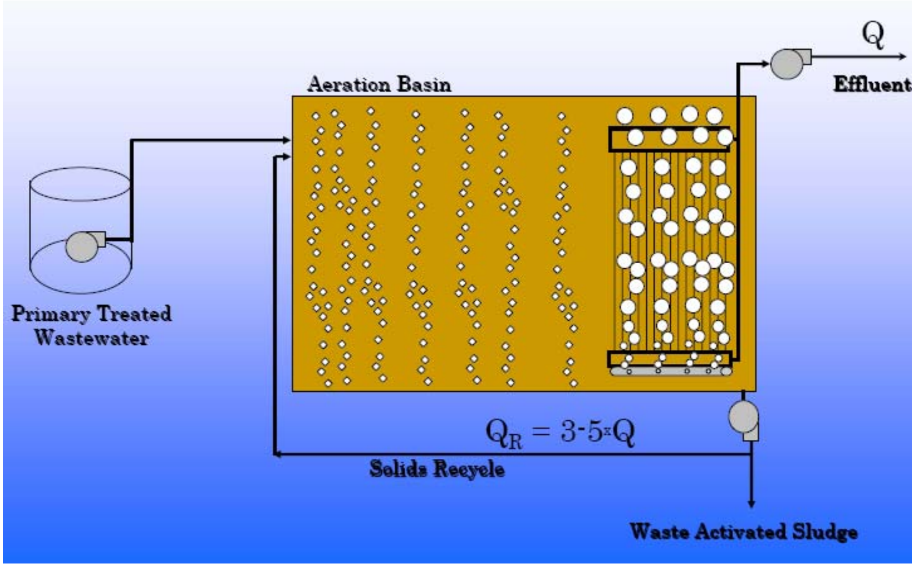


Figure 1.17 Principle of the immersed membrane activated sludge process

Their common features are:

- Microfiltration or ultrafiltration membranes with pore sizes in the range of between 0.01 to 0.4 μm;
- Direct immersion into the reactor where the biological treatment takes place;
- Operation in outside-in filtration mode under negative pressure and
- Renewal of the biomass to be filtered by airlift-induced circulation.

In the immersed membranes activated sludge process, membranes are used extensively, at low pressure and below critical flux, where fouling is minimal. This ensures simple, reliable and low-cost operation.

Chiemchaisri *et al.* (1992) investigated the organic stabilization and nitrogen removal using a household type hollow fibre membrane separation bioreactor of 62 l volume. The process employed direct solid-liquid separation by hollow fibre membrane inside an activated sludge aeration tank. Permeate flux obtained after 330 days of operation was 0.2 m/d under intermittent suction. High degree of organic stabilization was obtained in the system by operation without sludge wastage except for sampling purposes. Rejection of 4-6 log virus concentration by gel layer formed on the membrane surface was also observed.

Chiemchaisri & Yamamoto (1994) studied the effect of a short term temperature change on organic carbon oxidation, nitrogen removal and membrane permeate flux in a membrane separation bioreactor. The process was developed as a household wastewater treatment unit, employing direct immersion of hollow fibre membrane modules for solid-liquid separation in an activated sludge aeration tank. The organic carbon oxidation in the system was not deteriorated by a short term temperature change whereas nitrogen removal decreased significantly as the temperature dropped to 10°C. Reduction in the percentage of strict aerobic bacteria suggested that limitation of oxygen transfer probably resulted in the decrease of the amount of nitrifying bacteria and, thus, inhibition of nitrification at low temperature. A temperature decrease affected the permeate flux not only by increasing the viscosity of mixed liquor but also changing the properties of the cake layer, i.e. cake layer thickness and/or porosity. An hysteretic curve of gel and cake layer was used to show the effect of temperature changes on the resistance of gel and cake layer. By differentiating the resistances of the porous cake layer from those of the gel and the extracellular matrix, changes in the cake layer thickness and/or porosity of the cake layer could be used to explain the changes in the cake layer resistance.

Côté *et al.* (1997) conducted two pilot studies to demonstrate the process with high biomass concentration (between 5 and 15 g/l) and sludge ages of 10 and 50 days. The process provided a high degree of treatment in terms of suspended solids (100%) and organic matter (>96% for COD). Better than 6 log removal of total coliforms and better than approximately 4 log removal of naturally occurring bacteriophages were observed. Sludge production was 0.25 kgTS/kgCODd., about 50% smaller than a conventional activated sludge process. The immerse membrane filtration system was able to operate without chemical cleaning or handling the membrane modules and had an energy requirement for filtration of only 0.3 kWh/m^3 of wastewater treated.

Bouhabila *et al.* (1998) studied the influence of aeration conditions on the filtrate flux and compared the performance during start-up of three pilot-scale bioreactors with immersed hollow fibres operated at different sludge ages.

Cicek *et al.* (1998) investigated the long-term performance of a pilot-scale MBR system and its effectiveness in the degradation of high molecular weight compounds in wastewater by means of a 40 litres – MBR fed with synthetic wastewater.

Huang *et al.* (2000) treated synthetic wastewater with a submerged membrane bioreactor to investigate the organic removal performance, as well as the behaviour of soluble microbial products during long-term operation. Satisfactory COD, TOC and BOD removal efficiencies were achieved, averaging 90, 94 and 95% respectively. The accumulation of TOC in the supernatant of the bioreactor and its degradation after 5 months of operation was observed. Among this accumulation, macromolecules with a molecular weight (MW) > 100 000 accounted for 34%. A decrease in the supernatant TOC corresponded to a shift fro large to small molecules. The organic substances with a MW > 100 000 decreased from 34 to 16%, whereas those with a MW < 30 000 increased form 33 up to 52%. The accumulation proved to be inhibitory towards the metabolic activity of the activated sludge, as well as contributing to the poor membrane permeability of the mixed liquor.

Lesjean *et al.* (2000) tested two wastewater treatment processes at pilot scale to assess their performances and determine the most cost effective solution to upgrade the existing process: these are the BNR process and the MBR Biosep®. Suspended solids content was not detectable in the Biosep® effluent due to the microfiltration membrane. The Biosep® effluent was pathogen free and more than 99% of virus removal was achieved. Suspended solids level was higher in the BNR effluent than in the main plant effluent (respectively 34 and 10 mg/l) mainly because of bulking. TCOD reduction in the BNR was 56% compared to approximately 80% with the Biosep® process. In the Biosep® effluent TCIF was equal to soluble COD since the membrane retained the particles bigger than the pore size (around 0.03µm). the absence of BOD_5 in the Biosep® effluent showed that the biodegradable organic matter was completely removed by the process. Nitrification occurred in both pilot plants. As for the production of sludge the BNR process, which operated with a low sludge age (9 days) actually produced more sludge (29%) than the conventional plant. On the contrary, the Biosep® process operated at a very high sludge age (50 days) and the biological reactor produced 46% less sludge than the conventional plant.

Nah *et al.* (2000) applied a membrane bioreactor using submerged hollow fibre in laboratory scale conditions to treat household wastewater including toilet-flushing water. The bioreactor was aerated intermittently to alternate anoxic/oxic conditions while membrane filtration occurred during the aeration period to take advantage of the air bubbles for fouling control. After being operated for about 150 days, the initial flux and suction pressure were maintained almost constant at 0.01 m/h and 4-6 kPa respectively, indicating fouling control by air bubbling was very effective. With 10-15 h HRT and a very long SRT, 97% of TCOD and 100% SS could be removed. On average, removal efficiencies for total nitrogen and total phosphorus were 83% and 55% respectively. Ammonia and coliform bacteria were completely removed. Due to the long SRTand sufficient oxygen supply, fast and complete nitrification was accomplished regardless of operational mode, and denitrification was the rate-limiting step.

Pound *et al.* (2000) used hollow fibre microfiltration membranes to treat screened and degritted raw wastewater. The membranes were immersed directly in the suspended growth activated sludge reactor. Neither primary nor secondary clarifiers were used. Suspended solids ranged from 5000 to 2000 mg/l. The membranes could be maintained in service for long periods of time by using the pulsing-type backwash of 30 seconds every 15 minutes and reinforced with a weekly or semi-weekly extended backwash for 10 to 15 minutes with a relatively high chlorine solution. The MBR removed an average of 95% COD over the measured test period with MLSS ranging from 4660 up to 20780 mg/l. the average effluent COD of the pilot unit was 16 mg/l. With an average HRT of 2 hours at average flux and 1 hour at peak flux, the membrane bioreactor reduced the total N by about 35%. The bacteriological analyses demonstrated that the ZeeWeed membranes functioning in a suspended growth activated sludge system are capable of reducing coliform bacteria by a minimum of 6 logs down to a level of less than 100 MPN/100 ml in the permeate. The addition of disinfection to the treatment process train demonstrated a reclaimed water with a median total coliform concentration of less than 2.2 MPN/100 ml without exceeding a maximum of 23 MPN/100 ml in any sample. It was demonstrated that the system can produce an essentially pathogen-free effluent when confronted with naturally-occurring viruses, with more than 3-log removal occurring through the membrane and the remainder consistently achieved through the use of disinfection. Additionally, the challenged virological assay demonstrated that the membrane bioreactor system could produce a permeate from which a 4-log or greater removal of poliovirus, Type II, can be

achieved with a dose of 10 mg/l of chlorine and a 120-minute contact time. The membrane bioreactor system was capable of producing a permeate with a turbidity of much less than 2 NTU.
Huang *et al.* (2001) conducted four runs of a laboratory scale submerged membrane bioreactor for the treatment of domestic wastewater with HRT of 5,h and SRTs of 5, 10, 20 and 40 days respectively to clarify the effect of SRT on the performance and microbial behaviour. The membrane bioreactor process was capable of achieving over 90% removals both for COD and NH_4-N, on average almost independent of SRT. With prolonged SRT, concentrations of suspended solids and volatile suspended solids in the bioreactor increased accordingly, whereas sludge growth kinetic parameters, sludge yield and endogenous decay coefficients, declined slightly and exponentially, respectively. The mean sludge particle sizes at different SRTs were in the range 14.82 – 48.24 µm, providing a favourable environment for enhancement of mass transport. Characterized by an OUR, sludge specific activities both for organic decomposition and nitrification of NH_4-N varied with SRT. However, volumetric OUR of the MBR, representing the whole ability of the process for decomposing pollutants, were enhanced as SRT increased.

3.3.6 Application of membranes as tertiary treatment of wastewater

Disinfection

Microfiltration and ultrafiltration are being intensively studied in France and the USA for wastewater disinfection and removal of colloids and larger molecular weight organics. Because of the high quality of the treated water, membrane filtration is used in Australia, Japan and the USA for specific water reuse applications such as groundwater recharge, grey water recycling and industrial wastewater recycling. Moreover, the absence of bacterial regrowth and residual toxicity may give membranes important advantages over other processes for groundwater recharged and potable reuse.

Table 1.5. Comparison of technical-economic characteristics of advanced disinfection technologies (Lazarova et al., 1999)

Characteristics	Chlorination	UV	Ozone	MF	UF
Safety	+	+++	++	+++	+++
Bacteria removal	++	++	++	+++	+++
Virus removal	+	+	++	+	+++
Protozoa removal	-	-	++	+++	+++
Bacterial regrowth	+	+	+	-	-
Residual toxicity	+++	-	+	-	-
By-products	+++	-	+	-	-
Operating costs	+	+	++	+++	+++
Investment costs	++	++	+++	+++	+++

-: none; +: low; ++: middle; +++: high

If compared to other disinfection methods (see Table 1.5), membrane filtration turns out to be a highly efficient process for water disinfection.

Pathogens removal

One of the main drivers for MBR technology is the ability of the systems to disinfect, resulting in an effluent free from pathogenic microorganisms. This is an important consideration when discharge is to bathing waters or if the water is to be reused. Rejection of both bacteria and viruses by both MF and UF membranes is known to be significant (Table 6)

Table 1.6. Microorganisms rejection (adapted from Gander et al., 2000)

Membrane	Pore size (μm)	Average log reduction	Bacteria
Memtec	0.2	ND	TC
Memcor	0.2	3.8	FC
Renovexx	0.5 - 1.5	3.3	FC
Stork	0.05 – 0.2	2.5	FC
Starcosa	0.2	8	TC
DOW	0.2	<7	TC

In Sydney (Australia) pilot studies have been conducted on a large scale over the last few years by Peters and Pedersen (1991). The effluent from the secondary sedimentation tank was fed to a microfiltration unit. A comprehensive microbiological testing program established that all indicators of pathogenicity (bacteria and viruses) were removed by this system operated with gas backwashing. Testing for chemical quality showed significant reduction in BOD, turbidity and oil/grease as well as some reduction of heavy metals and phosphorus, suspended solids being zero. Consistent filtration rates over several months were achieved without significant biological membrane fouling. The study conclusively showed the capability of the microfiltration system to disinfect and clarify treated sludge (Table 7).

Table 1.7. Microorganisms rejection in the study by Peters and Pedersen (1991)

Parameter	Influent	Permeate	Removing efficiency
Total coliform (MPN/100 mL)	$8.5\text{x}10^4$ – $5.0\text{x}10^6$	0	99.9%
Fecal streptococci (MPN/100 mL)	$4.0\text{x}10^2$ – $2.4\text{x}10^5$	0	99.9%
Enterovirus TCID_{50}	10^2 - 10^6	No virus	99.9%
BOD (mg/L)	1 - 18	<1 - 7	83%
Turbidity (NTU)	6 - 37	0.6 - 2	92%
Total phosphorus (mgP/L)	2.5 – 9.4	1.8 – 7.9	22%

Dittrich *et al.* (2000) examined the possibility for MF to be a technically feasible and an economically competitive process for disinfection and phosphorus removal of secondary effluent. For bacteria and phosphorus removal, three different microfiltration systems (systems with flat sheet, tube and hollow-fibre modules) with a pore size of 0.2 μm were tested in small-scale pilot plants to find out whether they are suitable for municipal wastewater treatment. Total coliforms, *E. coli*, faecal streptococci and salmonella were removed to levels below the detection limit, less than 1 CFU/100 ml in the effluent of all three MF plants. Coliphage - as a surrogate organism for enterovirus - were significantly reduced with a 2-3 log removal, which means that the limit value for enterovirus laid down in the EU Bathing Water Directive can be met in the effluent of the MF plants. The average concentrations for total phosphorus (P_T) in the effluent were 60 μg/l for the Memcor and the DOW units and 90 μg/l for the Starcosa unit without the use of precipitants. With a low ferric dosage of 0.014 mol/m^3 prior to the MF, the average effluent P_T concentrations of all three MF units were lower than the target concentration of 50 μg/l (no polymer feed).

Lazarova *et al.* (2000) tested and evaluated some disinfection processes (peracetic acid, UV irradiation, ozonation, ultrafiltration and microfiltration) through bench and pilot scale studies. They achieved 3 log removal of total coliforms, faecal coliforms and faecal streptococci by 10 ppm of peracetic acid at 10 minutes contact time, by UV radiation at 35 mWs/cm^2 and by ozone at 5 ppm for 10 minutes contact time. The UF process showed complete removal of *Giardia*, bacteria and viruses. The permeate quality was excellent and made it favourable for groundwater recharge and urban applications. Similar results were observed for the MF process at the exception of viruses, which were detected in the permeate.

Organic matter removal

The presence of residual organic matter in treated waters is usually ascribable to a complex mixture of macro-organic molecules, derived from the degradation and decomposition of larger organic molecules (such as biological organisms, too), with a broad spectrum of functional groups, sub-structures and molecular weight distribution. These substances not only do affect the odour, colour and taste of water but also form complexes with heavy metals and pesticides and also react with chlorine, the most widely used oxidant for water disinfection, to from chlorinated disinfection by-products (DBPs). The latter, such as trihalomethanes (THMs) and haloacetic acids (HAAs) have been recently recognised to be human carcinogens. Among all the processes for organic residues from water UF has proved to be a valuable and effective technique in terms of removal efficiency though some drawbacks are often encountered such as process complexity and cost, flux decline due to the adsorption and deposition of foulants.

Aoustin *et al.* (2001) studied the impact of different parameters on ultrafiltration of natural organic matter with particular concern for the influence of solution conditions including pH, calcium concentration and type of organic as well as for operational parameters such as flux and membrane pore size. The fouling of UF membranes due to different organic fractions was studied by means of two UF membranes of different MWCO (10 and 100 kDa, respectively) with different water permeabilities (46 $\pm$ 5 LMH at 300 kPa and 620 $\pm$ 68 LMH at 100 kPa respectively). The first membrane gave high rejection and no flux decline whereas the second one did not achieve good rejection results and experienced high flux decline. The different behaviour was explained with a combination of a “critical flux” effect and varied pore penetration due to the different pore diameters of the membranes and ability of the organics to form aggregates with calcium.

Lopez-Ramirez *et al.* (2003) used a physical-chemical pre-treatment for a reverse osmosis unit for the reclamation of secondary effluents. The pilot plant was equipped with a variety of tertiary treatment units to prevent fouling and Biofouling of the cellulose-acetate reverse osmosis membranes used. The optimisation of pre-treatment involved application of various concentrations of lime to raise the pH to 10.3 – 12.1 and to stabilise the sludge generated, as well as different dosages of ferric chloride (15, 20 and 25 mg/l) for the coagulation and solid-liquid separation. Sodium hypochlorite (8 mg/l) and UV disinfection were used for microbiological control. The water quality obtained, under the optimum conditions (pH = 10.5; $FeCl_3$ = 25 mg/l; anionic flocculant = 0.5 mg/l; sodium hypochlorite = 8 mg/l) was high. Showing an average conductivity of 66 µS/cm and low COD values (4 mgO_2/l). the product water was suitable for injection into a groundwater aquifer to counteract seawater intrusion.

3.3.7 Differences between MBR and CAS

Activated sludge properties

The presence of a membrane for sludge separation has consequences in many ways. Defrance and Jaffrin (1999b) found out that filtering activated sludge from an MBR resulted in totally reversible fouling, whereas filtration of ‘conventional’ activated sludge led to irreversible fouling. MLSS concentrations are usually higher in MBR than in conventional activated sludge treatment. Adham et al.(2001) describe the results of a questionnaire sent around under four manufacturers (Kubota, Zenon, Mitsubishi and Suez- Lyonnaise des Eaux/Infilco Degremont Inc.) Twenty were returned, and the results show that applied MLSS concentration is around 10 mg/L. This influences rheological properties of the sludge. Defrance et al.(2000) compared conventional activated sludge with MBR activated sludge and found that MBR sludge was less viscous than conventional sludge. The same was observed by Rosenberger et al.(2002). Furthermore, with increasing shear rate, viscosity of the sludge decreases (Rosenberger et al., 2002), although in some cases the activated sludge behaves as a Newtonian fluid (Xing et al., 2001). Lastly, with increasing MLSS concentration, the viscosity increases (Ibid.). Another effect of the increased MLSS concentration is a decrease in a-factor5 Günder and Krauth, 1999. Cornel *et al.*(2003) measured a-values of activated sludge from full scale installations and found that with increasing MLSS concentrations the a-value decreased. With a MLSS concentration of 12 g/L, the average a-value was 0.6, whereas at conventional stabilisation plants, operating at 3-5 g/L MLSS concentration, values of about 0.8 are measured, see also Krampe and Krauth (2003). The maximum value enabling energy efficient operation of an MBR system is mentioned as 15 g/L (Günder and Krauth, 1999) and 10 mg/L (Itonaga *et al.*, 2004).

Activated sludge composition

It is quite difficult to generalise results from any installation, since each installation promotes different types of activated sludge. This has its effect on the microbial community that can be found in an activated sludge system. Nevertheless, it seems obvious that the presence of the membrane in an MBR system influences the biomass composition. Since no suspended solids are washed out with the effluent, the only sink is surplus sludge. From a secondary clarifier lighter species will be washed out, whereas in an MBR they will be kept in the system by the membrane. Furthermore, changes in SRT and higher MLSS concentrations might lead to changes in the microbial community. Witzig et al. (2000) describe results of measurements on the microbial characteristics of MBR sludge. Although significant changes were observed, compared to conventional activated sludge, the treatment efficiency with respect to COD-removal was the same. When applying Fluorescence in Situ Hybridization (FISH) to an MBR with extremely high sludge ages it was found that, compared to conventional activated sludge, a significantly lower fraction of all living bacterial cells (identified by DAPI) were detectable with EUB probes (Witzig et al., 2002). The majority of the cells were found to be in a non-growing state, reason why it is supposed that these cells are participating in the degradation process just to satisfy their maintenance energy requirements without further cell division, thus producing low amounts of excess sludge, see also Wagner and Rosenwinkel (2000).

Treatment efficiency/Removal capacity

Because the biological treatment in MBR is performed according to the principles known from activated sludge treatment, the types of conversion that can be achieved in MBR do not differ substantially from conventional activated sludge. COD, BOD and SS removals are high throughout all studies described in literature, which is mainly ascribed to the fact that the effluent is particle free (Côté *et al.*, 1997, Engelhardt *et al.*, 1998, DeWilde *et al.*, 2003). Mansell *et al.* (2004) performed measurements in which MS2 coliphage were seeded tot the influent of a Kubota MBR (characteristic pore size 0.4 μm) and a Zenon MBR (characteristic pore size 0.04 μm). Permeate concentrations showed a log removal range of 3.2 to 7.4 for the Kubota installation and 5.32 to 7.5 for the Zenon installation. All of the heavy metals detected in the influent were removed to levels below detection limit, as well as the VOC's and BNA's that were measured. Ahn *et al.* (2003) describe experiments in which phosphorus removal could be achieved in a lab-scale MBR treating household wastewater.

Average influent concentration for Ptot was 3.7 mg/L and effluent concentrations were averagely 0.26 mg/L. Effluent BOD was smaller than 10 mg/L, TSS < 1 mg/L. Cicek *et al.*(2000) describe experiments with an MBR equipped with ceramic membranes, and treating a synthetic feed. With varying SRTs (5, 10, 20 and 30 days) COD was removed for more than 98%. Also Kj-N was removed with efficiencies of more than 98%. Kubin *et al.*(2002) measured ammonium removal of more than 97%. Biological P-removal in a MBR is described by Adam *et al.*(2002). Ptot was always lower than 0.2 mg/L with sludge ages between 15 and 25 days. Investigations with P-spiking showed higher bio-P-potential in MBR compared to conventional activated sludge systems. Lesjean *et al.*(2002) describe experiments in which very low total nitrogen and phosphorus concentration were obtained with an MBR, with sludge ages of 16 and 25 days. Both pre-denitrification and post-denitrification were tested, without additional carbon source, where post denitrification seemed favourable. Innocenti *et al.*(2002) investigated the removal of heavy metals and nutrients by an MBR treating a mixture of industrial and municipal wastewater. The removal of Ag, Al, Ba, Cd, Co, Fe, Hg, Mn, Ni, V and Zn increased when SRT was increased from 10 to 190 days. As, B, Cu, Pb and Se removal decreased with longer sludge ages.

Sludge production and treatment

From small-scale lab studies a great advantage of MBR was the observed lower or even zero excess sludge production, caused by low loading rates and high SRT (Benitez et al., 1995). The amount of excess secondary sludge produced in larger MBR installations is somewhat lower than or equal to conventional systems (Günder and Krauth, 2000). When long SRT's are applied, sludge production of course decreases (Wagner and Rosenwinkel, 2000). The primary sludge production is higher, because of the higher degree of pretreatment. Sludge treatment is almost the same compared to conventional activated sludge systems. Recent developments in the USA show a trend towards lower MLSS concentration (<10 g/L) while the plant sizes are increasing (> 40,000 m3/day). SRT is selected based on the biological process requirements (Daigger *et al*, 2004). The dewaterability of waste activated sludge from MBR seems to be no problem, compared to aerobic stabilised waste sludge from conventional activated sludge systems (Kraume and Bracklow, 2003).

Space requirements

One of the advantages of MBR is its compactnes, because large sedimentation tanks are not needed. An interesting parameter in this respect is the surface overflow rates for the two systems. The overflow rate of a secondary clarifier is defined as the ratio of its flow and footprint i.e. the volume of water that can be treated per square metre of tank, see eq. 2-2. In practice, values around 22 m/d are used. For an MBR filtration tank, also an 'overflow rate' can be calculated. To this aim the packing density of the membranes has to be known, i.e. the amount of square metre of membrane area per square metre of tank. The overflow rate of a membrane tank can then be calculated as the product of the permeate flux and the packing density, see eq. 2-10.

$$OR_{MT} = packing\ density \cdot J$$

where OR_{MT} = overflow rate of the membrane tank [m/d]
packing density = membrane surface/tank surface [-]
J = permeate flux [m/d]

From several membrane suppliers the membrane packing density of the respective membrane tank is presented in Table 2-10. The overflow rate depends on the applied permeate flux, therefore results from calcualtions with two values of permeate flux are presented. With an average permeate flux of 15 L/m2Ph, the overflow rates of the membrane tanks are in the range 25-62 m/d which is up to three times higher than the overflow rate of a conventional secondary clarifier. Compared to an average overflow rate of 22 m/d with a secondary clarifier the space consumption for sludge water separation in an MBR is 10 to 60% lower when J=15 L/m2h, and 50 to 80% lower when J=25 L/m2Ph.

Table 1.8. Comparison of overflow rates of membrane tanks and clarifiers in CAS

Membrane manufacturer	Packing density (m^2 membr./m^2 membr.tank)	Overflow rate (m/d)

		J=15 L/m^{2}h	J=25 L/m^{2}h
Zenon	148	53	89
Mitsubishi	171	62	103
Kubota	68	25	41
Toray	137	49	82

A further reduction in foot print is caused by the higher MLSS concentration that can be applied in an MBR. Remark that the calculations do not take into account backflushings or relaxation periods which will reduce the ‘overflow rate’.

Membrane operation and maintenance

The most eye-catching difference between a conventional wastewater treatment system and a MBR is of course the application of membranes. Since most of the commonly applied membranes are quite sensitive, special attention should be paid to operate them properly and assure the required life time. With respect to the operation of membranes, there is a tendency towards nonfouling operation. This means that the membranes are operated with low flux rates, in order to prevent excessive fouling and penetration of the membrane with foulants. Flux rates between 10 and 35 L/m2h are commonly applied values nowadays. Furthermore, intermittent permeate extraction is applied to enhance air scouring effectiveness (Hong et al., 2002). To save energy, the aearion rate of the membranes may be related to the actual permeate flux (Howell *et al.*, 2004)

With respect to cleaning, common practice in submerged hollow fibre systems is the application of periodic maintenance cleanings. With intervals ranging from 7 days to about one month the membranes are backflushed or soaked with a solution containing cleaning agents, like oxidising agents. For plate and frame systems, which are not backflushable and are usually operated at lower fluxes, the intervals between chemical cleanings are even larger, up to months and a few times per year (see e.g. Gander *et al.*, 2000).

Cost comparison

High cost connected with MBR is often mentioned in discussions about applicability of MBR. It is interesting to evaluate the development in cost estimates over the past 7 years. Davies *et al.*(1998) made a cost comparison for two WWTPs, with capacities of 2,350 and 37,500 p.e.. With the assumptions they made (for example a membrane (lifetime of 7 years) they conclude that depending on the design capacity (i.e. 2 times DWF to be treated) MBR is competitive with conventional treatment up to a treatment capacity of 12,000 m3/day, see Table 1.9.

Table 1.9. Cost comparison MBR vs conventional (Davies *et al*, 1998)

Parameter		**MBR (Kubota)**	**Conventional**	**MBR/Conv**
Capital Cost				
2.350 PE	*	613.000	980.204	0,63
37.500 PE	*	7.292.524	3.642.259	2,00
Operating Costs				
2.350 PE	*/year	75.373	56.200	1,34
37.500 PE	*/year	602.101	264.730	2,27

*currency not specified

Engelhardt *et al.*(1998) after carrying out pilot experiments also made a cost calculation for an MBR with a capacity of 3,000 p.e., designed for nitrification/denitrification and treatment of 2*DWF. Investment costs were estimated at €3,104,000 (including pretreatment) and operational cost at €194,000/year. Adham and co-workers made a cost comparison for conventional activated sludge and MBR (Adham *et al.*, 2001). A comparison was made between MBR, oxidation ditch followed by membrane filtration and conventional activated sludge followed by membrane filtration. The exact assumptions and details of the cost estimate are not available, it can be concluded that MBR is competitive with the other treatment systems, see Table 1.10.

Table 1.10. Cost comparison between different treatment options

Alternative	Capital costs	MBR/Conv	Total Cost	MBR/Conv
	$		$/year	
Zenon MBR	5.068.627	-	783.000	-
Oxidation ditch+MF	5.587.800	0.91	876.000	0.89
Conventional activated sludge+MF	5.933.520	0.85	867.000	0.90

STOWA (2004) describes a cost comparison between an MBR installation and a conventional activated sludge system with tertiary sand filtration. The calculations are carried out for two new wastewater treatment plants with the aim of producing effluent with low concentrations of nitrogen and phosphorus. Investment costs are almost the same, and operating costs are 10-20% higher for MBR, depending on the capacity of the plant, see Table 1.11. The calculation does not take into account those parts that are the same for both treatment trains, like bar racks, waste sludge treatment, etc.

Table 1.11 Cost comparison MBR vs Conventional+sand filtration

Parameter – Capacity		**MBR**	**Conventional + sand filtration**	**MBR/Conv**
Capital costs				
10.000 PE	€	6.407.000	6.979.000	0.92
50.000 PE	€	23.091.000	22.901.000	1.01
Operating costs				
10.000 PE	€/year	748.000	686.000	1.09
50.000 PE	€/year	2.821.000	2.335.000	1.21

DeWilde *et al.*(2003) conclude that MBR will be more expensive in terms of capital and operational costs and that space availability is more likely to be a driving force for MBR application. Chang *et al.*(2001) report experiments with low cost membranes. The effect on investment cost is considerable, but operational problems hinder further application of low cost membranes. A drawback of the applied membranes is its limited disinfecting capacity.

Thus, it is clear that it is not easy to make a general economical comparison between MBR and conventional activated sludge systems. First of all, the reference system should not simply be an activated sludge system, but a system that produces an effluent of the same quality. Secondly, investment costs seem to converge for the two. If the difference between dry weather flow and storm weather flow (SWF) is small, MBR is more competitive.

Lastly, MBR is a modular system, i.e. easily expandable, which is often mentioned as an advantage of the system. However, this makes the system less competitive with conventional systems, since these become relatively less expensive per PE at larger scale.

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Chapter II. Experimental set-up

This chapter describes the experimental set up applied for the research activity. To achieve a widespread knowledge about the focused technology, three installations has been used:

1. the demonstration MBRs located in the Treviso WWTP, used to investigated for the carbon, nutrients and micropollutants removal;
2. the large pilot MBR located in the Falconara Vallechiara WWTP, used to investigate for the impact of the content of activated sludge on membrane fouling and to have a better understanding of the metals removal in ultrafiltration membrane systems;
3. the full scale MBR at Viareggio, supervised in details to carry out the full scale validation of the process.

In this chapter the pilot and the demonstration MBR installations are described, while the description of the full scale MBR of Viareggio is given in the last chapter of this digression. As far as the analytical plans, the descriptions are given in the following chapters just before the discussion of the results. This is to better transmit the link between the analytical activity and the findings pursued.

1. The demonstration MBRs

The demonstration membrane systems and the related facilities are located in the Treviso municipal WWTP, that is also the source of the real raw wastewater used to feed the MBRs.

2.1 The experimental flow-scheme

According to the experimental approach, the whole demonstration flow-scheme was engineered in a way to reproduce real scale problems as far as possible. All the equipments and facilities were taken from the industrial market, from the electro mechanics and the membranes to the software for data processing and acquisition. The whole flow scheme of the demonstration experimental set up is shown in figure 2.1.

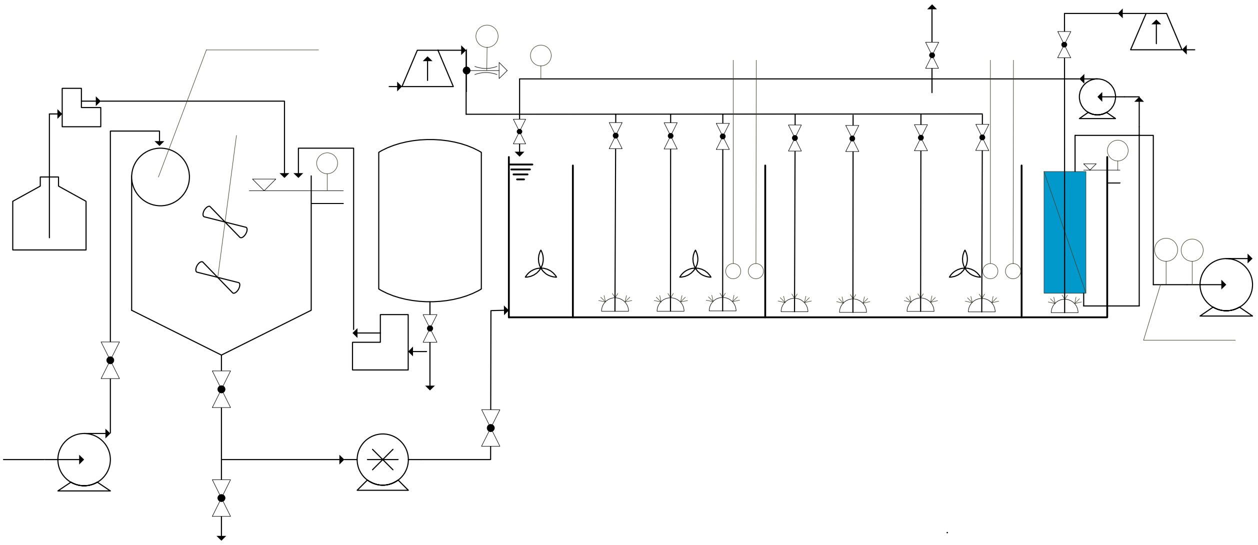

Figure 2.1. Instrumental flow-scheme of the experimental set up

2.1.1 Pre-treatments and external dosages

The influent wastewater is continuously taken after the primary treatments (screening and degritting) of the Treviso full scale WWTP by a centrifuge pump submerged into the ex-primary settler (figure 2.2). The flow is pumped to a fine screen (wedge wire geometry - openings 1 mm) (figure 2.3) and to the accumulation basin. This tank is made of stainless steel and has a volume of 10 m^3. It is equipped with an 8 paddles mixer that avoids sedimentation of the suspended solids. In this tank the feeding can be mixed with other influent streams (i.e.: external carbon sources, salts of nitrogen and phosphorus) that are stocked in tanks nearby (figure 2.4)

Fine screen (1mm)

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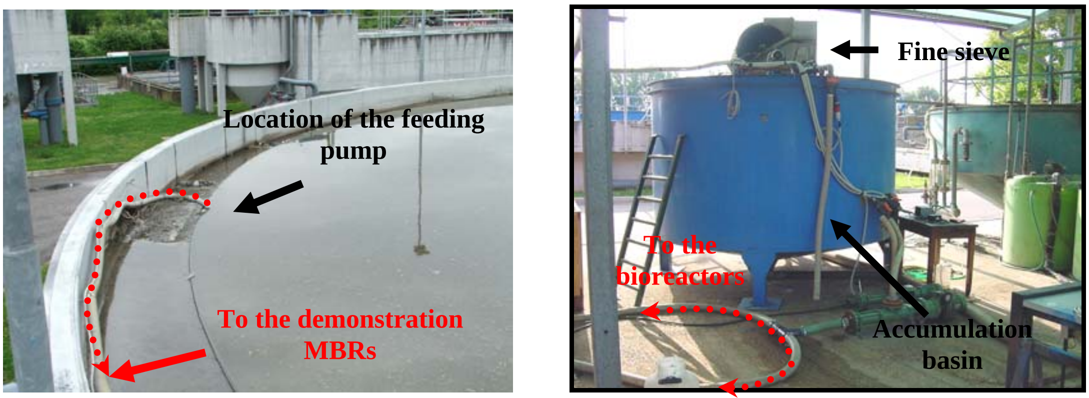


Figure 2.2 and 2.3. Raw wastewater inflow drawing and preliminary facilities

Figure 2.4. Tank to stock the external carbon source

The accumulation basin has an hydraulic retention time of 2.5÷5 hours, so also the real fluctuations of the municipal raw wastewater are partially maintained. After the accumulation tank, the flow is pumped to the MBRs by volumetric pumps equipped with manual frequency regulators, that allow to feed the plant with the desired constant flow.

2.1.2 The Membrane Bioreactors

The membrane bioreactors are realized in a stainless steel tank (figure 2.5a) which has an overall working volume of 22 m^3 and is divided into two parallel and hydraulically separated MBR lines of 11 m^3 (figure 2.5b).

Figure 2.5a The demonstration MBRs of Treviso

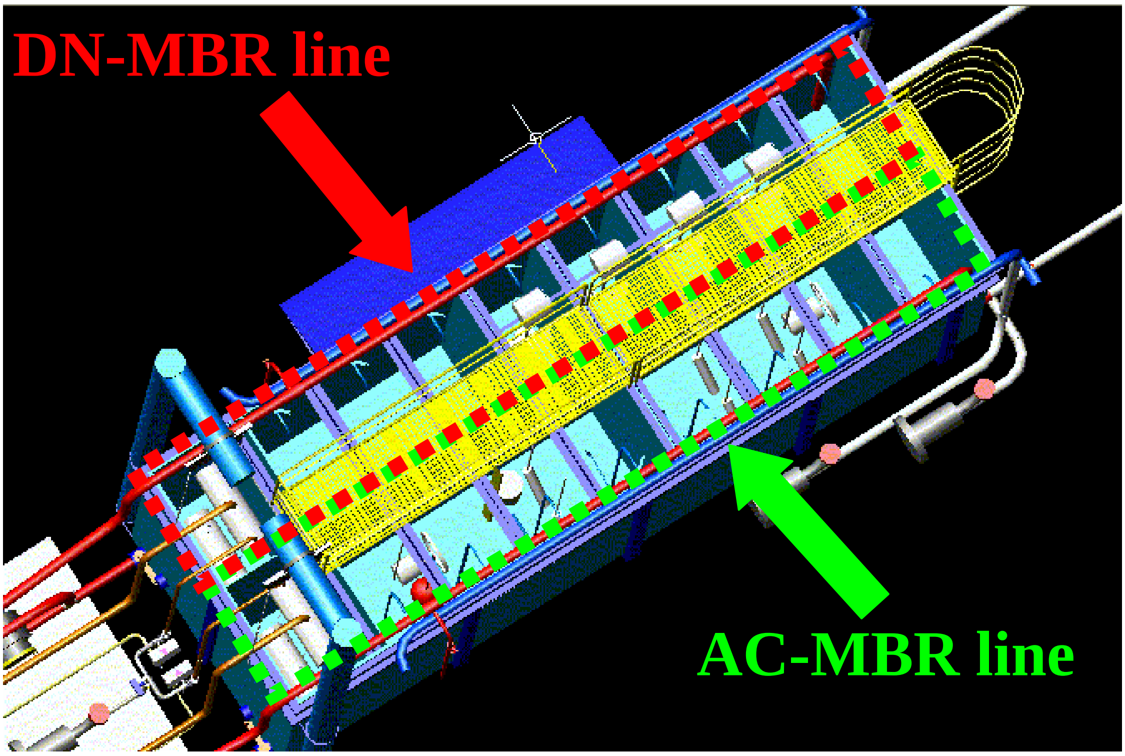


Figure 2.5b. 3D scheme of the demonstration MBRs

The first line is a dynamic system operating the intermittently aerated alternate cycles (AC) process (Battistoni and Chemitec, 1999; Battistoni *et al.*, 2003a; 2003b) and is the direct subject of this thesis, while the second line is less flexible and operated the common multizone denitrification-nitrification process and, in this thesis, is used only to compare the nitrogen removal in the two tanks (see chapter IV). As for the reactor volumes, the whole stainless tank is prearranged in a way to change the reactor volumes only installing stainless steel baffles (figure 2.6). The aeration is realized by micro-bubble tubular diffusers while submerged mixers are installed to keep suspended the activated sludge in anoxic periods (figure 2.7). Both the lines are equipped with the same submerged membrane modules which are described later in this chapter.

Figure 2.6. Modular plant

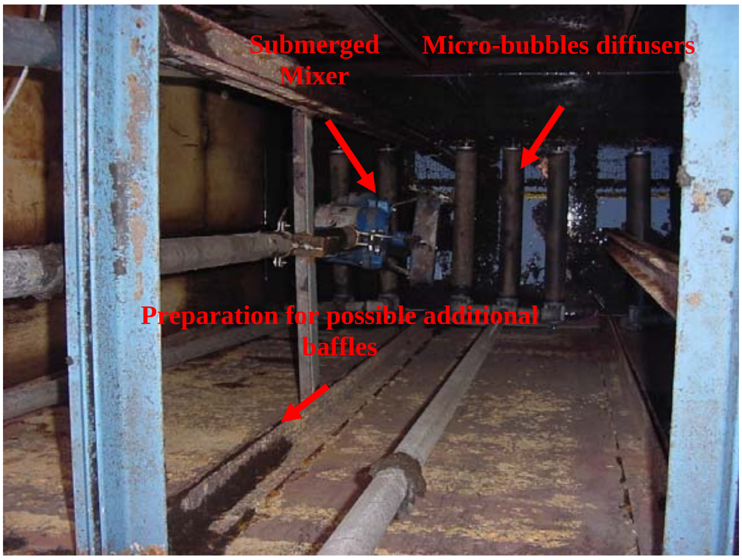


Figure 2.7. Micro-bubbles diffusers and submerged mixer

2.1.3 The Alternate Cycles-Membrane Bioreactor (AC-MBR)

The AC-MBR line (figure 2.8) is divided into four reactors in series: an anoxic selector provided only with submerged mixer; two completely stirred tank reactors (CSTRs) where the aeration and the mixing are automatically controlled according to the AC algorithm; finally the UF tank (1.4 m^3) which is equipped with submerged hollow-fibres membranes (see the following part of this paragraph).

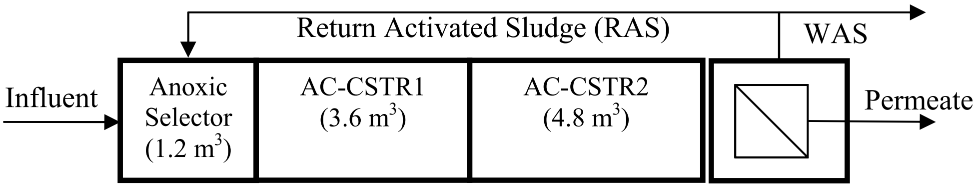


Figure 2.8 Configuration AC-MBR line

It is important to point out the aerobic/anoxic/anaerobic state of the activated sludge in the different reactors.

- The initial tank is intended to be a metabolic-based anoxic selector of floc-forming bacteria, so to prevent from the nocardioform foaming phenomena. However, the oxygen present into the tank (either dissolved or bound to other compounds - nitrates, sulphates etc) depends strictly on the return activated sludge from the membrane tank. In this last tank, in fact, the environment is always aerobic with DO levels up to 7÷8 mg L^{-1} and, consequently, a lot of oxygen could be recirculated to the initial tank. However, the low RAS required by the alternate cycles process allow to limit this possible drawback and to keep anoxic the activated sludge.

- The AC-CSTRs are, intermittently, aerobic and anoxic according mainly to a bending points based control strategy further discussed later.
- The membrane tank is always highly aerobic, because the aeration is here adopted to scour the membranes and to reduce the membrane fouling phenomena Therefore this is not only the section where the ultrafiltration is performed, but also an effective aerobic activated sludge bioreactor with a nominal HRT of 0.7÷1.4 hours.

The automatic control of the intermittent aeration

Intermittently aerated continuous systems using Oxidation Reduction Potential (ORP) and/pH and DO has been studied by many researchers in the past decade. These control systems are particularly attractive, in particular for small wastewater treatment plants, because of the considerably cheaper supplies of the sensors compared to the nutrients ones. However, it has to be pointed out that ORP and pH and DO are indirect measures of the nitrification and denitrification processes, therefore attention should be put on the control based on these signals. The first studies on this type of control dated back to the 80s and early 90s (Charpentier *et al.*, 1987; Wareham *et al.*, 1993; Hao *et al.*, 1996; Plisson-Saune *et al.*, 1996; Zipper *et al.*, 1998) and to date different control devices have been patented. Figure 2.9 depicts the typical ORP, DO, NO_3-N, NO_2-N, NH_4-N in an alternating aerobic-anoxic nitrogen removal bioreactor with extended aerobic and anoxic periods. As illustrated, the ORP in the reactor rises when aeration is switched on and drops when it is switched off- Two bending points may occur on the ORP curve: the "ammonia break point", caused by a sharp DO rise due to the depletion of ammonia nitrogen in the mixed liquor; and the "nitrate break point" or "nitrate knee", caused by the depletion of nitrate in the bioreactor. In the aerobic phase, also the DO has typical profiles which can be processed and used to identify the end of nitrification. Moreover, the DO measure is very important to fix absolute setpoints and avoid the over-aeration of the tank as following further discussed.

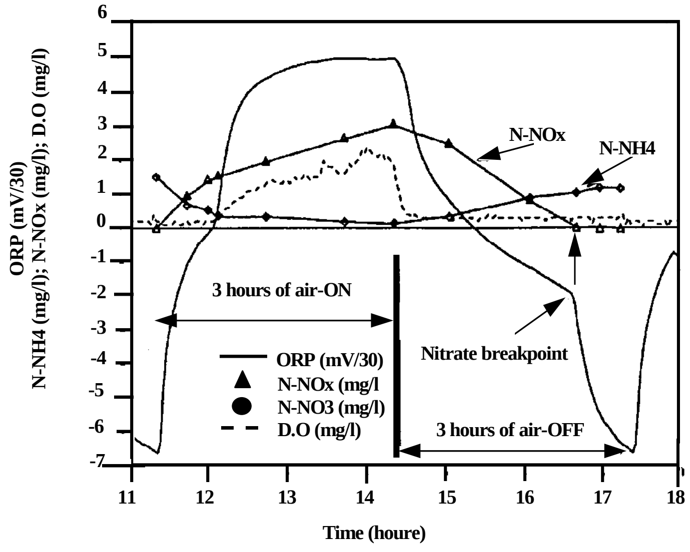


Figure 2.9 ORP, DO, NO_3-N, NO_2-N, NH_4-N typical profiles in an intermittently aerated bioreactor

According to the AC automatic control algorithm, the aeration of the AC reactors is a automatically controlled through a bending point based strategy which used the on-line curves of dissolved oxygen (DO) and oxidation reduction potential (ORP). Aeration is switched off (and submerged mixers are switched on) when the ammonia break point is detected, and is switched on (and submerged mixers are switched off) when the nitrate knee is detected. In this way, the lengths of the aerobic and anoxic phases are controlled to be just sufficient for complete nitrification and denitrification, respectively. However, the bending points are not always easy to be identified.

Ammonia break point on the ORP curve appears only when the DO is subject to a sharp rise from a low level to a significantly higher one at the end of nitrification. Similar difficulties may also be found with DO bending points (Olsson *et al.*, 2005). Furthermore, Paul *et al.* (1998) demonstrate that bending points are not detectable under particular conditions like over-aeration, under or over-loading, which can be almost common for real wastewater treatment system, especially for small treatment capacities. Finally, with a bending point based strategy, nitrification and denitrification come to their ends in the aerobic and anoxic phase, respectively. This is not necessarily an optimal strategy. For an intermittently aerated continuous system, high effluent ammonia and nitrate peaks may appear alternatively, resulting in high effluent nitrogen concentration, when the plant is over loaded with nitrogen. Therefore, the complete control algorithm has been provided with secondary branches which are based on setpoints of the time lengths of the aerobic and anoxic phases and of the absolute values of DO or ORP. These secondary branches represent a secondary safety level of the automatic control and are initially set by simulations with the activated sludge model, then they are adjusted after the initial trials operations of the plant so to reach the assessment which best fits the particular case study. Table 2.1 shows the setpoints which could be set to complete the automatic control of the process.

Table 2.1 Setpoints included in the secondary branches of the algorithm

	Aerobic phase		Anoxic phase	
	MAX	MIN	MAX	MIN
DO	X			
ORP	X			X
Time-lenght	X	X	X	X

The structure of the hardware (figure 2.10) is organized into two levels: the first controls the alternate cycles process; the second regulates the utilities used for the biological process.

In particular, the first level of hardware concerns the installed on-line signals (dissolved oxygen – DO- and oxidation reduction potential –ORP-) used to manage the intermittent aeration. The analog signals (4-20 mA) are transferred to the analog-digital (A/D) converter and then sent to the industrial PC (called “node card”), which is connected with the second level hardware. On the other hand, the second level hardware manages the electro-mechanics employed by the process. Principally, this second level guarantees the switching on of the blowers in the aerobic phase, contemporary to the switching off of the submerged mixers, and viceversa in the anoxic phases.

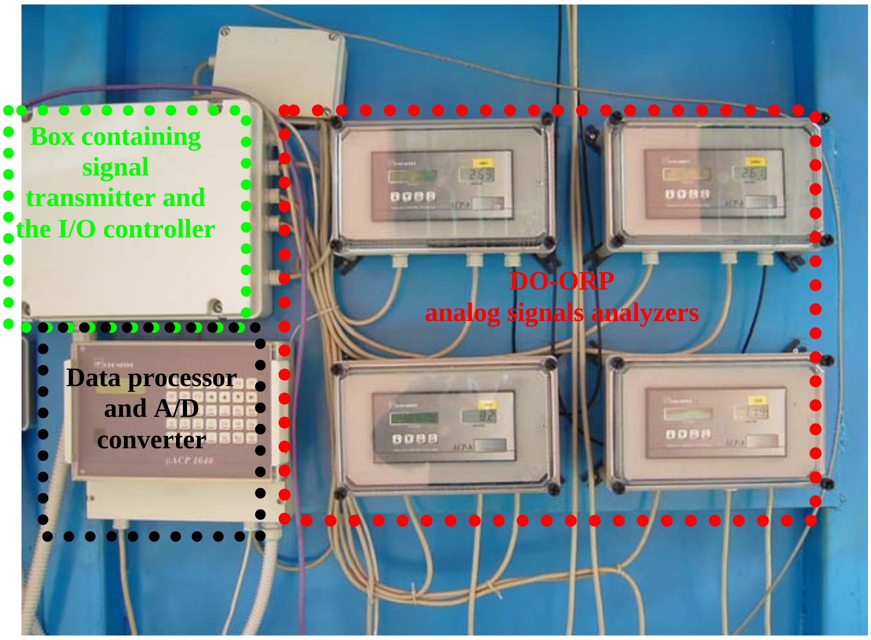


Figure 2.10. The hardware to control the AC process

The ultrafiltration membrane

Industrial modules of submerged hollow fiber membranes were kindly donated by the Zenon Environmental and adopted for the experimentation. The two parallel lines are equipped exactly with the same membrane area and also the membrane configuration as well as the measuring and control facilities are twins for the two parallel lines.

In particular, the ZeeWeed® 500 membrane module consists of hundreds of membrane fibers oriented vertically between two headers. The hollow fibers are slightly longer than the distance between the top and bottom headers and this allows them to move when aerated. It is the air that bubbles up between the fibers that scours the fibers and continuously removes solids from the surface of the membrane. Fibers have an outside diameter of 1.9 mm: they are flexible and have high tensile strength. Modules are generally assembled into cassettes which constitute the physical unit immersed in the process tank. Figure 2.11 shows the membrane module ZeeWeed® 500c used for the AC-MBR line. In this experimentation only three modules were immersed in each line because this was sufficient for the treated flowrates. This membrane is a barrier for the solid/liquid separation: the solid (the biomass) is retained within the reactor whereas the liquid (the treated water, or permeate) is discharged. Hollow fibers are self-supporting membranes with an outside diameter of less than 2 mm operated out-in with reference to water permeation. Since there is no distinction between the feed and the retentate this separation process is classified as a particular type of dead-end filtration.

During filtration, the membrane is intermittently aerated from the bottom with ON/OFF intervals of 10 seconds for the purpose of renewing the biomass to be filtered and agitating the hollow fibres. The permeation sequence can be set by the operator through a Program Line Controller (PLC). In particular, three sequences can be operated: (a) permeation/relaxation; (b) permeation/backwashing; (c) hybrid permeation/relaxation/backwashing. Over the whole experimentation the sequence "c" was adopted according to 4 repetitions of permeation/relaxation and permeation/backwashing at the 5th. The clean water stream (permeate) is stored in a vessel from which the effluent is withdrawn by overflow. The same permeate can be used in case of membrane backwashing.

The main characteristics of the membrane module are reported in Tab.2.2.

Table 2.2. Description of the ultrafiltration hollow-fiber module

Parameter	
Model	ZW-500c
Membrane shape	Hollow-fibres
Nominal pore size	0.04 μm (Ultrafiltration)
Filtration configuration	Submerged
Material	Poly-sulphone
Filtration mode	Negative pressure
Filtration direction	Outside - inside
Filtration area per module (m^2)	23.30
Modules per line (n)	3
Typical operating TMP, bar	0.1-0.6
Typical net flux, L/m^2h	15 – 30

Figure 2.11. UF membrane

Three protocols of chemical cleaning are used to control membrane fouling, two are performed to maintain the membrane permeability and the third is more intensive and it is carried out when the fouling phenomena have become unsustainable and no longer filtration is possible because of the elevated TMP. Following a brief description of the three protocols is reported:

1. Maintenance Cleaning in Place (mCIP): it consists of a sequence of relaxation and backwashing dosing a solution of hypochlorite or citric acid (concentration 0.2÷0.3 %) in the back flux. Its frequency is usually once a week or every two weeks. It lasts less than 1 hour and is carried out *in situ*, keeping the membrane submerged in the activated sludge;
2. Maintenance Cleaning in Air (mCIA): the cleaning protocol (sequence and chemicals) is similar to the mCIP, but it is performed *ex-situ* to increase the cleaning capacity of the chemicals. Since the membrane need to be moved from the tank, this cleaning is less frequent and usually is not included in the routinely operation and maintenance of the plant
3. Recovery Cleaning (RC): this intensive cleaning is either conducted *ex situ* or in the drained membrane tank to allow the membranes to be soaked in cleaning reagent. Recovery cleaning is performed immersing preliminarily the membrane module in the cleaning solution, then a longer sequence of permeation/relaxation/backwashing and an overnight soaking complete the cleaning. Therefore, at least one day is needed for the recovery cleaning.

The on-line sensors/analysers

Biological process

Besides the DO and ORP sensors used to control the alternate process, further on-line sensors/analyzers were installed into the MBR in order to evaluate the reliability of the commercially available systems, especially those which can represent a valid alternative to control the intermittent aeration. Table 2.3 lists the on-line sensors/analyzers installed into the demonstration plant together with the producer.

Table 2.3 On-line sensors installed into the demonstration MBRs

Measured parameter	*Producer*	*Method*
Ammonia	Danfoss (now Hach-Lange)	Colorimetric
Nitrates and nitrites	Danfoss (now Hach-Lange)	Photometric
Nitrates and nitrites	Hach-Lange	UV absorbance
Suspended Solids	Hach-Lange	Infrared and light scattering
Dissolved Oxygen	Chemitec	Potentiostatic
Dissolved Oxygen	Hach-Lange	Chemi-luminescence
Dissolved Oxygen	Endress+Hauser	Potentiostatic
Oxidation Reduction Potential	Chemitec	Potentiometric
Oxidation Reduction Potential	Endress+Hauser	Potentiometric

Membrane section

The filtration section is also provided with a number of on-line sensors and meters used to measure the permeate/backwashing flowrates, the operating TMP and, indirectly, the hydraulic level into the membrane tank. Moreover, the flowrate of the air for membrane scouring and the chemicals dosage are measured but the data are not logged. Table 2.4 shows the meters and sensors that concerns the membrane section.

Table 2.4 Sensors and meters for the membrane section

Measured parameter	*Producer*	*Method*
Permeate-backwashed flowrate	Endress+Hauser	Electro magnetic
Pressure	Endress+Hauser	Ceramic sensor

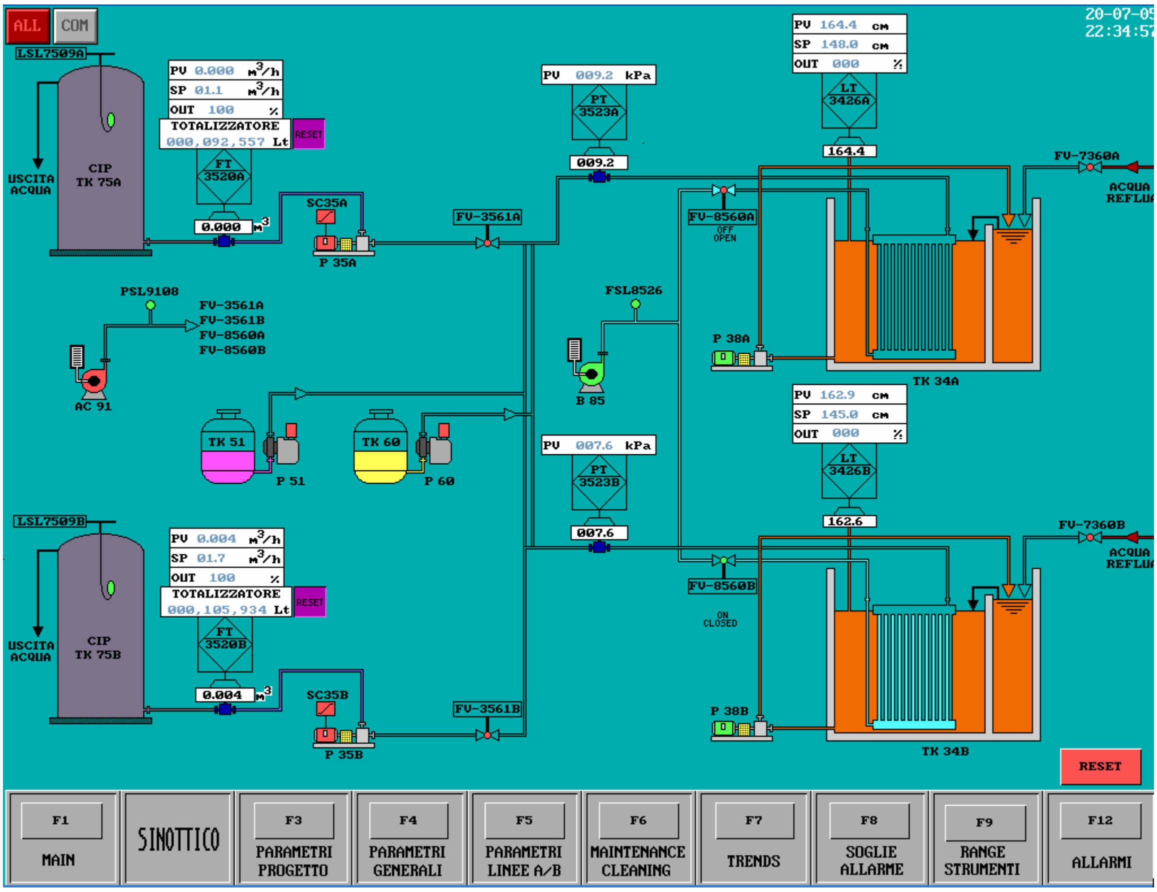
On-line data acquisition

Alternate cycles section

A software called “Gestimp”, usually adopted for the plant wide control in full scale systems has been adopted to monitor the biological sections of the experimental installation. This software includes different sheets dedicated to the different sections of a full scale real plant which operates the AC process. In this experimentation 16 analog (among the sensors listed in table 2.3) and 3 digital (coming from one blower and two submerged of the AC-MBR) signals were transferred through an RS232 cable from the industrial PC (Chemitec µACP1040) to the personal computer provided with Gestimp.

Membrane section

The membrane section was provided of a software to supervise, manage and control the filtration process Over the experimentation this system received six analog (permeate/backwashed flowrates, TMPs and levels in the membrane tanks) and nine digital signals (from the electromechanics of the membrane section). Through the same software it was possible to set the filtration sequence, the chemical cleanings, the permeate flowrates and the intermittence of the aeration for membrane scouring. Figure 2.12 shows the synoptic table where the different utilities can be individuated.



PV 0.000 m^3/h
SP 01.1 m^3/h
OUT 100 %
TOTALIZZATORE 000,092,557 Lt

PV 009.2 kPa

PV 164.4 cm
SP 148.0 cm
OUT 000 %

PV 162.9 cm
SP 145.0 cm
OUT 000 %

PV 007.6 kPa

PV 0.004 m^3/h
SP 01.7 m^3/h
OUT 100 %
TOTALIZZATORE 000,105,934 Lt

Figure 2.12 The synoptic table regarding the filtration section

2. The big pilot membrane plant

The big pilot membrane plant is located into the full scale municipal WWTP of Falconara Vallechiara (treatment capacity 85000 PE) and, precisely, in an area close to the secondary clarifiers and the disinfection.

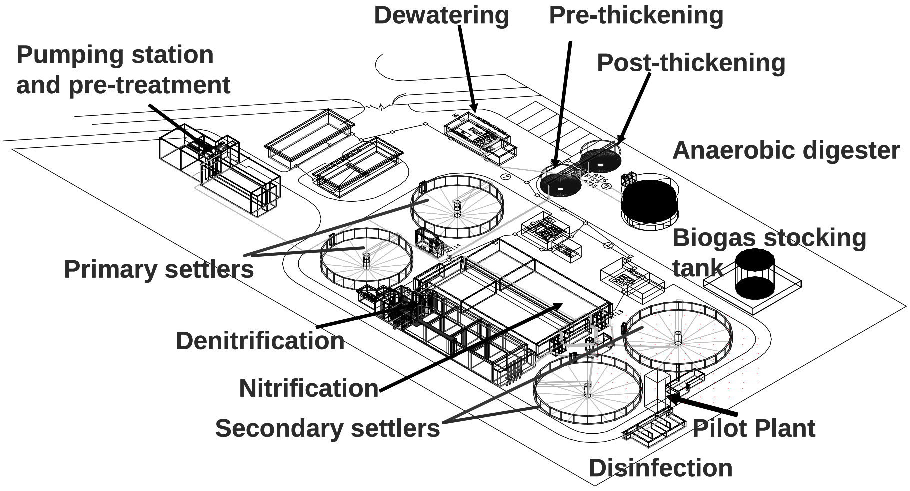


Figure 2.13 Location of the big pilot membrane plant

2.1 General description

The pilot plant is equipped with industrial hollow fiber module, manufactured by Zenon, which main characteristics are reported in Table 2.5 together with the main features of the reactor. It can operate at constant permeate fluxes, which can be set by a program line controller and a frequency regulator for the process pump. The filtration cycle is composed of suction (300 sec) and backwashing (30 sec).

At the end of each test, an intensive cleaning of the membrane was carried out submerging the module in hypochlorite solution (200÷600 mgCl L^{-1}) for 4÷12 hours, keeping always switched on the aeration to scour the membrane and, finally, performing 10÷20 minutes of suction/backwashing of the cleaning solution.

The pilot plant (figures 2.14, 2.15 a-b) was also equipped with a number of on-line sensors/analysers and meters that measured: TMP; permeate/backwashed flowrates; soluble COD, conductivity, turbidity into the permeate tank; temperature and suspended solids into the liquor to filtrate (MBR tank).

Table 2.5. Main characteristics of the membrane plant

Membrane Model	ZeeWeed 500	Membrane Type	Hollow fibre
Fibre external diameter (mm)	1.9	Membrane area (m^2)	21.6
Nominal pore size (μm)	0.04	Typical TMP (bar)	0,1 ÷ 0,6
Filtration type	Out to In	Permeate flux (LMH)	20 ÷ 30
Membrane configuration	Submerged	Reactor volume (m^3)	1.4
Module Dimension (mm) (height, width, thickness)	1000x700x200	Backwashing time	30 sec
Blower – Power (kW)	0.75	Mixer – Power (kW)	0.5
Analysis tank Volume (L)	210	Permeate tank Volume (L)	145

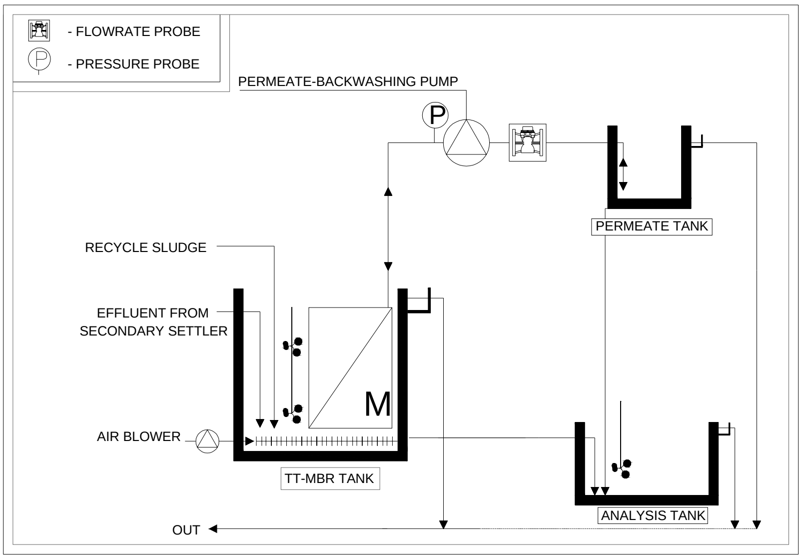


Figure 2.14. Simplified scheme of the pilot plant

Figure 2.15 a-b. The big pilot plant (a) and the facilities (b)

2.2 The plant configurations

The pilot plant can operate in two configurations: tertiary filtration (TF) (Figure 2.16a) and MBR (Figure 2.16b). During the TF test, the pilot plant is continuously fed with the secondary effluent from the full scale plant taken before the disinfection. As for the MBR configuration, a specification about the methodology is needed. In fact, the aim of the experimentation was to find out merely the effect of the membrane system, under different MLSS concentration, on micropollutants removal and on the sludge filterability. Hence, at the beginning of each test the reactor was fed with biomass taken from the full scale plant and the test lasted 5 days at most. According to this approach, the characteristics of the activated sludge into the MBR were always similar to those of the conventional full scale plant, in other words the modification of the biomass that can happen in MBRs was always avoided.

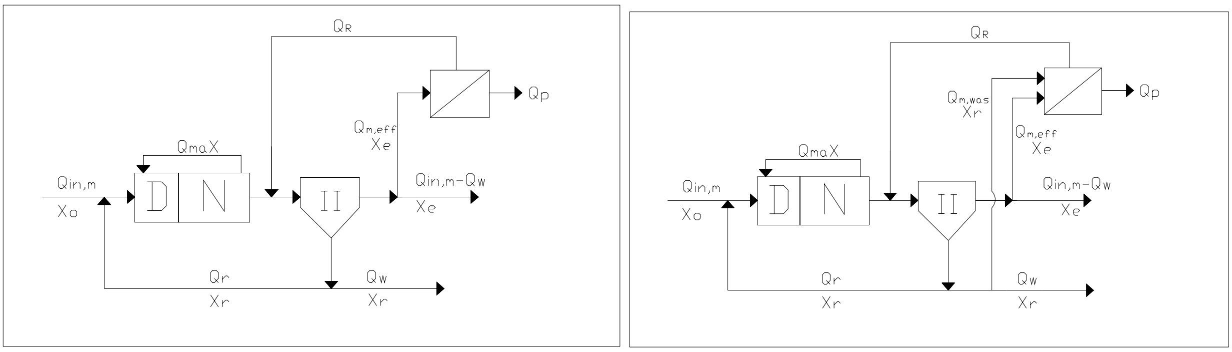


Figure 2.16 a-b. TF (a) and MBR (b) configuration

References – Chapter II

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Chapter III. Alternate cycles process: state of the art and upgrading design methodology

This chapter is aimed towards a better understanding about the alternate cycles process as a feasible way to improve the present italian scenario regarding the municipal wastewater treatment. Therefore, at first the italian scenario concerning the wastewater treatment facilities is briefly outlined. Secondly some information about the present options for alternating biological process are given. Then an empirical methodology to upgrade the existing plants by the adoption of the alternate cycles process is described. Finally the performances and further data coming from actually operating full scale plants are presented and discussed in order to understand the present state of application for this technology.

1. Policy for municipal wastewater treatment in Italy: "optimize what we have first"

A recent study commissioned by the Italian Environmental Protection Agency has outlined the scenario concerning the treatment of the italian municipal wastewater (APAT; 2005). The final report points out that at the moment more than 15000 WWTPs are operating in Italy and, although most of them have small treatment capacities (less than 2000 PE), the major part of the pollutant loads is treated by larger systems (treatment capacity larger than 100000 PE). The treatment capacity of all the existing structures can fit plentifully the national demand for the loadings of conventional pollutants (COD, N, P, SS). However, most of the plants have been constructed before 1990 and operate according to basic technologies that result, or will result, no longer suitable to meet the stringent required standard both for discharge and/or for reuse of the treated effluent. Therefore, there is a great interest in very performing and cost-effective technologies that can be applied not only to possible new plants, but also to retrofit the existing structures, so to improve drastically the quality of the treated effluents.

As far as the large WWTPs the study was deepened on a selected sample of 34 cases, with real treatment capacities in the range 30000÷400000 PE, which were considered representative of the whole italian scenario. The authors paid attention to: (a) the nutrients removal efficiencies; (b) the power requirements; (c) the excess sludge production; (d) the operation and maintenance (O&M) costs.

As far as the nitrogen removal, the configurations adopted for the biological process were: predenitrification-nitrification for 59%, pre and post denitrification for 6% and the remaining 35% has no denitrification at all. As a result, the content of total nitrogen in the treated effluent was in the range 10÷20 mgN L^{-1} in more than 90% of the cases.

As for the phosphorus, more than 50% of the analyzed plants does not operate any system to enhance the removal, nor biological nor physical/chemical. Therefore P is almost removed only by synthesis of new biomass. However, phosphorus is not a problem of major concern in Italy since a stringent normative law (Ministerial Decree 9/6/88) restricted drastically the presence of polyphosphates in detergents recipes. In fact, notwithstanding the lack of systems for P removal, the P content in the treated effluents was reported in the range 0,5÷2 mgP L^{-1} for more than 90% of the cases.

The power requirements of the selected plants were in the range 80÷110 Wh $PE^{-1}d^{-1}$ for almost traditional treatment schemes. These values increased up to 220 Wh $PE^{-1}d^{-1}$ for plants operating also tertiary treatments (i.e.: effluent ozonization, heat drying of the waste biosolids, etc.).

The net production of excess sludge from the plants, considered as final dry solid to dispose, is in the range 25÷35 gDrySolids $PE^{-1}d^{-1}$ for conventional plants.

The specific operating and managing (O&M) costs were evaluated both per cubic meter of treated water and per population equivalent (calculated considering a unitary discharge of 120 gCOD $PE^{-1}d^{-1}$), so to take into account possible dilutions of the influent wastewater. The O&M costs for conventional schemes were 6÷20 € $PE^{-1}year^{-1}$ and 0,08÷0,22 € m^{-3}, while they increased up to 14÷26 € $PE^{-1}year^{-1}$ and 0,17÷0,24 € m^{-3} for schemes with tertiary operation units. As for the main items that form to the overall costs, a descending order includes personnel and power requirements in the top positions.

The scenario about small WWTPs was not described due to a substantial lack of data. However, generally these systems adopt extended aeration processes, without any kind of biological denitrification or enhanced phosphorus removal. Furthermore, also specific power requirements and O&M costs can increase sensitively due to a normal scale-up well documented in literature (Metcalf & Eddy, 2003). However, the abandonment of this huge number of small systems is widely considered not convenient in many areas where it can involve the construction of long sewers system to collect all the wastewater discharges to large wastewater treatment systems.

In conclusion, the principle of "optimize what you have first" seems to be the winning strategy in Italy. Therefore, the strategy includes the up-grading of small and large existing WWTPs and the use of technologies that are both very performing for nutrients removal and cost-effective.

2. The alternate cycles system: a methodology for the WWTP upgrading

2.1 Features of instrumentation, control and automation in wastewater systems

The general methodology to adopt process control automation in waster systems has been well outlined by Olsson *et al.* (2005). The authors pointed out that in the context of control, wastewater treatment differs from most other processes on many aspects including: (a) disturbances; (b) process complexity; (c) operational objectives; (d) manipulatable variables; (e) sensors.

2.1.1 Disturbances

The disturbances are major reason why control is required and wastewater systems have a lot of them to cope with. Influent typically varies substantially both in its composition and in its flowrate, with time scales ranging between hours to months. Also, discrete events may occur from time to time. As a result, the plant is hardly ever in steady state, but it is subject to transient behaviour all the time. Furthermore, internal disturbances may be generated due to inadequate or inappropriate operations. Consistent performance must be maintained in the presence of these disturbances. Traditionally these disturbances were damped designing plants with large operating volumes, incurring in large capital costs. However, to date the treatment facilities are almost already constructed and the on-line control systems, which have been demonstrated to cope well with most of the disturbances, are a very attractive and appropriate solution both for new systems and for upgrading operation.

2.1.2 Process complexity

Biological wastewater treatment involves a large variety of biological and chemical reactions occurring in parallel mediated by a large consortium of microorganisms. A treatment system consists of multiple process units with strong interactions. The control action taken in one process unit may affect to a large extent of the performance of the downstream and even upstream (due to recycling) units. Obviously, the design of the process control has to take into account this complexity.

2.1.3 Operational objectives

The operational objective for a WWTP is generally expressed as to achieve the required standards with the least operation and maintenance costs. Therefore, two aspects should be considered when designing the process control: the particular way of expressing the discharge limits (i.e.: 24h- or 7d-average compliance with the limits) and the operation costs.

2.1.4 Manipulatable variables

Considering its complexity, a wastewater treatment system has a very limited number of manipulatable variables. These typically include air flows to control aeration and a number of internal recycling flows, and the excess sludge wastage flow. Best control aims to achieve the best performance that a particular manipulatable variable is capable of delivering towards the operational objectives, rather than to achieve a pre-specified value of the operational objectives.

2.1.5 Sensors

The lack of reliable sensors has been a major obstacle for the control and automation of wastewater treatment systems. However, in the last years a rapid development of sensors has led to attractive solutions of process control design. To date the costs of nutrients sensors are still quite high and other solutions of process control are preferred (i.e.: the alternate cycles process, base on the redox potential and the dissolved oxygen). Probably the next future will see a drastic change of control implementation under the widespread use of nutrients sensors.

2.2 Alternate cycles control design: a general procedure

The alternate cycles process has been recently recognized as good method to up-grade existing systems. In fact at the moment this process has been or is going to be applied in about 40 full scale italian WWTPs, which mostly come out from retrofitting operation. The methodology to retrofit the existing WWTPs by the adoption of the alternate cycles process is simple and involve very modest capital expenditure. In fact, the modifications of the existing civil structures are often not necessary. Generally, existing bioreactor needs only modification of the facilities in order to provide uniform air supply (fine bubbles diffusers are the optimal solution), for the aerobic phases, and mixing (submerged mixers are suggested), to keep suspended the biomass in the anoxic phases. Furthermore, the on-line sensors used to control the process, DO and ORP, are very reliable and operate a very consolidated technology that involve very affordable prices. This is why these sensors are already commonly applied in many WWTPs. To have a clear idea of the cost for the plant retrofitting, Battistoni *et al.* (2003) reports an overall specific investment costs of 53 € PE^{-1} to retrofit a plant with treatment capacity of 700 PE.

As far as concern the methodology to upgrade the municipal WWTPs by the alternate cycles biological process, Battistoni *et a.l* (2003) developed a simplified mathematical model that could be used to predict either nitrates and ammonia variations inside the reactor or in the effluent considering a completely stirred tank reactor. The model is based on few hypothesis: nitrification and denitrification follow a zero order kinetic, nitrates influent to the plant are not significant, total influent nitrogen can be assumed as ammonia (TKN to NH4-N ratio in the influent is 1.2); the nitrification potentiality of the biomass can well satisfy the requirements of the influent ammonia loadings. On the basis of these assumptions, a simplified solution for ammonia and nitrates mass balance during oxic and anoxic phases can be found according to Eqs 3.1-3.2 and 3.3-3.4 respectively.

$$NO_X - N = K_n X * t \qquad \text{Equ. 3.1}$$

$$NH_4 - N = NH_4 - N_{t1} + \frac{NH_4 - N_{IN} * Q}{V} * t - \left(\frac{NH_4 - N_{t1} * Q}{V} + K_n X \right) * t \qquad \text{Equ. 3.2}$$

$$NO_X - N = NO_X - N_{t_0} - \left(\frac{NO_X - N_{t_0} * Q}{V} + K_n X \right) * t \qquad \text{Equ. 3.3}$$

$$NH_4 - N = \frac{Q}{V} NH_4 - N_{IN} * t \qquad \text{Equ. 3.4}$$

$$t_c = \left(\frac{K_n X}{K_n X - \frac{Q * NH_4 - N_{IN}}{V}} \right) * \frac{NO_X - N_{MAX}}{K_d X} = \frac{NO_X - N_{MAX}}{\frac{Q * NH_4 - N_{IN}}{V}} \qquad \text{Equ. 3.5}$$

Where

NO_X-N=Nitric and nitrous nitrogen (mg L^{-1})

NH4-N=Ammonia nitrogen (mg L^{-1})

Kn=maximum nitrification constant (d^{-1})
Kd=maximum denitrification constant (d^{-1})
Q=influent flowrate (m^3d^{-1})
V=working volume of the bioreactor (m^3)
X=mixed liquor suspended solids (mg L^{-1})
t=time (d)
t_c=duration of the cycle (d)
$_{IN}$=influent
$_{t0}$=beginning of the anoxic phase
$_{t1}$=beginning of the aerobic phase
$_{max}$=maximum value

In the ideal conditions the duration of a cycle can be related to kinetic rates for nitrification and denitrification and influent characteristics or to the process performances according to eq.3.5. Therefore, once that K_d and K_n are established, the durations of anoxic and oxic phases can be calculated according to the influent nitrogen contents. Furthermore, the simplified model is useful to design the retrofitting of existing plants through the adoption of the alternate cycles process. My first activity was to further develop a methodology to upgrade municipal WWTPs by the application of the alternate cycles process that was first carried out on pilot scale and then validated on a full scale system. Following this experimentations are described and discussed.

2.2.1 Development on pilot scale

The bench scale pilot plant had a basic configuration like the small WWTPs. It was composed of one activated sludge tank (23 L), where the AC process was performed and one secondary clarifier (5.2 L). Real municipal wastewater was used to feed the plant. The desired nitrogen and carbon speciation (soluble and suspended) was reached according to the following procedure: the raw wastewater was settled for two hours, the clarified supernatant and the settled solids were separately collected. Both were stored at 4°C at most for four days. Feeding was daily prepared mixing fractions of settled solids and supernatant wastewater according to the previously determined ratios. Hourly the feeding flow-rate was automatically adjusted in order to reproduce the typical fluctuations of municipal wastewater collected by sewers systems and finally influent to the municipal WWTPs (figure 3.1).

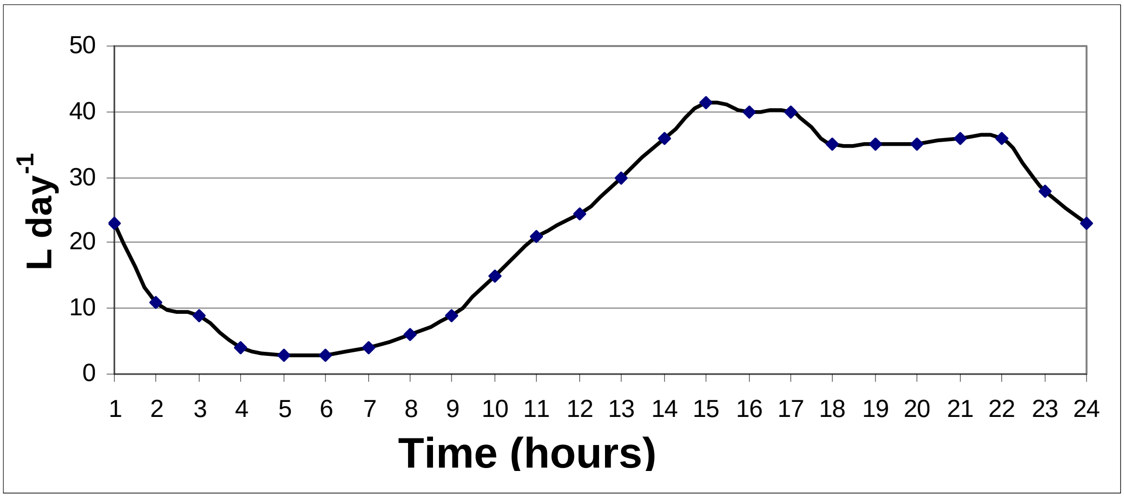

Figure 3.1 Hourly variation influent to the pilot plant

Using real municipal wastewater mixed according to the method mentioned before, the pilot plant was fed with different nitrogen loading rates (NLRs). This parameter is supposed to be a fundamental design datum for the biological reactor. Therefore, taking into account the typical per capita daily discharges of pollutants, the NLRs were related to the specific volume of the biological tank (Vsp expressed as litres per capita) according to eq. 3.6.

$$NLR = \frac{LTN_{in}}{V} = \frac{TN_U}{Vsp} \qquad \text{Eq. 3.6}$$

Where:
TN_u: total nitrogen unit loading factor (typical value in Europe: 12 g TN capita $^{-1}$ day $^{-1}$)
V_{sp}: specific per capita volume of the biological tank (litres per capita)
LTN_{in} : load of total nitrogen in the influent (kgTN day^{-1})
V: total volume of the biological tank (L)

An overview on the Italian existing and obsolete municipal WWTPs pointed out that: plants for small communities (treatment capacity less than 10000 PE) are almost operating the extended aeration process and actually work with V_{sp} of about 200 litres per capita; larger plants (more than 20000 PE) are almost operating a biological predenitrification-nitrification configuration and actually use up about 100÷130 litres per capita. Furthermore, considering the areas with combined sewers systems, WWTPs are often coping with diluted wastewaters and the bioreactor can operate with Vsp of 350÷400 litres per capita. Therefore, in the pilot experimentation six steady state periods were carried out according to NLRs from 0.03 to 0.1 kgN m^{-3} d^{-1} (table 3.1), in order to comply with the existing scenario concerning the municipal wastewater treatment.

Table 3.1. Nitrogen loading rates and per capita tank volume

Run	Loading	NLR (KgTN m-^{3} day^{-1})	Vsp ($L_{reactor}$/capita)
1	High	0.103	117
2	Medium – high	0.079	152
3	Medium	0.062	192
4	Medium-low	0.052	233
5	Low	0.039	304
6	Diluted – (wet weather)	0.028	434

Both raw wastewaters and activated sludge, respectively to continuously feed and initially seed the plant, were withdrawn from the same full scale plant. The operating parameters (table 3.2) were in ranges similar to those commonly adopted for full scale real systems.

Table 3.2. Operating parameters in the pilot system

Run	pH	Alk mg$CaCO_3$ L^{-1}	NLR (kgTN m^{-3}day^{-1})	MLSS (g L^{-1})	MLVSS/MLSS	SRT (day)	SVI (ml/g)
1	7.8	440	0.103	4.2 ± 0.9	0.67 ± 0.02	16	149
2	7.7	395	0.079	4.2 ± 1.1	0.68 ± 0.02	16	171
3	7.9	464	0.062	4.0± 0.3	0.67 ± 0.02	16	141
4	7.8	436	0.052	3.8 ± 0.4	0.66 ± 0.02	15	158
5	7.9	447	0.039	3.4 ± 0.8	0.63 ± 0.02	12	173
6	7.8	358	0.028	3.6 ± 0.6	0.62 ± 0.01	11	141

The MLSS content was lowered for diluted and low loaded runs, when hydraulic overflows are expected and the sludge settling property should be improved. Consequently, the sludge retention times (SRTs) were 15÷16 days for the more loaded periods, 11÷12 days for the low and diluted wastewaters. However, the SRTs were always sufficient to guarantee the suitable fraction of autotrophic bacteria for complete ammonia nitrification.

The influent municipal wastewater came from a combined collection system, therefore the COD/TKN ratio ranged from 6.7 to 9.5 and the readily biodegradable COD (rbCOD) was from 8 to 19% on the total COD (see table 3.3 for the main average physical-chemical characteristics).

Table 3.3. Physical and chemical characteristics of the influent

Run	NLR	TSS	COD	sCOD	rbCOD	TKN	TN	TP
	(kgTN $m^{-3}day^{-1}$)	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mgN L^{-1}	mgN L^{1}	mgP L^{-1}
1	0.103	406	436	91	52	62	65	6.5
2	0.079	361	409	91	50	49	52	5.4
3	0.062	364	482	109	68	54	58	6.4
4	0.052	253	353	107	67	45	47	5.4
5	0.039	344	357	74	29	38	40	4.9
6	0.028	195	268	59	22	20	28	2.0

The average effluent characteristics are given in table 4 and show the impact of different NLRs on the AC process. However, the effluent quality achieved always high quality standard within the range experimented.

Table 3.4 Physical and chemical characteristics of the treated effluent

Run	TSS	COD	SCOD	NO_x-N	NH_4-N	TKN	TN	PO_4-P	TP
	mg L^{-1}	mg lL^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mgN L^{-1}	mgN L^{-1}	mgP L^{-1}	mgP L^{-1}
1	2.0	33	27	6.1	5.3	8.3	14.3	2.1	3.0
2	2.0	35	29	3.5	2.4	4.5	8.0	1.6	2.2
3	2.5	35	25	6.2	2.7	4.7	10.9	2.5	2.9
4	2.4	33	24	5.9	2.3	4.3	10.2	2.3	2.6
5	1.5	32	25	5.0	1.1	3.8	8.8	1.6	2.0
6	1.2	35	28	3.0	0.2	2.9	5.9	1.0	1.4

The impact of low and high influent loadings is easily understandable even after a quick examination of the on-line patterns of DO and ORP. Figures 3.2-a and 3.2-b show the typical profiles respectively for medium-high and low-diluted strength wastewaters.

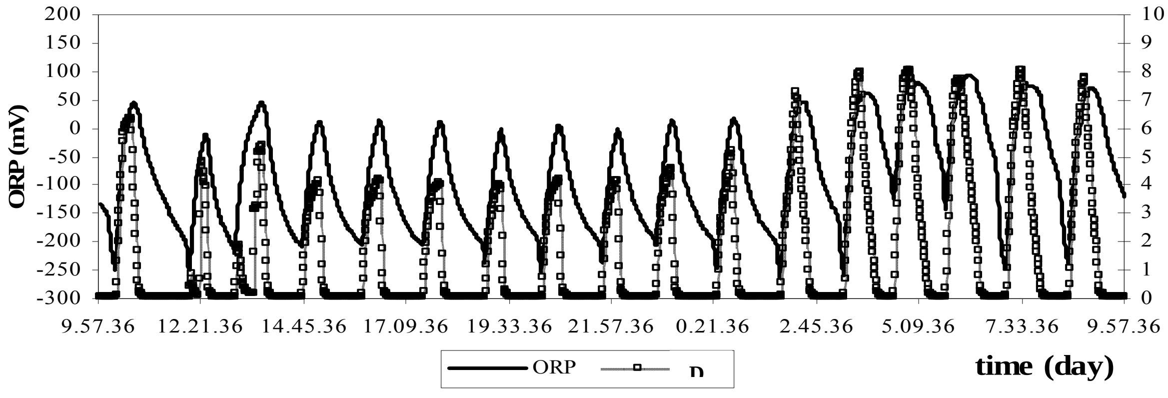

Figure 3.2a. Cycles per day during high nitrogen loading

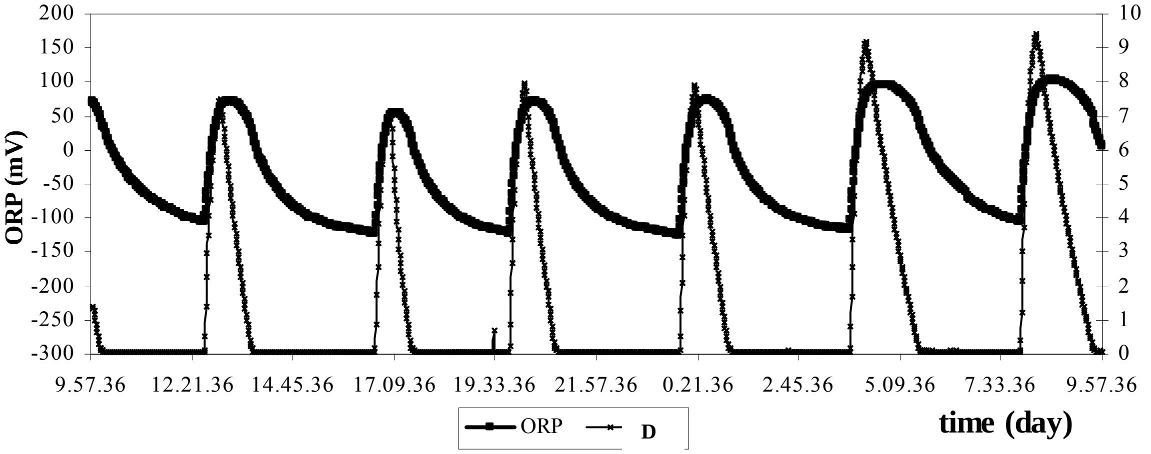

Figure 3.2b. Cycles per day during low nitrogen loading

The durations of the aerobic-anoxic phases were heavily influenced by the over-aeration phenomena. The air supply was unchanged run by run and the number of cycles per day was generally driven by the de-nitrification rates. Therefore about 17÷19 cycles per day were performed with high loadings, on the contrary no more than 7÷8 cycles were observed for low NLRs when the biodegradable carbon was wasted during the aerobic phase because of the over-aeration.

The analysis of all the cycles lets define the relationship between oxic and anoxic phases durations and NLRs. Generally the system had longer denitrification times respect to the nitrification (figure 3.3).

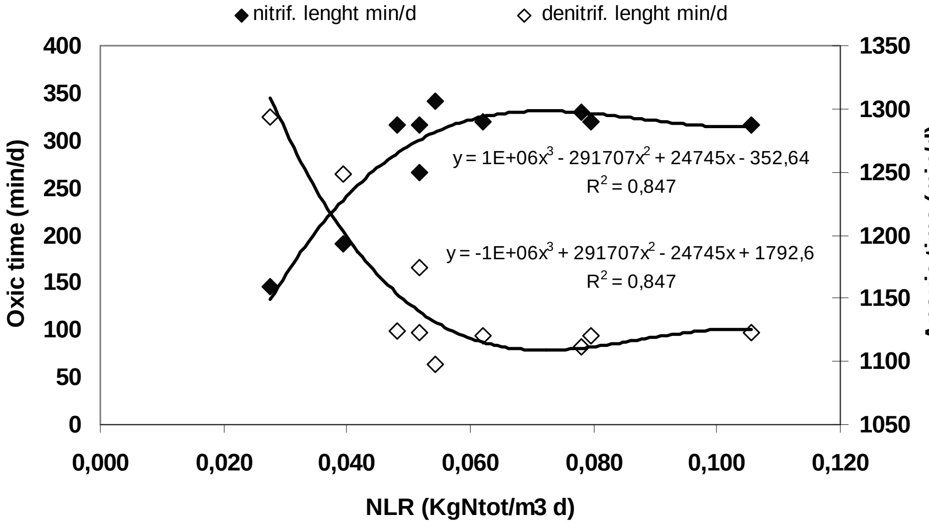

Figure 3.3. Durations of the aerobic and anoxic phases within a day

Nitrification in the range 300÷350 min d^{-1} is required for NLRs higher than 0.05 kgTN $m^{-3}day^{-1}$, while low loadings (0.028 kgTN $m^{-3}day^{-1}$) correspond to minimum nitrification and maximum denitrification time. Figure 3.3 confirms the behaviour of the AC process outlined by the DO and ORP curves (figures 3.2-a and 3.2-b). Starting from low NLRs, the lower loadings can well represent the hydraulic overloading of wet weather conditions, when over-aeration reduces the rbCOD that should be used for the following anoxic biological denitrification. Depending on the nitrification and denitrification rates, the durations of the anoxic and oxic periods reached a plateau for NLRs higher than 0.05 kgTN $m^{-3}day^{-1}$. This is a fundamental factor to design the plant up-grading. In fact, once known the durations of the aerobic and anoxic phases reached in the plateau of the curves, the NLRs can be fixed depending on the required standard for the treated effluent and the kinetic constants. Therefore, since the existing plants allow a reliable determination of the nitrification rate, equ. 9 gives the NLR that can safely be treated by the intermittent system

$$NLR_{treatable}=K_n*t_{aerobic\_plateaux}*MLVSS \qquad \text{(equ.9)}$$

The experimental durations of the oxic and anoxic phases were compared with the theoretical values coming from the simplified mathematical model.

In order to validate the simplified model, the maximum nitrification and denitrification rates were measured daily as maximum specific utilization rates of ammonia and nitrate by respirometry tests according to Kristensen *et al* (1992). Table 3.5 show the results obtained.

Table 3.5 Range for biological nitrification and denitrification rate

	Kn	Kd
	kgNH4-N/kgMLVSS*d	Kg NOx-N/kgMLVSS*d
Average	0.10	0.03
Min	0.03	0.02
Max	0.18	0.08
St. Dev.	0.02	0.02

Applying the simplified mathematical model, a good agreement between the experimental and theoretical results was found out (figure 3.4).

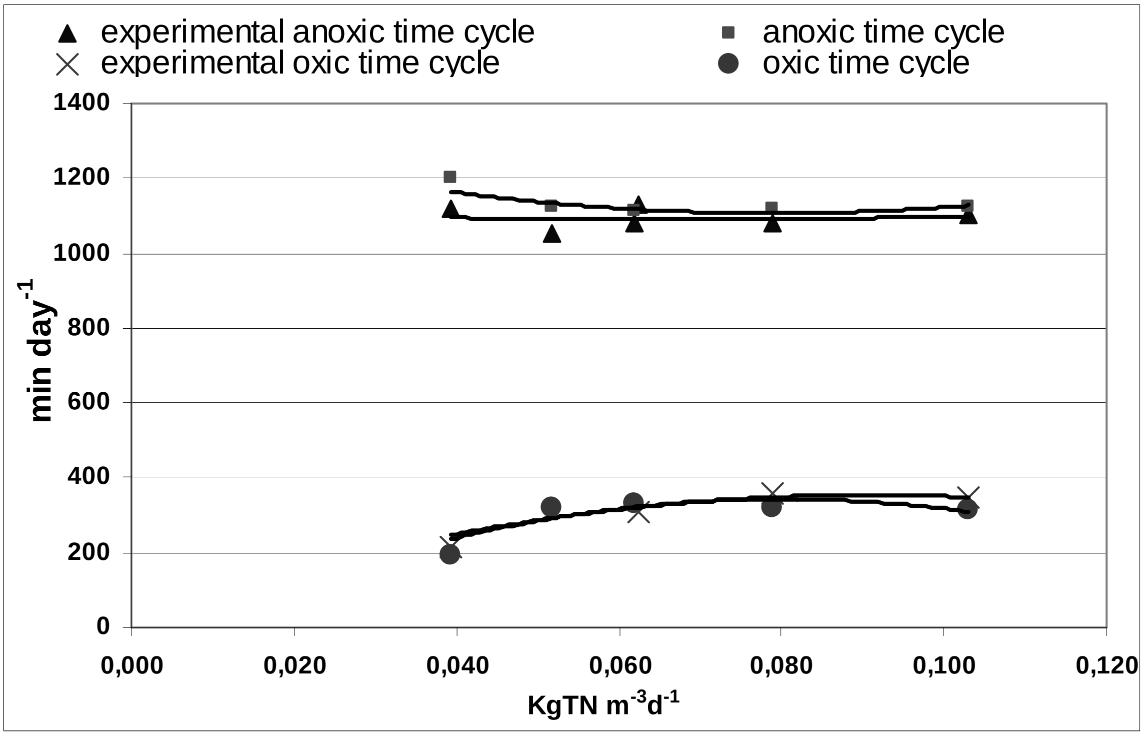

Figure 3.4. Durations of the anoxic/oxic cycles: comparison of theoretic and experimental results

The better agreement with the model was found out for the aerobic phases, while the anoxic had greater discrepancy especially in case of low loadings and consequent over-aerated conditions. This phenomenon was due to the imprecision of applying always the maximum denitrification constant rate, even when the over aeration caused shortage of readily biodegradable carbon for the denitrifying biomasses. On the other hand, the nitrification rate was rather invariant and corresponded to the maximum measured by the respirometry tests. Therefore, once known the nitrification rate and the duration of the aerobic phase, the simplified model could be used to know the design NLRs. As example of application, in this case the application of the proposed design strategy would lead to choose a maximum NLR of 0,1 kgTN m^{-3} d^{-1}, corresponding to 117 $L_{reactor}$ per capita. However, the result from the model should be adjusted by a safety factor ranging between 1.3÷1.5, in order: (1) to provide the AC plant of the sufficient treatment capacity also in case of seasonal over-loadings, (2) not to exceed with the V_{sp}, so to avoid over-aeration phenomena.

2.2.2 Full scale validation of the methodology

Since kinetic relations can change depending on different availabilities of carbon substrate and its degrees of biodegradability, aerobic and anoxic times can change accordingly and higher NLRs can be adopted for the upgrading. A full scale case study of upgrading is the Viareggio WWTP, where the nitrification and denitrification rates were respectively 0.04 and 0.08 kgN $kgMLVSS^{-1}$ d^{-1} and involved the durations of aerobic and anoxic phases shown in figure 3.5.

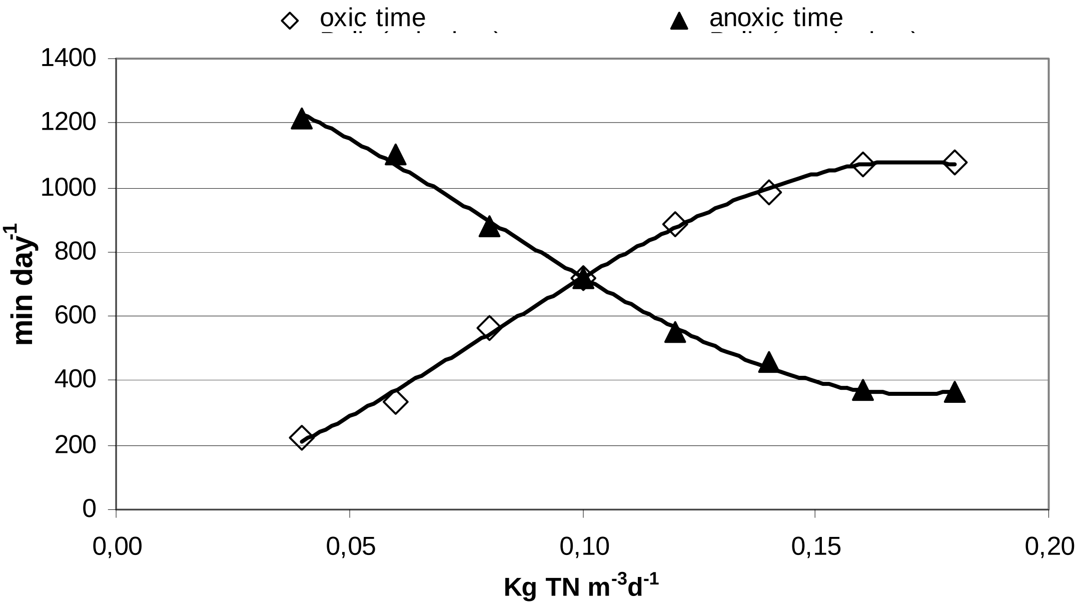

Figure 3.5 Aerobic/anoxic durations in a full scale WWTP

The aerobic time per day in the full scale case study is about 1100 minutes that allow a design NLR of 0.15 kgN m^{-3} d^{-1}, corresponding to about 80 litres of reactor per capita. This nitrogen loading has been really treated successfully from the full scale plant and can clearly confirm the theoretical calculations.

In the light of the before discussed validations, the simplified model can be used on the basis of three assumptions: (1) the influent C/N ratio is higher than 6÷7; (2) the maximum aerobic time is at most 1000÷1100 minutes per day; (3) the maximum nitrification and denitrification rates are reliable.

3. Performances of the alternate cycles process in conventional real WWTP

The success of the alternate cycles process is demonstrated by the number of papers published (Battistoni et al; 2002; 2003; 2006) in the last decade. In this paragraph the main findings that regard full scale application are briefly reviewed discussing: the nutrients removal efficiencies; the performances and the reliability of the control device; the O&M cost.

3.1 Nutrients removal

Aeration control based on the bending point detection can be also a non-optimal strategy. In fact for an intermittently aerated continuous system, high effluent ammonia and nitrate peaks may appear alternatively, resulting in high effluent nitrogen concentration, when the plant is overloaded with nitrogen. This is why the second safety level of the alternate cycles logic control provide set points on the DO and ORP levels and on the durations of the anoxic-oxic phases. Following the real performances are resumed to show that this strategy can be effective and reliable.

Battistoni *et al.* (2003) applied the alternate cycles process to a full scale small WWTP with treatment capacity 700 PE. This plant was easily retrofitted by three steps: (1) the volume of the basins, the blower and pump power, and the flow rate were verified to define the hydraulic and mass loading rate which could actually be treated; (2) the actual pollutant loads were measured, and their consistencies with the plant structures were verified; (3) the on-line sensors/analyzers for on line measurement of DO and ORP signals and the device for the automatic control were installed. The authors monitored the plant over a whole year so to include both dry and wet weather periods which changed the characteristics of the influent coming from a combined sewers system. The rbCOD was generally in the range 5÷16% and the C/N ratio was about 9 in in dry and 6 in rainy periods. In such a scenario, the effectiveness of nitrogen removal was evaluated by means of nitrogen mass balance. The effective nitrogen removal was greater than 70%. Furthermore, the authors pointed out the flexibility of the process control respect to the influent characteristics. In particular, the aerobic and anoxic phases changed according to the hourly or seasonal fluctuations of the influent characteristics allowing for the optimization of the nitrogen removal performances.

In a recent paper Fatone et al (2006) has monitored a 2500 PE alternate cycles plant over one year operation. The authors pointed out the real removal efficiencies of 95% and 77% respectively for the ammonia nitrification and nitrates denitrification. In this study also the activated sludge settling properties were investigated in order to verify if the dynamic conditions involved by the intermittent process could lead to problems of sludge settlement. The authors performed periodically the gravity flux curves and found the good effect of an anoxic selector before the AC bioreactor. As a matter of fact, no excess of effluent solids was observed also at severe liquor temperature (8÷10 °C).

A larger real WWTP (about 20000 PE) operating the alternate cycles has been described by Battistoni *et a.l* (2003). Also in this case the data presented in the paper came from the retrofitting of an existing plant where the alternate cycles process was successfully performed in the former longitudinal primary settler. The plant treated mainly municipal wastewater with C/N ratio in the range 9÷12 and rich in nitrogen (TKN_{in} 30÷ 45 mg L^{-1}). As expected, the nitrogen removal was substantially improved. Moreover, although the phases were only aerobic-anoxic, the luxury uptake phenomenon was observed thanks to the presence of suitable rbCOD in the influent. As a result, the yearly averaged P biological removal was around 60%. In conclusion, the alternate cycles process has been proposed as possible solution to achieve the standard for discharge in sensitive water bodies. Finally a recent paper (Battistoni *et al.*, 2007) has proposed the couple Alternate Cycles-Food Waste Disposers for the integrated management of organic kitchen waste and municipal wastewater in small decentralized towns. The authors applied this integrated solution to a rural town (less than 1000 inhabitants) located in a scarcely populated italian area (113 inhabitants/km^2). The existing WWTP, formerly operating an extended aeration process, was retrofitted with the adoption of the alternate cycles technology and the performances of nitrogen removal increased drastically. The alternate cycles process was considered very suitable for the integrated treatment because it is able to face the possible peaks of loading coming from the gound foodwaste. As a result the total nitrogen in the treated effluent passed from 30÷40 to 1÷10 mgN L^{-1} and the payback time of the integrated system was evaluated in 4÷5 years.

3.2 Performances and reliability of the control device

Paul et al (1998) showed that mass over or under-loading, over or under-aeration, nitrification inhibition and the insufficient carbon availability are the main factors involved in hindering the flex points of the DO and ORP profiles with time. Therefore, it is interesting to know the success of the bending point detection in real case studies. With further concern to the 700 PE plant, Battistoni *et al.* (2003) showed that the end of the optimal denitrification phases was easier (82% percentage of success) to detect than the denitrification (47%). The reason was ascribed to the over-aeration which often occurred during nights and wet weather events. However the right set-points stemmed the problem allowing for high performances. The authors finally concluded on the feasibility of the control strategy and the reliability of the control device. In larger plants the detection of the bending points was more successful for nitrification because the aeration of the sludge fitted more the demand from the inflow. Problems for the detection of the nitrates knee were observed for diluted wastewater when the C/N ratio decreased up to 4÷6. However, the setting of appropriate set points optimized the removal performances as far as possible. In conclusion, a control strategy that works according to two levels (bending points and set-points) is reliable for municipal applications.

3.3 Power requirements and O&M costs

The alternate cycles process is also renowned thanks to its power requirements lower than conventional processes. This advantage comes from the best use of the oxygen bound to nitrates when oxidising the organic compounds, moreover the lack of mixed liquor recycle allows savings in terms of pumping power requirements. These facets result in the specific power requirements published by Battistoni *et al.* (2003) the were in the range: 119÷193 Wh PE^{-1} day^{-1} for the over-aerated 700 PE plant and up to 35÷45 Wh PE^{-1} day^{-1} for the 25000 PE plant. Compared with the traditional activated sludge processes, the alternate cycles systems can lead to save 20÷35% of the power requirements. In the case study, the sustainability of the technology has been evaluated also in terms of O&M costs. On the basis of the real data along one year operation, the plant had an average treatment capacity of 2426 PE and the overall O&M costs were 1,63 € PE^{-1} $month^{-1}$, which come from the sources given in figure 3.6.

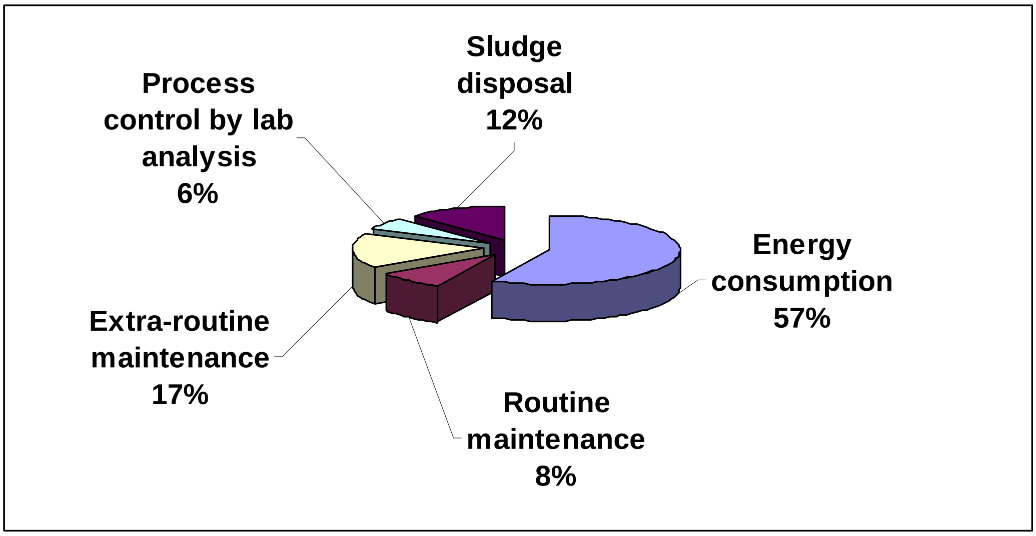

Figure 3.6. Splitting of costs for a 2500 PE alternate cycles WWTP

In the light of the success gained from the alternate cycles process, the idea of coupling this intermittent process to the membrane technology was rather easy to be taken. Therefore, following chapter will deal with the demonstration study of the alternate cycles-membrane bioreactor process.

4. Conclusions and future perspectives of the AC process

To date the alternate cycles process can be considered a consolidated system ready for its widespread industrial application in the field of biological wastewater treatment.

The technology can be used to retrofit existing municipal plants allowing also for the increase of the treatment capacity in terms of nitrogen loadings. As a matter of fact, in case of carbon source sufficient for the biological denitrification, the AC process can effectively treat up to 0,14÷0,16 $kgN \cdot m_{reactor}^{-3} d^{-1}$. This specific load, compared with the 0,06÷0,09 $kgN \cdot m_{reactor}^{-3} d^{-1}$

typically adopted for municipal systems, involve the possibility to exploit the existing facilites to treat also liquors rich in nitrogen. Further to the possibility to increase the nitrogen treatment capacity, the alternate cycles process has demonstrated that requires lower power than the conventional systems, thanks mainly to the better exploitation of the nitrate-bound oxygen and the low total recycles of activated sludge. Actually the full scale AC conventional plants need less power than conventional plants both for small systems (119÷193 Wh PE^{-1} day^{-1} for an over-aerated 700 PE plant) and for larger ones (up to 35÷45 Wh PE^{-1} day^{-1} for a 25000 PE plant). Moreover, the AC process has proved also to be suitable for the integrated management of the organic kitchen waste and municipal wastewater thanks to its relevant flexibility, able to face the peaking loadings coming from the ground foodwaste.

Next perspectives of the technology are addressed towards a twofold front: (1) the retrofitting of the existing WWTPs in order to create networks of plants automatically controlled and remotely managed; (2) the coupling to the membrane technology in the alternate cycles – membrane bioreactor system which is dealt with in the next chapters of this thesis.

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Chapter IV. AC-MBR process in a demonstration study: carbon and nutrients removal

Membrane solid-liquid separation in place of sedimentation in secondary settler offers several advantages that have been discussed in the first chapter. Although the benefits that can come from the membrane bioreactors have been widely stated, the debate about the most appropriate plant configuration is still open. In the first chapter the different MBRs, sidestream or submerged, have been illustrated concluding that the submerged modules are the most common solution for industrial application, mainly because of the lower power requirements. As for the biological treatment within the membrane bioreactor, the plant configuration plays a fundamental role for the optimization of removal performances and reduction of operating costs. In this chapter, different possible schemes for submerged MBRs are preliminarily described as from the literature; later the intermittent processes are better illustrated, so to introduce the demonstration study on the alternate cycles-MBR that is the major topic of this chapter.

1. MBR configuration for municipal application

1.1 Overview

Several interesting solutions have been proposed for submerged MBRs: most of them have been tested only at lab or pilot scale, but others have been commercialized and applied in industrial cases. Some configurations have been proposed for industrial wastewater. Bae *et al* (2003) proposed a MSBR (Membrane Sequencing Batch Reactor) for the treatment of diary industry wastewater and the same alternate configuration has been proposed to treat a mix of municipal and industrial wastewater (Innocenti *et al*; 2002). A novel membrane bioreactor with aerobic granular sludge (MGSBR) was applied for the treatment of synthetic wastewater with municipal characteristics. The authors pursued the main goals to control membrane fouling by changing the configuration of aerobic sludge and to study the feasibility of the system for municipal applications. Leiknes and Ødegaard (2007) proposed the moving bed biofilm membrane bioreactor (BF-MBR) and concluded that this system has the potential of operating with volumetric loading rates of 2÷8 kgCOD m^{-3} d^{-1}, HRTs up to 4 h and membrane fluxes up to 50 LMH, while the conventional activated sludge membrane bioreactors (AS-MBR) are reported to operate 1÷3 kgCOD m^{-3} d^{-1}, HRTs in the range 4÷10 h and membrane fluxes 15÷25 LMH. As expected, the multizone suspended activated sludge configuration is both the most studied and the most diffused in full scale applications. Ramphao *et al* (2005) recently concluded that incorporating membranes in biological nutrients removal activated sludge systems makes a profound difference to the design of the plant. The authors pointed out that getting free from the sludge settling properties increase the flexibility of the system because the mass fraction in the anaerobic/anoxic/aerobic tanks can be controlled with the inter-reactor recycle ratios. As a result varied plant schemes have been experimented and the membranes are usually included in the aerobic volume. Furthermore, also the worlds largest municipal MBRs adopt a multizone scheme, in fact both Nordkanal (Engelhardt *et al.*, 2006) and Brescia (Montagnoli *et al.*, 2003) are operating the classical biological predenitrification-nitrification system.

Even with concern to suspended activated sludge systems, the intermittent management of the aeration has been proposed by several authors to enhance carbon and nitrogen removal and optimize the oxygen supply. Yeom *et al.* (1999) experimented in lab scale an intermittently aerated MBR using a submerged hollow fiber membrane to treat real household water including toilet flushing water. The authors found out that fast and complete nitrification were accomplished and the denitrifications appeared to be the rate limiting step for total nitrogen biological removal. The performances were very satisfactory, however the long lack of anoxic phases in the membrane tank could produce unsustainable fouling phenomena (Jin *et al.*, 2006). Furthermore, the alternation of the phases was controlled by simple time set-points, limiting the flexibility of the process for the typical loads fluctuations in municipal wastewater. Kim et al (2007) performed a full scale MBR with modified intermittent aeration (MIA) and installing the submerged hollow fiber membranes into a separate tank which was always aerobic and located after the intermittent reactors. The authors controlled the sequence of the aeration/non-aeration by time set points and by the alternate management of the sludge recycle from the membrane tank. The process was investigated for 200 days of operation giving removals of C,N,P respectively of 95.2, 72.7, 71.4%. However such a control of the phases can be too rigid respect to the influent fluctuations, therefore it requires a large equalization basin increasing the capital cost. The on-line control of the intermittent aeration can optimize the flexibility of alternate MBRs and allowing also applications in small plants with very fluctuating inloading. Very successful application of intermittent aeration automatically controlled and membrane bioreactor has been proposed by Veolia Water with the BIOSEP® process (Tazi-Pain *et al*; 2002) that started experimentations in 1993 and built the first industrial plant in 1995. According to BIOSEP® the alternate phases are regulated on the basis of the redox signal and both nitrification and denitrification are performed in the same tank where also the submerged hollow

fiber membranes are installed. To date this process has been widely applied for municipal and industrial wastewater treatment and its market is still growing. However and obviously, due probably to the industrial patent there is a lack of scientific information about the real performances and the mechanisms that regulate the process.
The on-line control of the intermittent aeration in a membrane bioreactor has been implemented also in demonstration study. Here, the alternate cycles process has been coupled to the submerged ultrafiltration membranes according to the plant configuration described in the chapter II.

1.2 The approach of the study: demonstration scale and real low C/N wastewaters

This demonstration study was aimed to evaluate the real potential of the AC-MBR process for the upgrading of existing municipal treatment systems, achieving the reuse purpose at sustainable investments and O&M costs.
As discussed in the previous section, more than 6000 small WWTPs are actually operating in Italy. Actually, the available facilities could be sufficient for all the municipal needs and a sustainable improvement of the adopted technologies could improve the quality of the treated effluents, up to reach, in most cases, the reuse for non potable purposes. Such a policy could be interesting also to re-establish the equilibrium in the water balance for the rural and scarcely populated areas. As far as the characteristics of the wastewater typically influent to municipal wastewater, a reference to the sewers system may allow to understand the italian scenario. The sewers systems, in fact, are mainly combined and often affected by infiltration and dilution. This phenomenon can likely be coupled to low C/N ratios, that make difficult the total nitrogen removal. Therefore, this study was focused on the treatment of real low C/N wastewater by the AC-MBR process. The study was aimed to explore the potential of the AC-MBR technology for the treatment of wastewater with low availability of biodegradable carbon source for nitrogen removal. The effect of increasing load of influent nitrogen was studied so to define the real treatment capacity of the system in the view of its application in municipal systems.

2. Methodology

2.1 Raw wastewater and influent characteristics

The AC-MBR was continuously fed with real wastewater coming from the municipal full scale WWTP of Treviso (northern Italy). A two year monitoring of the influent raw wastewater pointed out the main characteristics given in table 4.1.

Table 4.1. Typical characteristics of the raw wastewater influent to the full scale WWTP

pH	Alkalinity	TSS	COD	rbCOD	NH4-N	TKN	NO3-N	PO4-P	TP
	mgCaCO3/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
7,4÷7,8	230÷350	80÷100	90÷160	17÷21	11÷15	20÷23	0,4÷1	0,7÷1,2	1,8÷2,2

The high infiltration into the sewers system led to wastewater very hard to be biologically treated for total nitrogen removal In fact, the C/N ratio is in the range 4,5÷6 and is supposed not to allow for high denitrification efficiencies. However, it must be pointed out that these wastewater characteristics can be usual when the groundwater table level is high and the sewers system is subject to infiltration phenomena. Therefore, the experimentations were carried out keeping always low the C/N ratio and increasing the inloadings of carbon and nutrients. The experimentation lasted around 500 days, carrying out nine steady state periods, which main chemical/physical characteristics of the influent are given in table 4.2.

Table 4.2 Macropollutants into the influent stream

	TSS	COD	SCOD	N-NH4	N-NO3	TN	TP
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Run1	90±88	112±53	33±16	11,7±4,5	0,4±0,4	21,9±6,9	1,7±0,7
Run2	89±73	93±54	23±25	15,2±3,0	0,9±0,5	23,9±5,9	1,9±0,6
Run3	94±9	217±73	108±53	16,2±2,5	0,5±0,2	23,5±4,0	2,8±0,8
Run4	286±107	285±217	58±48	15,4±10,7	0,1±0,1	32,3±15,2	4,8±1,4
Run5	190±82	169±47	32±14	37,7±4,6	0,5±0,6	45,1±6,0	10,3±2,0
Run6	271±187	291±154	52±20	23,4±3,5	0,2±0,1	52,2±9,2	9,0±2,8
Run7	208±156	245±116	51±18	16,9±9,2	0,3±0,4	39,5±20,6	6,1±2,8
Run8	155±49	149±40	42±24	56,8±3,8	0,5±0,3	66,0±5,1	8,6±1,4
Run9	582±72	413±138	37±21	53,5±11,6	0,5±0,3	78,1±17,1	14,8±2,2

While in runs 1,2,5,8 the influent COD was internal to the raw wastewater, different external carbon sources were used in run 3,4,6,7,9. In run 3 the acetic acid was dosed, in run 4,6,7,9 the liquid phase of the organic fraction of the municipal solid waste (OFMSW$_L$) coming from the full scale co-digestion plant of Treviso (Pavan *et al*; 1998) was used. Also with concern to the external carbon source, the experimental approach aimed to the treatment of real sewage so to reduce the possible scale-up of the results for a full scale application of the technology.
In particular, the OFMSW$_L$ was obtained through a screw press operating in the full scale plant that treats the wastewater and OFMSW according to the scheme of figure 4.1. Really, in this demonstration study the OFMSW$_L$ was separated from the solid fraction before the fermentation, therefore a lower amount of Volatile Fatty Acids was expected in this external carbon source.

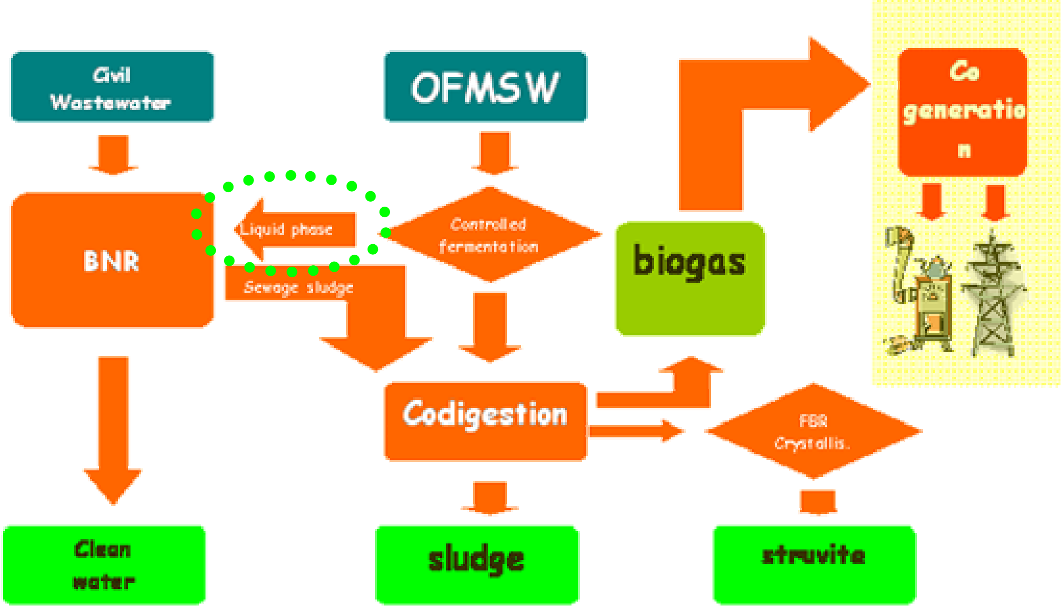


Figure 4.1 Scheme of the Treviso full scale wastewater and organic waste treatment system

However, this methodological approach had to cope with the operation and the maintenance of the parallel full scale plants that provided the substrates for the demonstration study. This drawback led the experimental strategy to be adjusted accordingly, this is why no external carbon source was dosed in run 5 and 8, or why in run 3 acetic acid was used. Also, the characteristics of the OFMSW$_L$

were very variable just as it is really observed in the full scale plant. Table 4.3 summarizes the ranges found out over the experimental periods.

Table 4.3. Characteristics of the $OFMSW_L$ dosed as external carbon source

TSS	COD	sCOD	NH4-N	TKN	PO4-P	TP
mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
200÷1000	7000÷15000	2500÷3000	80÷120	400÷500	4÷8	5÷10

In order to study the maximal treatment capacity of the AC-MBR process in terms of nutrients removal, also external nitrogen and phosphorus were dosed using a solution of NH_4Cl and $(NH_4)_2HPO_4$. Table 4.4 summarize the influent assessment over the 9 experimental runs.

Table 4.4. Assessment of the liquor influent to the demonstration MBR

	External carbon source	N-P dosage
Run1	No	No
Run2	No	No
Run3	Acetic acid	No
Run4	$OFMSW_L$	No
Run5	No	Yes
Run6	$OFMSW_L$	Yes
Run7	$OFMSW_L$	Yes
Run8	No	Yes
Run9	$OFMSW_L$	Yes

As a result, except for run 3 and 4 the carbon availability was supposed to be limiting for the biological nitrates denitrification (Hu *et al.*, 2003) (see table 4.5).

Table 4.5. Typical ratios in the influent sewage

	rbCOD/COD	COD/TN	COD/TP
Run1	0,19	5,1	66
Run2	0,19	3,9	49
Run3	0,48	9,2	78
Run4	0,19	8,4	59
Run5	0,15	4,5	20
Run6	0,14	5,1	32
Run7	0,15	6,7	37
Run8	0,16	2,2	17
Run9	0,07	5,2	28

In order to pursue the possible real industrial applications of the results, the experimental scheme was engineered also to reproduce the typical fluctuations influent to the Treviso municipal treatment system (see, for instance, fig. 4.2 which is referred to run 1) so to study the dynamic answer of the AC-MBR process.

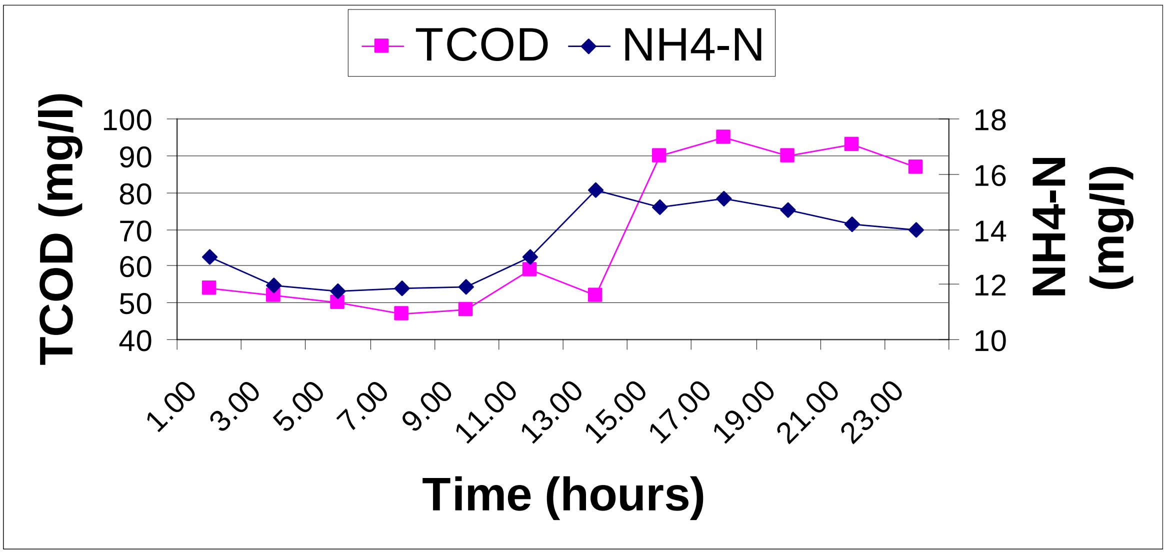


Figure 4.2. Fluctuations observed in the influent (run 1)

As far as the specific volumetric loading rates (table 4.5), MBRs are reported to operate under organic volumetric loading rate (OLR) of 0,25÷16 kgCOD m^{-3} d^{-1} (Stephenson *et al*, 2000). However, most of these conditions can likely occur in industrial applications, but are rarely observed in municipal systems where typical values are in the range 0,6÷1,2 kgCOD m^{-3} d^{-1}. Moreover, in case of diluted wastewater these values can also decrease up to 0,2÷0,4 kgCOD m^{-3} d^{-1}. Therefore the plant was fed with OLR typical of municipal applications.

Table 4.5. Loading rates of C,N,P

	Organic Loading Rate	Nitrogen Loading Rate	Phosphorus Loading Rate
	kgCOD/m^3d	kgN/m^3d	kgP/m^3d
Run1	0,24	0,05	0,004
Run2	0,29	0,07	0,006
Run3	0,67	0,07	0,009
Run4	0,59	0,07	0,010
Run5	0,42	0,09	0,022
Run6	0,61	0,11	0,019
Run7	0,76	0,12	0,020
Run8	0,40	0,22	0,028
Run9	1,35	0,25	0,048

Particular attention should be paid to the NLR, because this is on of the key performance indicators for the nitrogen removal efficiency of a wastewater treatment system. Typical NLRs usually adopted to design real municipal WWTPs are in the range 0,06÷0,09 kgN $m^{-3}d^{-1}$ and these values can decrease up to 0,04÷ 0,05 for diluted wastewater (Ingildsen, 2002). These usually do not represent the maximal treatment capacities of the treatment systems, that could be better exploited by treating secondary streams rich in nitrogen. Therefore, from table 4.5 it is clear that the experimental study was aimed to study the maximal treatment capacity an intermittently aerated membrane bioreactor could support. The expected result is to know-how this technology can be indicated for the up-grading of the existing treatment plants for the treatment of municipal wastewater and other liquid waste rich in nitrogen. Furthermore, the critical lack of biodegradable carbon source in the influent was useful to study the most critical scenario. In the context before outlined, the phosphorus is a side, but not less important, aspect. In fact also the maximal treatment capacity in terms of phosphorus removal was investigated.

2.2 The monitoring plan and the operating parameters

2.2.1 Monitoring plan

The facets of the AC-MBR systems were studied from different points of view in order to construct a complete scenario which can include the know-how of the system. The following scheme summarizes the types of activity and their scopes.

Activity	Data Processing	Scope
Physical/Chemical Analysis	Mainly mass balances	Efficiencies and behaviour of the system
Respiration based batch tests	Analysis of selected single cycles	Identification of the kinetic rates
Respiration based field tests	Analysis of selected single cycles	Identification of the field kinetic rates
Statistical analysis of the on-line signals	On-line data processing	Feasibility and reliability of the process control automation

Table 4.6 shows the parameters analyzed and the frequency of the analyses.

Table 4.6. Physical/chemical analysis during the experimentation

Sampling	Parameter	Frequency
Influent, effluent	COD, sCOD, NH4-N, TKN, NO_3-N, NO_2-N, TP, PO_4-P, TSS, pH, Alkalinity	3 per week
Activated sludge	MLSS, MLVSS	
Waste Activated Sludge	MLSS, MLVSS, N%TS, P%TS	1 per week

Table 4.7 shows the respiration based analysis, both in batch and on field.

Table 4.7 Repirometry based test to control the activated sludge activity

Test		Frequency
Ammonia Uptake Rate		1/run
Nitrates Uptake Rate	Carbon source = Acetate	1/run
	Carbon source = $OFMSW_L$	1/run*
Phosphorus Release and Uptake Rate	Carbon source = Acetate	1/run
Filed study on the cycles	Carbon source = Real influent	1-2/run

* when substrate is available

Finally, the statistical analyses of the cycles was carried out every week and reported every run.

2.2.2 Operating parameters

In line with the approach of all the experimentation, the choice of the operating parameters was done with the aim to work with values reproducible and sustainable for full scale application. This point will be further developed in the last chapter dedicated to the full scale validation of the process. By now, it is sufficient to know that high MLSS into the bioreactor can influence severely the oxygen transfer and the power requirements for air supply (Krampe and Krauth, 2003; Germain *et al*, 2007), therefore this experimentation was carried out under the main operating conditions resumed in table 4.8.

Table 4.8 Operating parameters in the demonstration study

	T	HRT	SRT	MLSS	MLVSS/MLSS	Recycle ratio
	°C	h	d	kg/m^3	%	%
Run1	20	11,0	42	5	62	1,5÷2
Run2	13	7,8	48	8	66	2÷2,5
Run3	11	7,8	50	9	70	2÷2,5
Run4	19	11,5	36	5	68	1,5÷2
Run5	23	11,5	23	6	60	1,5÷2
Run6	22	11,5	22	7	65	1,5÷2
Run7	19	7,8	25	7	64	1,5÷2
Run8	17	7,3	30	7	62	1,5÷2
Run9	15	7,3	32	8	59	2÷2,5

The temperature into the plant was never so low as to severely inhibit the biological processes. The apparent inconsistency of the different operating parameters (MLSS vs SRT, or VSS/SS vs T) is due to the high heterogeneity of the feeding. However, it is important to point out the range of operated MLSS (5÷9 kgMLSS m^{-3}) and HRTs (7,3÷11,5), which is considered completely suitable also for industrial municipal applications in small and large systems. Finally, the total number of recycles within the reactor was as low as required by the alternate cycles process. This value was slightly increased for higher MLSS (run 9) in order to avoid critical biomass concentration into the final membrane tank.

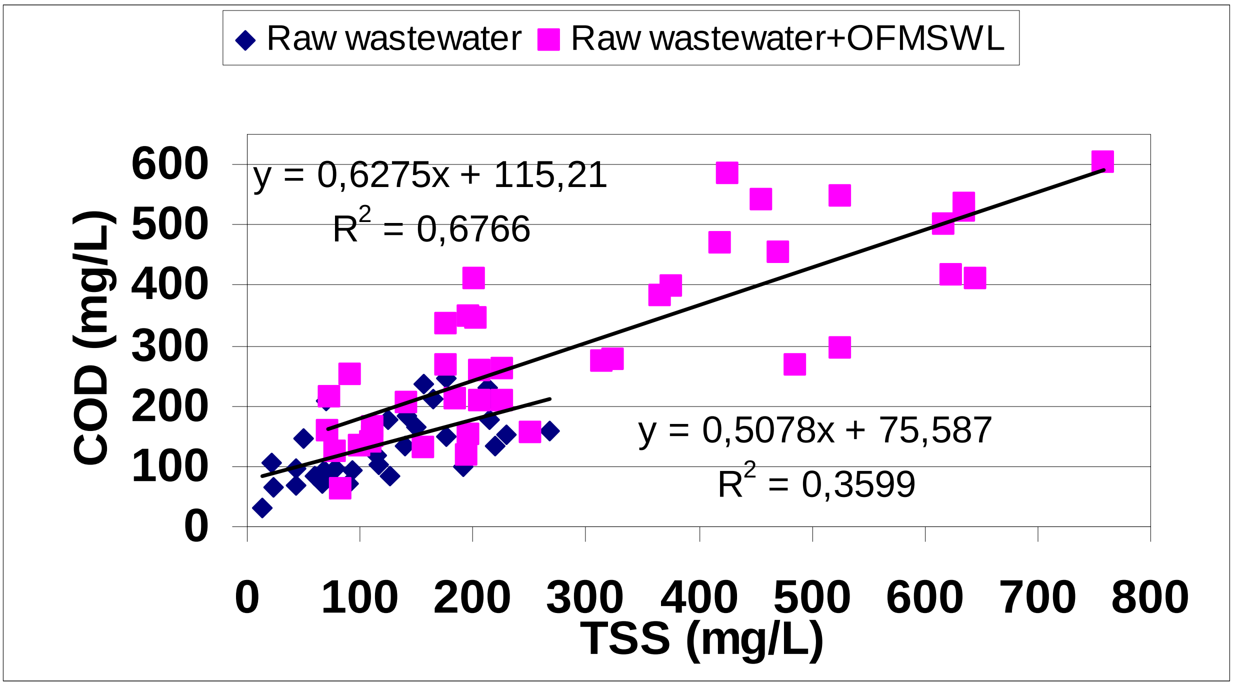
3. AC-MBR behaviour: results and discussion

3.1 Carbon

Reported volumetric loading rates range between 1.2 to 3.2 kgCOD m^{-3} d^{-1} and 0,05 to 0,66 kg BOD5 m^{-3} d^{-1} with corresponding removal efficiencies >90% and 97%. Steady state effluent BOD concentrations have been consistently <10 mg L^{-1}, irrespective of the wide range of influent concentrations encountered, e.g. from >100 mg L^{-1} (Murakami *et al.*, 1999) to > 250 mg L^{-1} (Martyn *et al.*, 1999). Although many loading rates are similar to those for activated sludge, removal efficiencies are higher. Cotè *et al.* (1997) attributed the improved COD removal to the combination of complete particulate retention by the membrane, including suspended COD and high molecular weight organics, as well as the avoidance of biomass washout problems common in activated sludge. In particular, a secondary benefit is the provision of stable conditions for the growth of specialised micro-organisms that are able to remove slowly degradable components. Performance appears to be relatively insensitive to HRT with values between 2 and 24 h resulting in very high removal percentages. Sludge age also appears to have little influence on effluent quality. Therefore, the COD removal was not expected to be a major problem in this demonstration study.

The influent COD has been characterized in terms of total COD, soluble COD and rbCOD. The experimental data showed no strict relation between the total COD in the feed and the total suspended solids both with and without the external carbon source dosage (see Pearson coefficients in figure 4.3).

Figure 4.3. COD-TSS in the inflow



However, both with only raw wastewater and with the $OFMSW_L$ the slope of the trends are similar. This evidence, coupled to the fact that the rbCOD/COD did not change significantly in the two cases, seem to demonstrate that the solids suspended in the raw wastewater and those coming from the $OFMSW_L$ have similar characteristics. However, the discussion on the biological denitrification will allow for considerations also on the biodegradability degree of the particulate COD. The COD removal was in the range 88÷98% (table 4.9).

Table 4.9. COD removal

	CODin	CODout	Removal
	mg/L	mg/L	%
Run1	112±53	11±7	90
Run2	93±55	5±14	95
Run3	217±73	4±4	98
Run4	285±217	8±6	97
Run5	201±47	19±23	91
Run6	291±154	34±17	88
Run7	245±116	24±14	90
Run8	149±40	18±15	88
Run9	413±138	7±6	98

Lower removals were probably due to irregular discharges of liquid wastes from small local factories, located in the catchments area, which increased the content of non biodegradable soluble COD. The system did not suffer from severe fluctuation of the influent loadings, in fact the removal in run 4 were stable and very high in spite of the high standard deviation. With further concern to the use of the carbon source in the biological tank, in the next paragraph the key performance indicator related to the removal of total nitrogen will be finally discussed.

3.2 Nitrogen

The complete retention of micro-organisms by the membrane can encourage the growth of specialised microorganisms such as *Nitrosomonas* and *Nitrobacter*. Complete nitrification has been demonstrated in MBRs at sludge ages of 5-72 d and organic loading rates of 0.05÷0.66 kg BOD m^{-3} d^{-1}. Sludge age have been shown to have an influence on nitrification in MBRs, with reported ammonia removal efficiencies increasing from 80 to 99% on increasing the sludge age from 10 to 50 days (Coté *et al.*, 1997) and from 94 to 99% on doubling the sludge age from 5 to 10 days. Total nitrogen removal is reported to be also very high both in intermittent MBRs and for configuration with separate anoxic tank. Using intermittent aeration, Cheimchaisri et al. (1999) found out 92.6% denitrification in a submerged MBR. Suwa et al (1992) related denitrification to BOD loading such that no denitrification occurred below a loading rate of 0,438 kg m^{-3} d^{-1} and thereafter increased linearly with loading rate. The type of external carbon source was found to have also an effect, MBRs giving 90% nitrogen removal can be operated at double the loading rates with methanol instead of acetic acid (Ghyoot *et al.*, 1999). The maximum loading rate for complete nitrification (0,16 kgN $kgMLSS^{-1}$ d^{-1}) was found by Ghyoot *et al.* (1999) and this dropped by 50% when a positive displacement pump used for recirculating the biomass was replaced with a centrifugal pump, so to demonstrate also the impact of biomass shear.

In this demonstration study the influent nitrogen was very variable for both concentration and form, especially for the incoming of organic nitrogen (table 4.10).

Table 4.10. Organic nitrogen and TKN/NH4-N influent to the plant

	Norg	**TKN/NH_4-N**
	mg/L	mg/L
Run1	9,8	1,8
Run2	7,8	1,5
Run3	6,8	1,4
Run4	16,8	2,1
Run5	6,9	1,2
Run6	28,6	2,2
Run7	22,3	2,3
Run8	8,7	1,2
Run9	24,1	1,5

Table 4.10 infers the different sources of nitrogen influent to the demonstration MBR. In fact when only nitrogen internal to the raw wastewater was incoming (run 1, 2 and 3), the organic nitrogen was in the range 7÷10 mg L^{-1}, while it increases up to 17÷29 when the $OFMSW_L$ was dosed (run 4,6,7 and 9). On the other hand, the TKN/NH_4-N indicates also the periods when ammonia chloride was dosed (run 5-9).

The dissertation that concerns nitrogen behaviour in the system is organized into three parts: (1) the removal efficiencies; (2) the influence of the influent loadings and operating parameters; (3) the validation of the bending point based control strategy.

3.2.1 Nitrogen removal efficiencies

The removal efficiencies were evaluated from the nitrogen mass balance. This was calculated according to the eq.4.1, while the nitrification and denitrification performances were studied according to four parameters: the nitrifying efficiency referring to the total incoming nitrogen (En, in eq.4.2) and to the amount of the only form of nitrogen that can be nitrified (Enn, in eq.4.3); the nitrogen removal efficiency referring either to the total incoming nitrogen (Ed, in eq.4.4) or to the nitrified nitrogen, NOx-N (Edd, in eq.4.5).

$$LTN_{den} = LTN_{in} - LTNq_W - LTN_{out} \qquad \text{eq.(4.1)}$$

Where: LTN_{den} = total denitrified nitrogen mass loading (kg/d);
LTN_{in} = total nitrogen mass loading in the influent (kg/d);
$LTNq_w$ = total nitrogen mass loading in the waste biological sludge (kg/d);
LTN_{out} = total nitrogen mass loading in the effluent (kg/d).

$$En\ (\%) = (LTN_{nit} / LTN_{in}) * 100 = [(LTN_{den} + LNO_X\text{-}N_{out} - LNO_X\text{-}N_{in}) / LTN_{in}] * 100 \qquad \text{eq. (4.2)}$$

Where: $LNOx\text{-}N_{out}$= NOx-N mass loading in the plant effluent (kg/d);
$LNOx\text{-}N_{in}$= NOx-N mass loading in the plant influent (kg/d);

$$Enn\ (\%) = [LTN_{nit} / (LTKN_{in} + LTKN_{qr} - LTNq_w - LN_{nb\ org\ out})] * 100 \qquad \text{eq. (4.3)}$$

Where: $LTKN_{in\ 1}$ = total Kjeldahl nitrogen mass loading in the influent (kg/d);
$LTKN_{qr}$ = total Kjeldahl nitrogen mass loading in the ricirculation flow-rate (kg/d);
$LN_{nb\ org\ out}$ = not biodegradable organic nitrogen mass loading in the effluent (kg/d).

$$Ed\ (\%) = (LTN_{den} / LTN_{in}) * 100 \qquad \text{eq. (4.4)}$$
$$Edd\ (\%) = [LTN_{den} / (LTN_{den} + LNO_X\text{-}N_{out})] * 100 \qquad \text{eq. (4.5)}$$

The removal performances are reported in table 4.11.

Table 4.11 Nitrogen removal efficiencies

	N removal	En	Ed	**Enn**	**Edd**
	%	%	%	**%**	**%**
Run1	76	94	69	**96**	**73**
Run2	82	97	80	**99**	**82**
Run3	96	97	93	**99**	**96**
Run4	94	98	91	**99**	**92**
Run5	68	94	65	**95**	**69**
Run6	87	91	82	**95**	**89**
Run7	88	94	84	**96**	**89**
Run8	36	82	35	**83**	**43**
Run9	71	76	58	**78**	**76**

Owing to the low C/N ratio, nitrates denitrification was always the limiting process for total nitrogen removal, while the ammonia nitrification reached always very satisfactory efficiencies, being quite complete in runs 1-7 and close to 80% in run 8-9. These evidences are obviously reflected by the real efficiencies Enn>Edd. Figure 4.4 resumes the boundary conditions and the performances for total nitrogen removal.

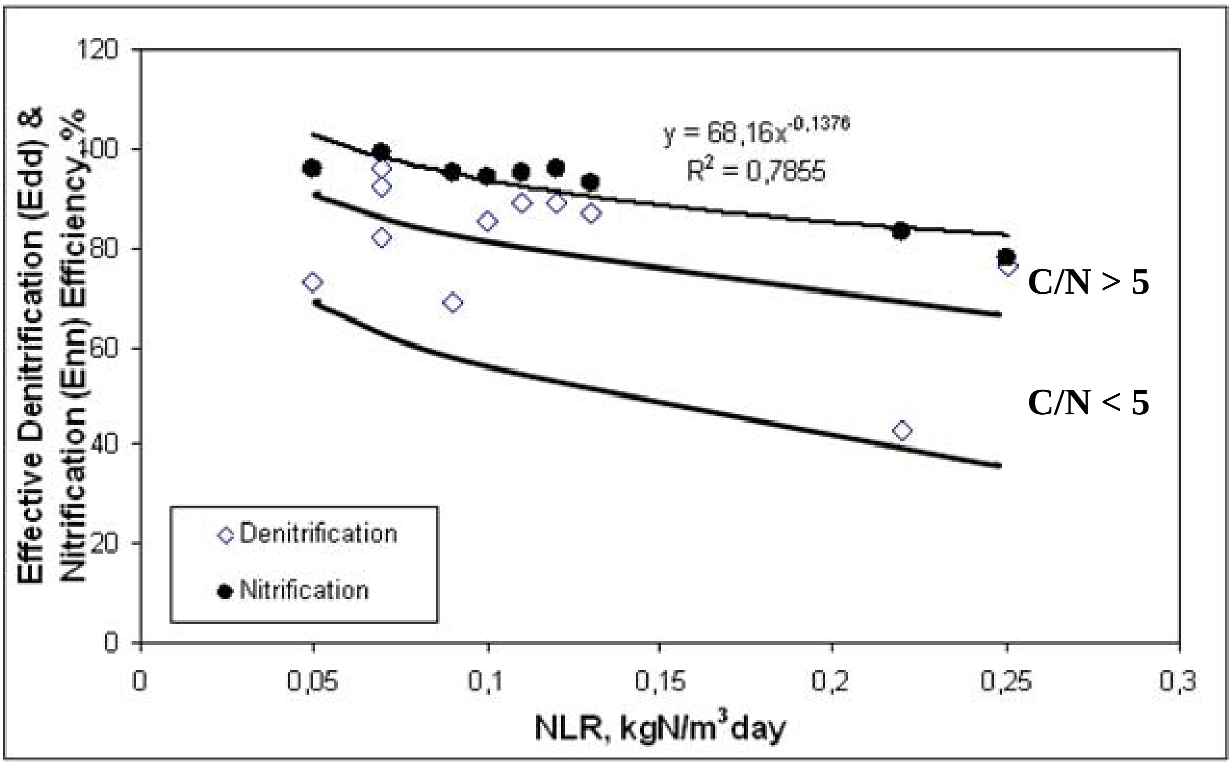


Figure 4.4 Removal efficiencies and boundary conditions for total nitrogen removal

To have a better understanding in terms of quality of the treated effluent, table 4.12 shows the effluent nitrogen concentrations.

Table 4.12 Nitrogen in the treated effluent

	TNout	NO3-Nout	NH4-Nout	NLR	COD/TN
	mg/L	mg/L	mg/L		
Run1	5,3±2,4	5,2±2,1	0,1±0,1	0,05	5,1
Run2	4,2±1,8	4,1±2,0	0,1±0,8	0,07	3,9
Run3	1,0±0,5	0,9±1,9	0,1±0,1	0,07	9,2
Run4	2,5±1,1	2,0±2,4	0,4±0,2	0,07	8,4
Run5	12,9±3,0	12,4±4,4	0,5±0,2	0,09	4,5
Run6	4,9±3,3	4,4±3,0	0,4±0,2	0,11	5,1
Run7	4,4±2,2	3,6±2,2	0,7±0,4	0,12	6,7
Run8	35,0±9,3	12,5±6,2	20,5±8,8	0,22	2,2
Run9	17,4±15,9	7,3±1,7	9,2±11,7	0,25	5,2

*Italian limit for re-use: TN=15 mg/L; NH4-N=1 mg/L

From table 4.12 the global rates for nitrification and denitrification were calculated according to the equ 4.6 and 4.7

$$Kn = \frac{L_{nitrified}}{(t_{phaseaerobic} * VSS_{AC} * V_{AC}) + (VSS_{MembTank} * V_{MembTank})} = 0.8 \div 4.0 \frac{mgNH_4 - N}{gVSS * h} \qquad \text{equ. 4.6}$$

$$Kd = \frac{L_{denitrified}}{VSS * ((t_{phaseanoxic} * V_{AC}) + V_{AnoxSel})} = 0.7 \div 2.0 \frac{mgNO_3 - N}{gVSS * h} \qquad \text{equ. 4.7}$$

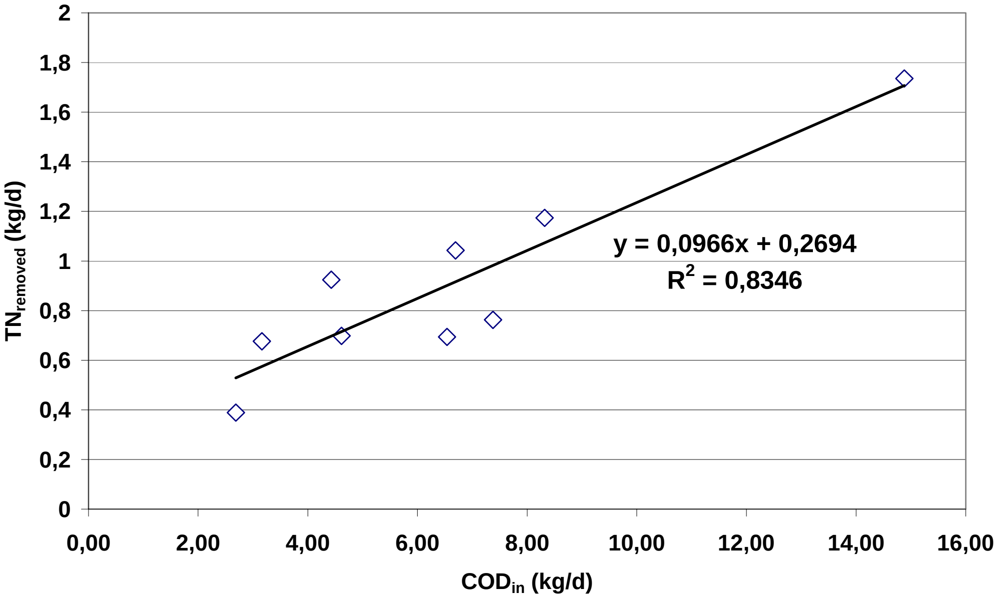
where the lower values for Kn were observed in case of limiting NH_4-N. As for the denitrification, the values were in the range 0,7÷1,2 and 1,3÷2 respectively with and without external carbon source. However, these values are revealing only for a global effect. The specific rates were better investigated, once a run, by field analysis that monitored the nitrogen forms over two following aerobic and anoxic phases. Samples of mixed liquor were taken every 10 minutes from both the CSTRs and from the permeate, then they were analyzed for NH_4-N, NO_3-N, NO_2-N. The resulting rates which come out from the field analysis pointed out that the ammonia nitrification was carried out mainly in the CSTR1 according to rates 1,5÷2,0 mgNH_4-N/gVSS*h and for loading higher loading also in CSTR2. As for the denitrification, the main role of the CSTR1 was more evident because of the low availability of the carbon for nitrates reduction. However, the difference between the two CSTRs in series was more remarkable when the external carbon source was dosed, while both the reactors denitrified at similar rates when the only raw wastewater was dosed. This evidence can indicate that endogenous carbon was used for nitrates denitrification with a rate of 0,7÷1,5 mgNO_3-N/gVSS*h.

The global effect of the different carbon sources was not very evident from the global mass balances because the C/N ratio was limiting for the denitrification process. However, the batch respirometry NUR test pointed out the potential impact of acetate and $OFMSW_L$. As a result, the specific denitrification rate associated to the acetate was in the range 2÷3 mgNO_3-N/gVSS*h while the $OFMSW_L$ involved a rate of 3÷4 mgNO_3-N/gVSS*h. Furthermore, it is important to point out that no significant differences were observed in the different run. This can indicate that the heterotrophic composition of the activated sludge was almost similar and did not change with the different loadings influent.

Key performance indicator for nitrogen removal

Since the available organic matter and the biological volume largely limit the nitrogen removal performances, the key performance indicators should consider these aspects. The use of the biological volume will be indirectly illustrated later, discussing the limiting nitrogen loading rate (NLR). On the other hand, figure 4.5 shows the removed total nitrogen per available amount of total organic matter.

Figure 4.5 Key performance indicator for nitrogen removal: use of carbon source



The system was able to remove 0,0966 kg of total nitrogen per kg of total influent COD that is in agreement with the data reported by Ingildsen (2002). However, in the demonstration AC-MBR plant the best use of the carbon source was sometimes not achieved because of over-aeration phenomena during the aerobic phases. Therefore, figure 4.5 can be taken as indicator of the minimal performance for the use of the carbon source in the system.

3.2.2 Feasibility of the alternate cycles control algorithm and realiability of the control device

Within the treatment of a subject like the nitrogen, the feasibility of the process control algorithm must be considered. In fact, as mentioned before, the alternate cycles process is based on the control of the aeration of the bioreactor on the basis of the bending points on DO and ORP that are linked to the nitrogen forms into the bioreactor. Aeration is switched off when the ammonia breakpoint is detected, and is switched on when the nitrate knee is detected. In this way, the lengths of the aerobic and anoxic phases are controlled to be just sufficient for complete nitrification and denitrification, respectively. However, this is not necessarily an optimal strategy. In fact for an intermittently aerated continuous system, high effluent ammonia and nitrate peaks may appear alternatively, resulting in high effluent loading concentration when the plant is overloaded in ammonia. Moreover, Paul *et al* (1998) pointed out that the bending points on DO, ORP and pH are not detectable under certain conditions (over-aeration, over-loading, inhibition). Therefore, the control algorithm of the alternate cycles system includes also secondary branches which correspond to the setpoint based control. This is a secondary safety level which ensures sufficient removal performances also under the impossibility of bending points detection. Table 4.13 shows the setpoints included in the complete algorithm.

Table 4.13. Setpoints included in the secondary branches of the algorithm

	Aerobic phase		Anoxic phase	
	MAX	MIN	MAX	MIN
DO	X			
ORP	X			X
Time-lenght	X	X	X	X

These setpoints are initially appointed as a result from Activated Sludge Model 2 (ASM2) (Henze *et al.*, 2000) simulations, then they are better adjusted after the initial trial operation, because they are strictly depending on the particular treatment system (i.e.: influent loadings and process boundary conditions).

Although the control algorithm can dispose of different safety levels, a software that can validate its reliability has also been engineered and installed in the full scale plants. It carries out the statistical analysis of all the cycles performed and gives, as output, both the end-reason (bending point detection, DO or ORP or time setpoint) for the change of phase and the lengths of the phases (average, minimal, maximal). This software is used, besides the classical mass balances, to make a detailed diagnosis of the process behavior so to, eventually, adjust the setpoints or intervene directly on site.

The operation of the alternate cycles process is evaluated and discussed taking into account two main evidences: the before discussed removal performances of the process, which gives objective and unquestionable information about the efficiency of the process, and the statistical analysis of the cycles, which gives the information on the real detection of the bending points (optimal condition) or the intervention of the setpoint branches of the control algorithm. Both the cited approaches contribute to evaluate the reliability of the plant configuration and the control strategies.

The software for the statistical analysis of the cycles works as described below. Given a selected operation period, it processes the data logged (analog signals from the DO-ORP sensors and digital ON/OFF signals from the blowers) and gives output information on: the *end-reason* (detection of bending point, set point on DO or ORP, set point on maximum time) which caused the aeration switching on or off; the sensor that has detected the bending point; the durations of the anoxic and oxic phases (average, minimum and maximum). Table 4.14 shows the output from the elaboration of more than 5000 cycles over the whole experimental period. In this table the optimal condition, that is the detection of the bending point, is called α, while ß and γ represents respectively the cases when the time and the DO-ORP set points were exceeded.

Table 4.14 End-reason during the whole experimentation

	Aerobic phase			Anoxic phase		
	α	ß	γ	α	ß	γ
	%	%	%	%	%	%
Run1	93	7	0	74	0	0
Run2	67	1	32	96	4	0
Run3	98	2	0	100	0	0
Run4	73	0	27	100	0	0
Run5	75	4	19	72	28	0
Run6	98	2	0	80	23	3
Run7	94	4	2	86	7	7
Run8	53	33	14	25	75	0
Run9	59	41	1	58	42	0

From the table 4.14 one can observe as the detection of the ammonia break point was almost common, so almost complete nitrification was always observed. The non-optimal conditions are in agreement with influent loadings: in run 4 and 5 over-aeration often occurred in the nights when the aeration demand was much lower than the supply; in run 6 and 7 the influent oxidizable nitrogen fits the air supply; in run 8 and 9 a nitrogen over-loading involve the detection of the ammonia break points only for around 50% of the events, while the aeration is stopped for the achievement of the set maximal time-length. As far as the anoxic phases, as expected the optimal conditions depended mainly on the C/N ratio. It is important to point out that the set point on the aerobic phase allowed to stem the waste of biodegradable COD linked to over-aeration phenomena. As a result in run 4 a COD/N equal to 8,4 involved over-aeration for 27% of the events, but 100% of nitrates break points were found out in the anoxic phases. Even under nitrogen over-loadings (run 8 and 9) the nitrates break points were detected with lower but satisfactory frequency. This means that such a dynamic alternate system is usually able to optimize its own performances thanks to its flexibility, but it is fundamental to impose the right setpoints that mark the boundary lines of the process. Figures 4.6 and 4.7 shows clearly the links between the two methods used to validate the control algorithm: the relations between the nitrification and denitrificaton efficiencies and the success in controlling the aeration at the end of the processes, as from the output of the statistical analysis.

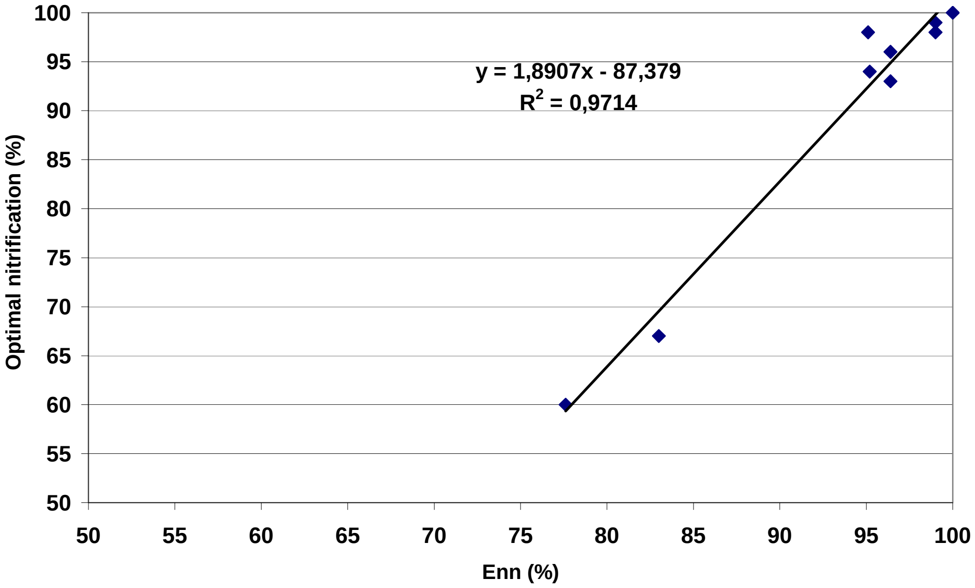


Figure 4.6. Real nitrification efficiencies and optimal control of the aerobic phases

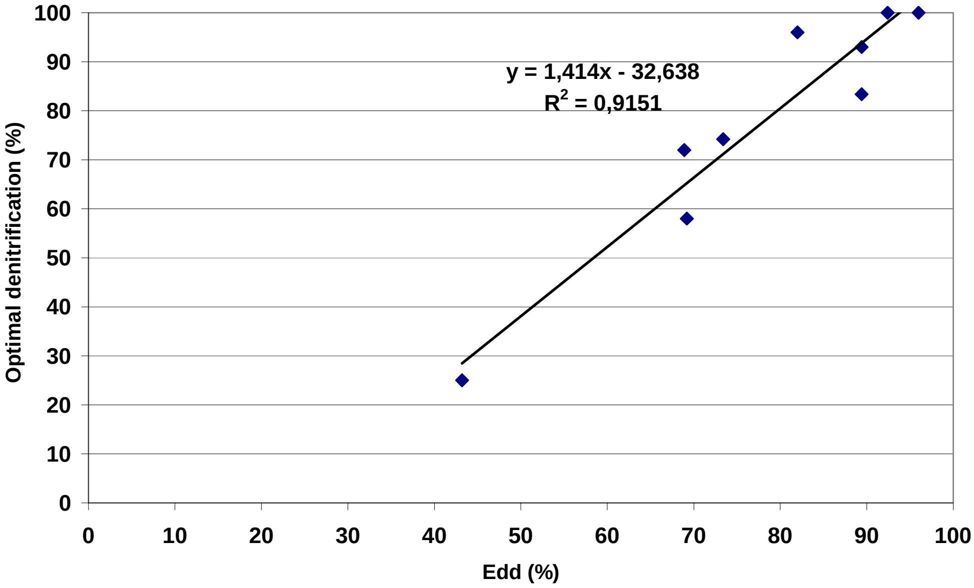


Figure 4.7. Real denitrification efficiencies and optimal control of the anoxic phases

The reliability of the control device is clearly proved observing figures 4.6 and 4.7 where there are linear correlations between process efficiencies and optimal control of the aeration. These evidences indicate that the statistical analyses may give also gross estimation about the nitrogen removal performances of the process.

As expected the time-lengths of the aerobic-anoxic phases are typical of a system under crtitical conditions for the denitrification step. Table 4.15 reports the values found out over the whole experimentation.

Table 4.15 Time lengths of the aerobic and anoxic phases

	Cycles per day	Aerobic phase	Anoxic phase
		min/day	min/day
Run1	18	241	1199
Run2	13	345	1095
Run3	17	631	809
Run4	27	393	1044
Run5	17	158	1282
Run6	19	226	1212
Run7	25	370	1070
Run8	10	242	1198
Run9	11	314	1126

The evaluation of the process behaviour through the on-line signals can be also immediate, from the simple observation of the DO-ORP signals. For instance, figures 4.8 a-b and 4.9 a-b show the profiles of DO (a) and ORP (b) typically observed in case of sufficient and non-sufficient carbon for the complete denitrification, respectively.

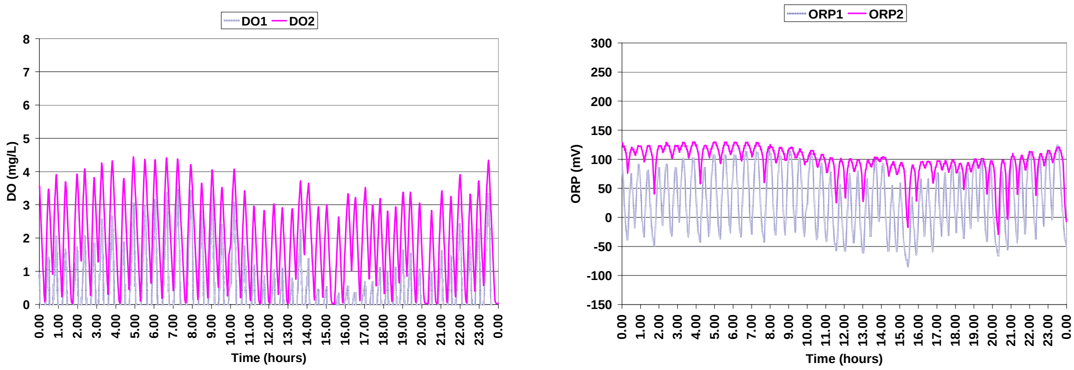


Figure 4.8. DO (a) and ORP (b) profiles ion case of sufficient carbon source for the complete denitrification

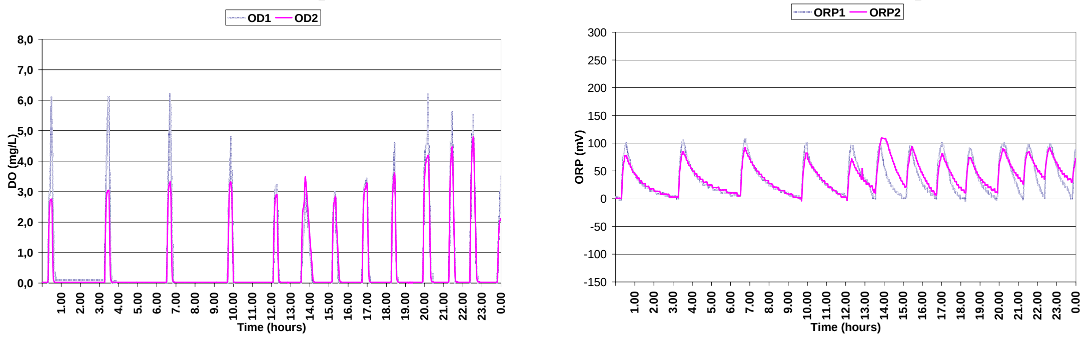


Figure 4.9. DO (a) and ORP (b) profiles in case of non-sufficient carbon source for the complete denitrification

From table 4.11 and figures 4.8; 4.9 one can clearly observe that the denitrification was the driving step for the whole alternating process.

However, how much flexible is the process? In the previous chapter the simplified model has been based on the assumption that the carbon source was sufficient for the complete nitrates denitrification. In that case the NLRs was found to address the process. In order to understand the behaviours of the system treating low C/N wastewaters the anoxic and aerobic phases have been plotted versus the C/N ratios and the NLRs, respectively (figure 4.10 and 4.11).

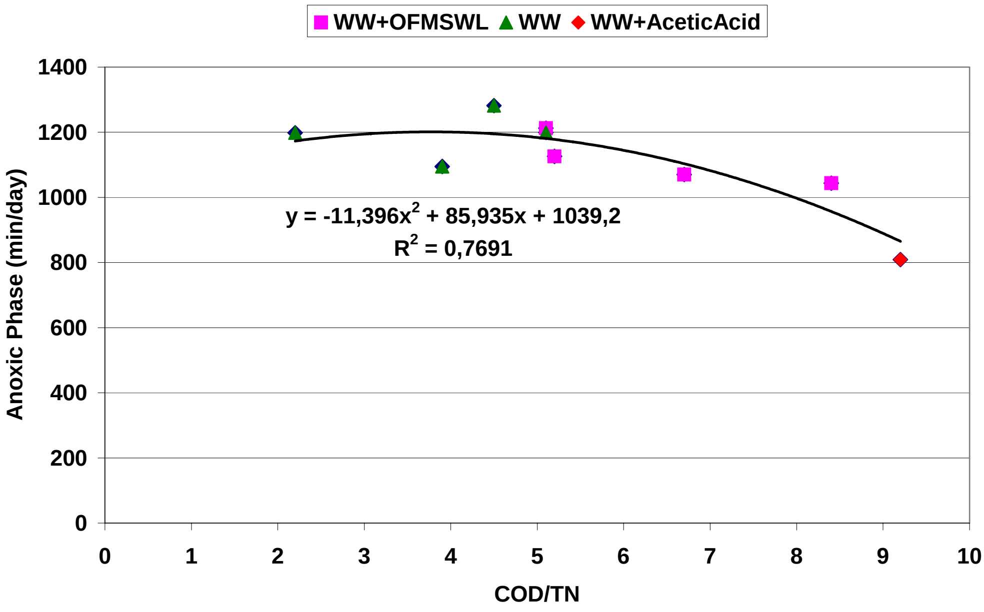


Figure 4.10 Anoxic phases and COD/TN ratio

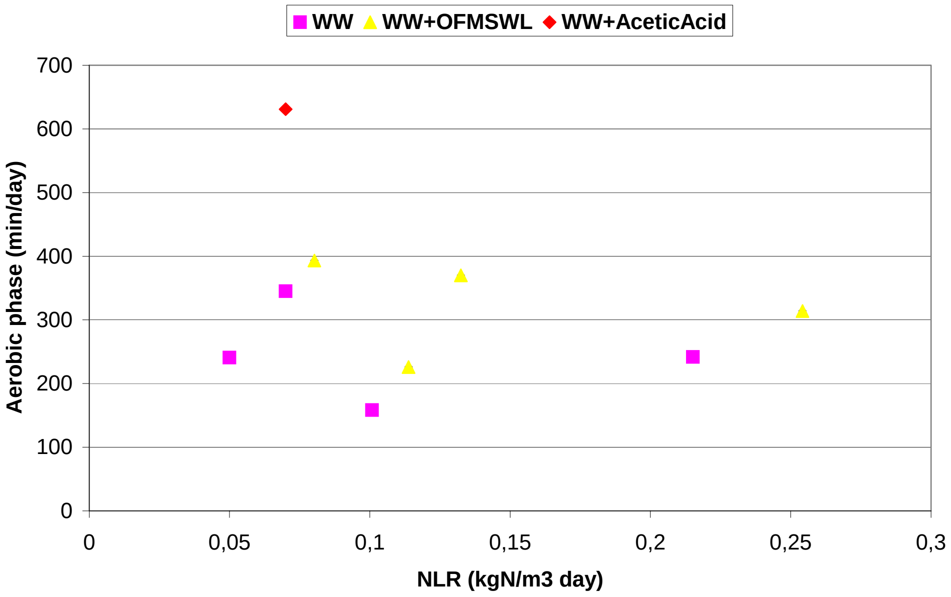


Figure 4.11 Aerobic phases and NLR

Figures 4.10 and 4.11 confirm that the denitrification drove always the alternating system. In fact the C/N ratio practically dictated the time-lenghts of the process, which lost completely its flexibility for C/N ratio lower than 5. This ratio can be considered also the maximum capacity of the alternating process, in other words when it becomes rigid and behaves similarly to a multizone process, in separated aerobic and anoxic tanks. Furthermore, it must be emphasized that the curve of figure 4.9 interpolates well the data concerning different types of carbon sources and, consequently, different biodegradability degrees of the influent. This point was better investigated plotting directly the time lengths of the anoxic phases with respect to the rbCOD/TN ratio (figure 4.12).

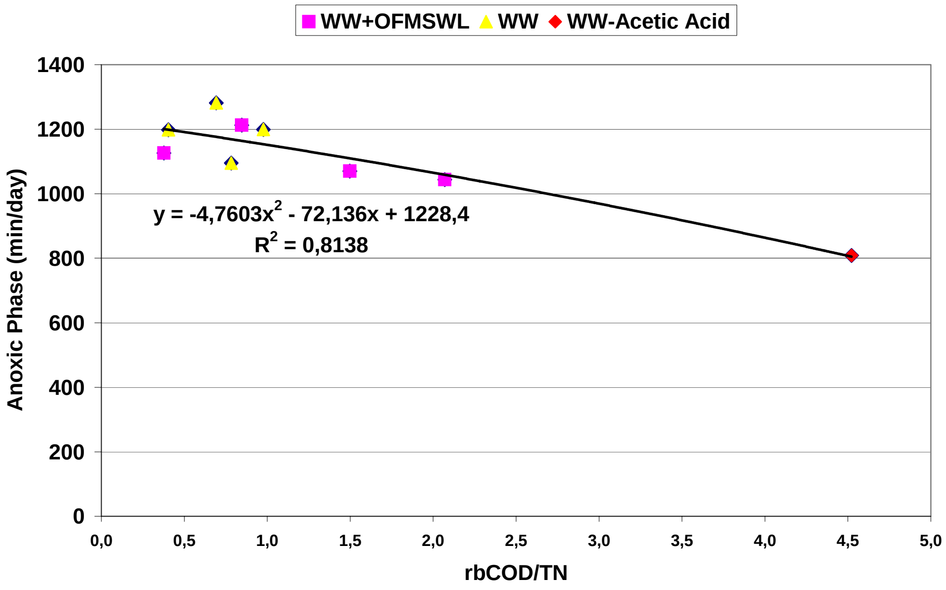


Figure 4.12 Anoxic phases and rbCOD/TN ratio

Figure 4.12 substantially confirms the results from figure 4.10. Here the loss of flexibility is observed for rbCOD/N<1 when the system is not longer able to change its behaviour on the basis of the more or less biodegradable carbon source. This seems to indicate that most of the nitrates denitrification is performed using endogenous carbon source.

3.3 Phosphorus

Generally phosphorus removal is a major area of interest as the need to reduce the nutrients loads becomes more important. However, as already mentioned in this thesis, phosphorus contents in italian municipal wastewater is almost low thanks to the reformulation of the detergents that limits the use of polyphosphates. Therefore, in Italy the phosphorus problem has been successfully faced directly *on the source* and the wastewater treatment systems usually are not under critical conditions for phosphorus. As a matter of fact, also the very stringent limits established by the recent European directives are generally easily achieved by chemical/physical precipitation. However, in the rest of the Europe and also worldwide phosphorus is of major concern. Reported phosphorus removals range from 11.9% (Coté *et al*, 1997) to 75% (Ueda and Hata, 1999). Assimilation alone does not account for all phosphorus removal. Stable phosphorus removal however, has been demonstrated by metal coagulant dosing achieving a removal efficiency of 80% or more at molar ratios of 1:1 Al or Fe:P (Buisson *et al*, 1998).

As far as the alternate cycles process control, it is based on the forms of nitrogen into the bioreactor to optimize nitrification and denitrification, but the phosphorus removal is not supposed to be enhanced. In fact, full scale plants operating the AC process make usually use of chemical/physical precipitation. However, Battistoni et al (2006) pointed out that the phosphorus release and luxury uptake has been observed in AC real WWTPs feed by real municipal wastewater rich in rbCOD. The resulting total P removal was reported to be some 60% for only biomass assimilation. In particular, phosphorus release was found out at the end of the denitrification phase, when the mixed liquor was on the boundary line between anoxic and anaerobic conditions; the luxury uptake was observed as soon as the aerobic phase began. Therefore, the alternate cycle process can result a biological nutrients removal (BNR) intermittent process. However, with conventional configuration with the secondary clarifiers the phosphorus biological removal is not enhanced, because of the lack of a final aerobic step which can continuously induce the uptake. Hence, in the effluent the P concentration is almost fluctuating. Differently, the configuration of the AC-MBR process can enhance the phosphorus removal thanks to the role of the final aerobic tank where the UF membranes are submerged. Further, owing to the low recycles operated by the AC systems, the effective HRT in the final aerobic tank is increased as well as the biomass concentration. This can allow for the completion of the phosphorus luxury uptake and for the effective enhancement of the P biological removal.

Batch test on the P release/uptake were performed in order to investigate the possible presence of Phosphorus Accumulating Organisms (PAO) and/or Denitrifying Phosphorus Accumulating Organisms (DPAO) into the activated sludge (figure 4.13).

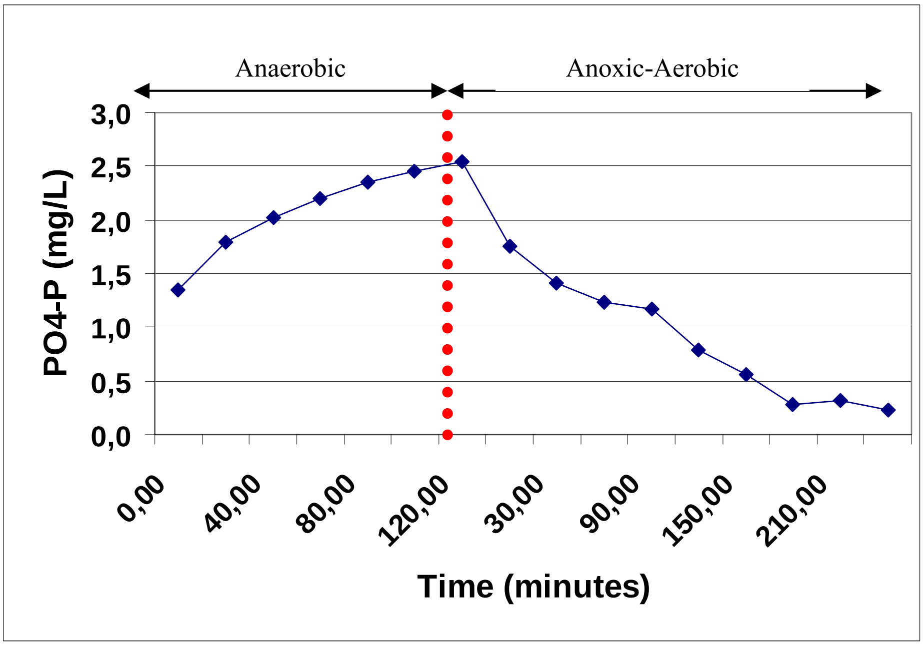


Figure 4.13. Respirometry batch test for P release/uptake

Using acetate as substrate, the batch test pointed out a phosphorus anaerobic release rate in the range 0,18÷0,23 gP $kgVSS^{-1}$ h^{-1} and an uptake rate of 0,15÷0,25 gP $kgVSS^{-1}$ h^{-1}.
Turning back to the demonstration plant, P removal was obtained mainly by biomass assimilation as can be observed in figure 4.14.

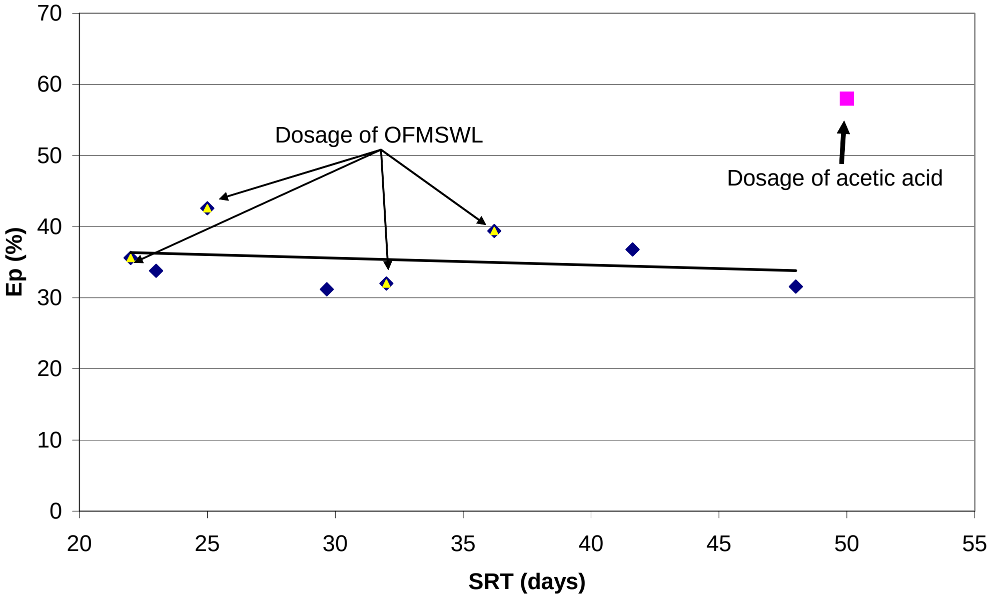


Figure 4.14 Phosphorus removal and SRT

The P was removed in the range 30÷42% except in run 3 when the addition of acetic acid involved a removal close to 60%. Otherwise the $OFMSW_L$ did not enhance the biological phosphorus removal. The effect of the acetic acid was also observed by the field analysis of the cycle. Figures 4.15 a-b and 4.14 a-b show the trends of DO, ORP, PO_4-P, NO3-N, NH4-N within a cycle in the run 2 and 3.

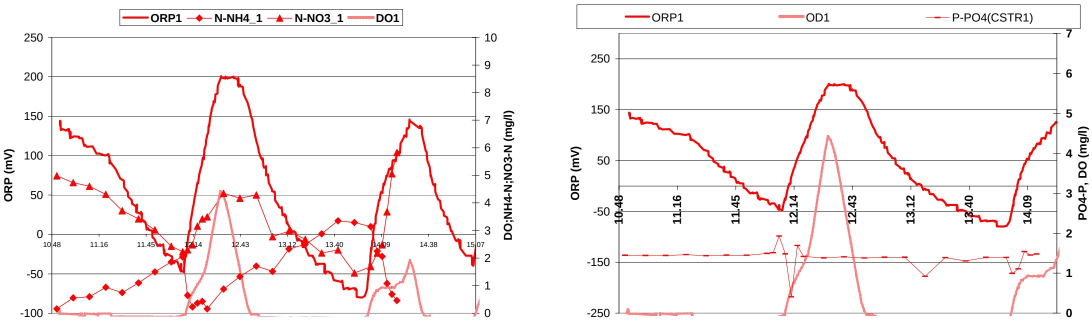


Figure 4.15 a-b PO4-P in the AC reactor - run 2

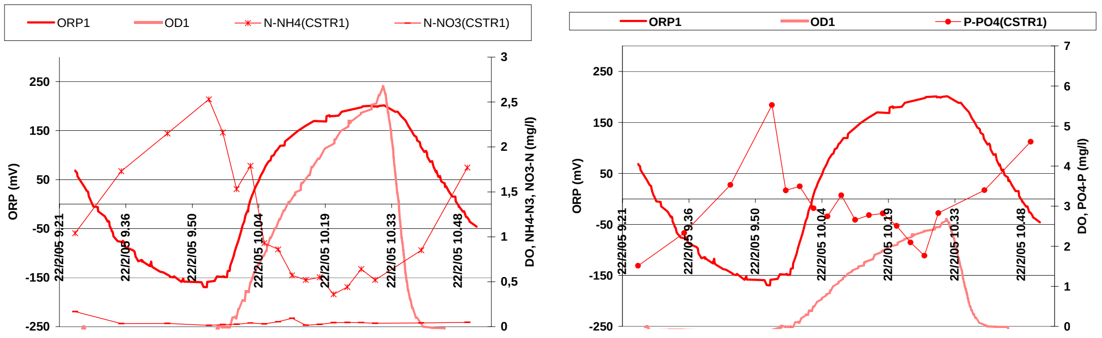


Figure 4.16 a-b PO4-P in the AC reactor - run 3

The phosphorus release and the following uptake in the AC reactor were studied together with the behaviour of the nitrogen forms. While in run 2 the nitrogen was characterized by the typical behaviour of anoxic denitrification and aerobic nitrification and the phosphorus was contemporary constant, during run 3 the NO3-N was almost constant despite the typical variation of ammonia nitrogen and the phosphorus showed contemporary an anoxic/anaerobic release and the classical aerobic uptake. This could be ascribed to the simultaneous ammonia nitrification and nitrates denitrification and a remarkable P release/uptake due to the abundance of suitable carbon substrate. The results concerning the phosphorus were also confirmed by the mass balance its verification through the measurements of the P content in the wasted activated sludge.

3.4 AC-MBR vs DN-MBR

How the intermittent aeration is preferable with respect to the multizone schemes in separated tanks was investigated comparing the AC-MBR plant with the parallel MBR which operated the conventional predenitrification-nitrification.

As for the DN-MBR configuration, the working volumes of the different reactors are reported in table 4.16.

Table 4.16 Working volumes of the DN-MBR demonstration plant

Anoxic Tank	Aerobic Tank	Membrane tank (aerobic)
m^3	m^3	m^3
4,8	4,8	1,4

From table 4.16 one can observe that the overall partition of anoxic-aerobic volume was 44-56 %, where the anoxic volume was large enough both to cope with low denitrification rates and to reproduce typical volume partition of many full scale conventional WWTPs.

Both the MBRs were fed with the same sewage and also adopted similar SRTs that involved similar biomass concentrations, so to indicate that the sludge yields were comparable. This phenomenon was observed in spite of the fact that the AC process exploited much more the nitrates-bound oxygen to oxidize the organic matter, which should involve anoxic sludge yields that are reported to be lower than the aerobics. The comparative study was possible only for the last six runs because of the frequent maintenance for the DN-MBR line.

As far as the removal performances, figure 4.17 shows the removals of COD.

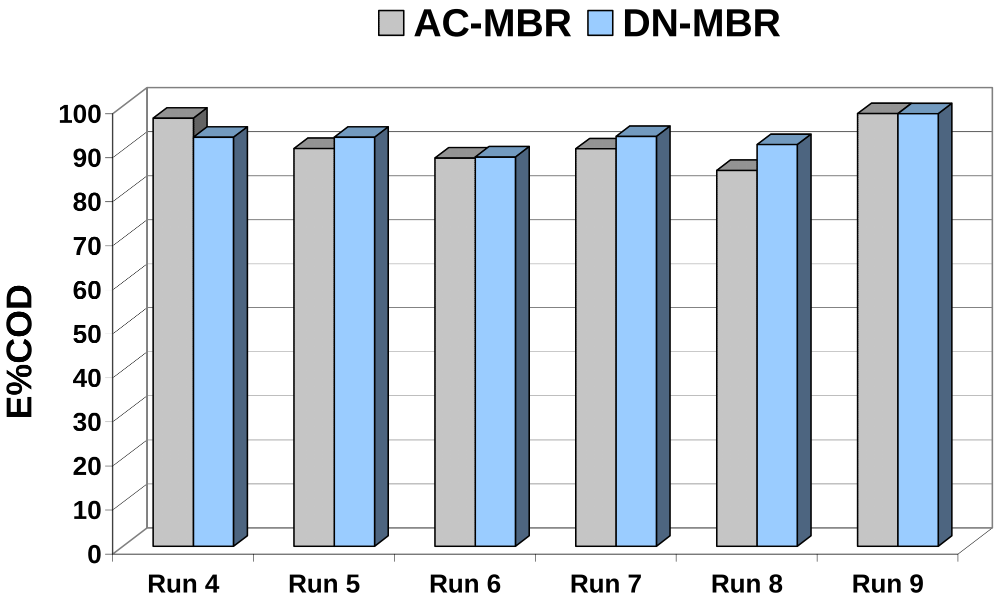


Figure 4.17. COD removal in the two parallel AC-MBR and DN-MBR

As expected the COD removals were almost the same and even the slight differences are attributed to analytical uncertainties.
The situation is expected to be quite different for the nitrogen removals because while the AC is a dynamic system that can cope with the influent fluctuations, the DN is a more static system characterized by longer response times. Figure 4.16 a-b shows respectively the NH$_4$-N and the NO3-N in the treated effluent from the two membrane systems, while figure 4.17 compares the total nitrogen

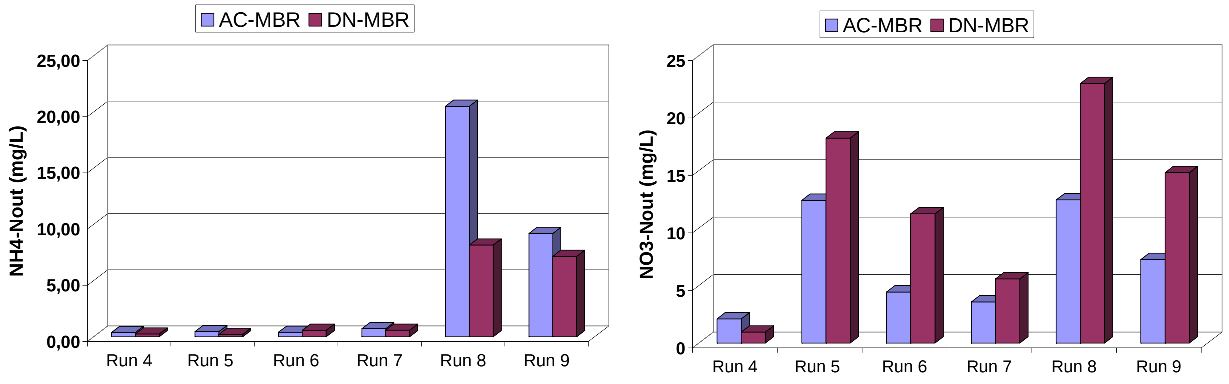


Figure 4.18. Comparison AC-MBR and DN-MBR: NH$_4$-N and NO$_3$-N in the treated effluents

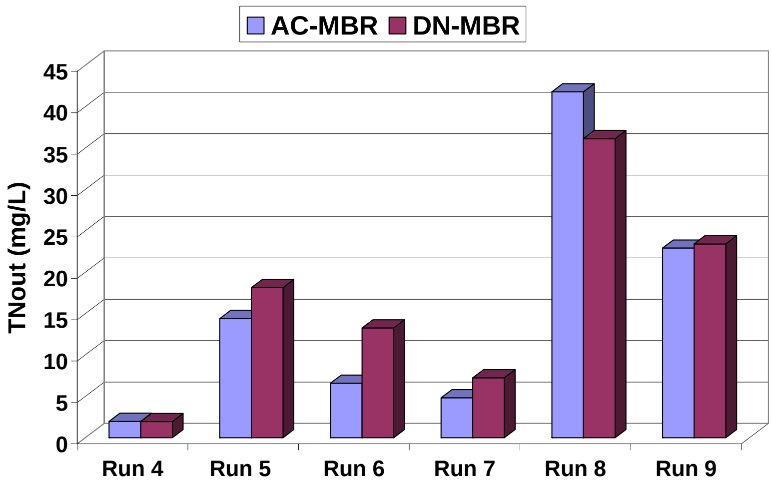


Figure 4.19. Comparison AC-MBR and DN-MBR: TN in the treated effluents

The nitrification was similar in the two systems up to NLR equal to 0,12÷0,13 kgN m^{-3} d^{-1} while the DN-MBR was more performing in run 8 and 9. On the other hand, the denitrification was always better in the AC-MBR, just as expected. As for the total nitrogen, the effluent contents from the AC-MBR were always lower than the DN-MBR except for the run 8. To evaluate these results one should consider the coupled effect of C/N ratio and NLRs and, contemporary, the effective aerobic and anoxic phases into the system. In run 4-7 the rigid DN-MBR was characterized by too long aerobic HRTs that causes also waste of COD which could have been used for nitrates denirtrification. As a result, the total nitrogen effluent from the AC-MBR is lower than the effluent from the DN-MBR of 1÷7 mgN/L. The situation changed remarkably when the nitrification potentiality of the plant was not adequate to the influent loadings, as occurred in runs 8-9 when the effluent ammonia increased severely. However, the AC-MBR could face the inloadings for C/N>5 (run 9) when the dynamic system maintained its flexibility and consequently optimized the phases. On the contrary, with C/N<5 the AC-MBR became static and does not allow for sufficient ammonia nitrification when NLRs>15 kgN m^{-3} d^{-1}. In these cases, it is better to adjust the control system so to operate according to fixed absolute time setpoints which optimize the ammonia nitrification.

3.5 ASM2 simulation

Several authors have dealt with the theoretical and mathematical basis to the design the intermittently aerated continuous bioreactor (Hanhan *et al*, 2005). However, to date the design of these systems is mainly based on empirical evidences as pointed out also in the chapter III. Moreover, several authors have pointed out the necessity to modify the default kinetic rates of the ASM2 (Henze *et al*, 2000) to have a reliable simulation of the processes involved in membrane bioreactors.

In this study, the validation of the ASM2 for the process in intermittent membrane bioreactors has been attempted using the default kinetic rates. According to the software based on this model, the configuration of the plant must have a secondary settler as last operation unit, the scheme was set according to figure 4.20.

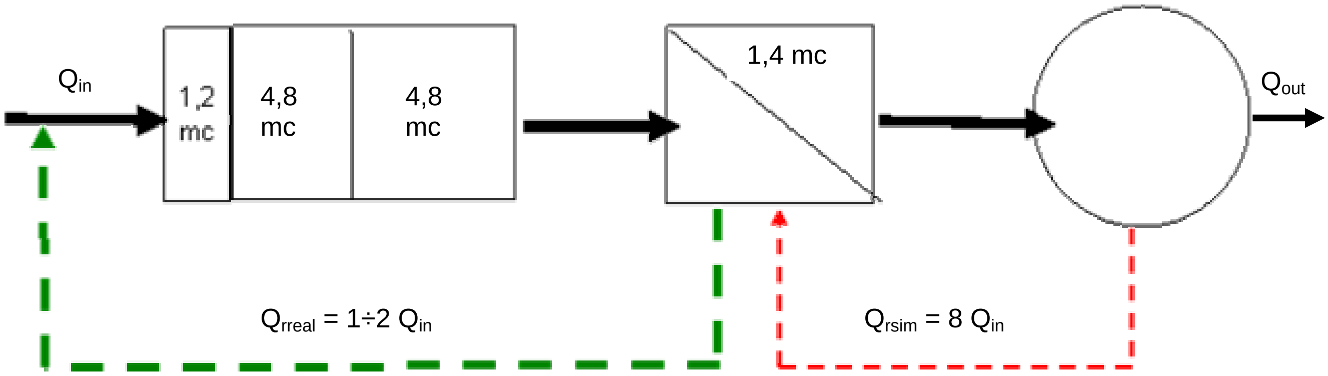


Figure 4.20 Plant configuration set for the simulation with ASM2

As one can observe from figure 4.20, the process was simulated with four completely mixed tank reactors in series and a final secondary clarifier, where a very low HRT has been imposed providing an high number of sludge recycles.

As for the oxygen level in the reactors: no air supply was provided in the first reactor, the intermittent aeration of the alternating reactors was set according to the time lengths really observed in the demonstration plants over the 9 runs, the membrane tank was provided by continuous aeration.

The experimental results and the output of the ASM simulations are reported in table 4.17

Table 4.17 Comparative simulation and experimental

Effluent ASM2 simulation										
NH_4-N	mg/l	0,2	0,2	0,2	0,1	0,6	0,8	0,4		
NO_x-N	mg/l	4,2	4,5	2,4	1,9	8,7	5,0	3,1		
PO_4-P	mg/l	0,7	0,6	1,3	1,9	4,2	3,0	2,7		
Effluent experimental										
NH_4-N	mg/l	0,1	0,1	0,1	0,4	0,5	0,4	0,7	20,5	9,2
NO_x-N	mg/l	5,2	4,1	0,9	2,1	12,4	4,4	3,6	12,5	7,3
PO_4-P	mg/l	0,9	1,3	1,2	4,8	10,3	9,0	6,6	5,2	5,6
Delta										
NH_4-N	mg/l	0,1	0,1	0,1	-0,3	0,1	0,3	-0,3		
NO_x-N	mg/l	-1,1	0,4	1,5	-0,2	-3,7	0,6	-0,5	-12,5	-7,3
PO_4-P	mg/l	-0,2	-0,7	0,1	-2,9	-6,1	-6,0	-3,9	-5,2	-5,6

As for the effluent nitrogen, the results from the ASM2 and its default kinetic rates were found in acceptable agreement with experimental results in runs 1-7. The almost complete ammonia nitrification resulted both from the experimental results and from the ASM2, while the proportional error for the effluent nitrates (see equ. 4.8) was in the range 7÷30% except for run 3 when, however, the difference was of 1,5 mg L^{-1}, which is considered still acceptable from an applicative standpoint.

$$\frac{(NO_X - N_{exper}) - (NO_X - N_{simul})}{(NO_X - N_{exper})} \cdot 100 \qquad \text{equ. 4.8}$$

As far as the $P_{effluent}$, the agreement between ASM2 and real results was not find out. The incapability of the software was attributed to the default biomass yield. This value was higher than the real and involved higher phosphorus removal by biomass assimilation. In conclusion, it can be said that the ASM2 can be used *as it is* to have gross information on the nitrogen forms effluent from AC-MBR systems. On the other hand, the system is not suitable to simulate phosphorus biological removal with acceptable exactness, because the biomass assimilation is over-estimated.

4. Conclusions

The results from the long-term operation of a demonstration membrane bioreactor intermittently aerated have been presented and discussed in this chapter. The technology was proposed for the treatment and reuse of municipal wastewater and the key performance indicators proved its reliability for this type of application. Four main topics have been analyzed in details: (1) the behaviour and the maximal potential of the AC-MBR system with respect to the nitrogen and phosphorus removal; (2) the reliability of the control strategy for application under the different conditions tested; (3) the comparative evaluation with a parallel multizone predenitrification-nitrification scheme; (4) the capability of the ASM2 to simulate the process with the default kinetic rates.

The main remarks of the study are the following:

- the system was able to adjust the alternation of anoxic and aerobic phases according to the influent characteristics for NLR and C/N in the range 0,16÷0,18 kgN m^{-3} d^{-1} and 5÷6, respectively. These values are assumed to mark the border lines for an effective nitrogen removal which can meet the reuse standard. Therefore, the AC-MBR can be adopted both for new systems and also to upgrade existing ones, increasing the treatment capacity and achieving the agreement with the reuse standard at the same time;
- the use of the available carbon source with concern to the total nitrogen removal was quantified in some 0,1 kg of total nitrogen removed per kg of total influent COD. However, this value was achieved in systems often affected by over-aeration phenomena and, therefore, could be taken as indicator of the minimal performance;
- the control strategy was validated at demonstration scale and the bending point based strategy seemed suitable for the treatment of wastewater poor of carbon source for denitrfication. Furthermore, the complete control algorithm was able to face critical boundary conditions thanks to the setpoint based secondary branches;
- as far as the phosphorus biological removal, the AC-MBR scheme proved to be able to enhance the performances by triggering luxury uptake phenomena. However, this was observed only in case the influent sewage contained external acetate. On the other hand, in the other runs the rbCOD was removed only by assimilation for the biomass growth;
- the comparative evaluation of intermittent and multizone schemes pointed out the better performances of the alternating processes for total nitrogen removal operating NLRs in the range 0,05÷0,16 kgN m^{-3} d^{-1}. The better performances were attributed to the enhanced denitrification, while the complete ammonia nitrification was almost achieved in both the systems. The incoming of nitrogen loadings higher than 0,18 kgN m^{-3} d^{-1} caused limitations for the ammonia nitrification in the alternating processes, causing high effluent levels of ammonia. In the light of this scenario, the bending point based control is not preferable because can involve too long anoxic phases and too high ammonia accumulation in the reactor which cannot be completely oxidized in the aerobic phases. The setpoint based control is, therefore, to be set in order to guarantee the nitrification.
- the effluent nitrogen forms as simulated by the activated sludge model, using the default kinetic rates, were found in acceptable agreement with the real effluent from the demonstration AC-MBR in the range 0,05÷0,16 kgN m^{-3} d^{-1}. On the other hand, the behaviour of the phosphorus was not simulated correctly probably due to different kinetic rates for sludge yield. In conclusion, if operating in the range of NLRs before mentioned, the ASM2 can be used as it is to have gross information about the process and also to arrange the first absolute time setpoint on the secondary branches of the control algorithm. These values must, anyway, be adjusted after the initial trial operation of the plant.

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Chapter V. Metals occurrence and removal

Trace quantities of many metals, such as Cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni) and zinc (Zn) are important constituents of most waters. Most of these metals are necessary for growth of biological life, and absence of sufficient quantities of them could limit growth of algae, for example. However, many of these metals are classified as priority pollutants, because the presence of any of these metals in excessive quantities interferes with many beneficial uses of the water because of their toxicity to higher organisms, micro-organisms and plants (Niece, 1999; Ehrlic, 1997; Lester et al, 1979).

The sources of metals in wastewater include the discharges from residential dwellings, groundwater infiltration, and commercial and industrial discharges. For example cadmium, chromium, lead, and mercury are often present in industrial liquid wastes. These are found particularly in metal-plating wastes and should be removed at the site of the industry rather than be mixed with the municipal wastewater. However, this last situation can likely occur, especially in presence of small factories which cannot afford proper effective treatment systems. As a consequence, also the municipal wastewater treatment systems often must cope with metals removal. This necessity is even more compelling in the light of the recent EU Water Framework Directive (Dir. 2000/60/EC), which included Cd, Pb, Hg, Ni and their compounds in the list of priority substances (Annex X) that have an high level of concern for the improvement or the conservation of the water bodies quality standard.

This chapter deals with the metals occurrence and removal in conventional and membrane systems for municipal applications. In particular, prior to examine the behaviour of membrane systems, the topic is appropriately weighed defining the occurrence and removal of metals in real municipal italian WWTPs. Finally, the discussion is focused on membrane systems leading to final considerations about the proper design and operation and maintenance (O&M).

1. Occurrence and removal of heavy metals in municipal wastewater treatment systems: literature analysis

Metals are generally present in wastewaters both at trace and high levels. Some metals are generally present at concentrations of 1 or more mg/L, namely, iron, aluminium and zinc, while other metals, especially very toxic heavy metals, are present at low or trace levels, sometimes close or under the detection limits. However, the metals levels in municipal wastewater are very variable, mainly because they are almost correlated to the presence of industrial discharges in the catchments area. Despite this great variability some generalisation could be attempted. Haung and Wang (2001) did not find significant correlations among metals concentration and distribution (i.e., soluble or particulate phase) and other wastewater parameters, like pH, alkalinity, COD, and ionic strength. In the end metal distribution relied almost entirely on the concentration of solids in wastewater samples. Balmer (2001), reported the results of some Danish and Swedish studies concerning the metals loading in wastewaters originated by households (toilets and water consumption), that is the so called "unavoidable" part of pollutants load into municipal wastewater. Table 5.1 shows typical load ranges for some heavy metals.

Table 5.1. Heavy metals load from toilets and water consumption in households and relative concentrations in municipal wastewaters

Metal	**Daily specific load**		**Concentration (*)**	
Cd	mg/PE·day	0.013	µg/l	0.07
Cr	mg/PE·day	0.2	µg/l	1
Cu	mg/PE·day	2.5	µg/l	12.5
Pb	mg/PE·day	0.12	µg/l	0.6
Hg	mg/PE·day	0.05	µg/l	0.25
Ni	mg/PE·day	0.3	µg/l	1.5
Zn	mg/PE·day	14	µg/l	70

(*) On the basis of an average production of 200 litres/PE·day

Clearly, the metals content in drinking water can be very different, depending on the origin of the fresh water, but metals will be always present at levels below the safety threshold. The total amount of metals originated from households was determined on the basis of data collected in Swedish municipalities without industrial areas and without combined sewers (no runoff storm wastewater). Table 5.2 summarises loads and concentrations of heavy metals from wastewater produced in municipal areas.

Table 5.2. Global heavy metals load and concentrations from households

Metal	**Daily specific load**		**Concentration (*)**	
Cd	mg/PE·day	0.05 – 0.1	µg/l	0.25 – 5
Cr	mg/PE·day	1 – 1.4	µg/l	5 – 7
Cu	mg/PE·day	6 – 17	µg/l	30 – 85
Pb	mg/PE·day	1 – 4.9	µg/l	5 – 25
Hg	mg/PE·day	0.02 – 0.05	µg/l	0.1 – 0.25
Ni	mg/PE·day	1 – 2	µg/l	5 – 10
Zn	mg/PE·day	20 - 50	µg/l	100 – 250

(*) On the basis of an average production of 200 litres/PE*day

These "unavoidable" loads can be variable, according to different habits of life and pipeline materials characteristics. Isaac *et al.* (1997) found that corrosion of drinking water distribution system can contribute significantly to copper and lead presence in wastewaters. In particular, they showed that corrosion may account for some 13-51% of Cu load and 9-67% for Pb load in wastewaters entering a WWTP in east USA. Balmer (2001) reported that corrosion of copper from pipelines accounts for 70% of Cu WWTP sludges in Sweden.

Moreover, in catchments with combined sewers, storm water will contribute to pollutants loading because of the surface runoff. The composition of storm water runoff is highly variable in terms of concentrations and also over time. In fact, only the first flush of runoff water presents high concentrations of metals, after that they go down to trace levels. Balmer (2001) reported data for drainage waters and storm water detected in Sweden, while Gromaire-Mertz *et al.* (1999) reported data of run off waters monitored in central Paris.

Table 5.3 summarises these data for some heavy metals detected in the first flush runoff waters.

Table 5.3. Metals concentrations in drainage and runoff storm water (first flush)

		Balmer, 2001		Gromaire-Mertz et al., 1999		
		Drainage water	**Storm water**	**Roof water**	**Yard water**	**Street water**
Cd	μg/l	0.09	0.34	1.3	0.8	0.6
Cr	μg/l	4.7	2	-	-	-
Cu	μg/l	7.3	85	37	23	61
Pb	μg/l	0.75	30	493	107	133
Hg	μg/l	0.002	0.06	-	-	-
Ni	μg/l	53	5	-	-	-
Zn	μg/l	32	170	3422	563	550

In their study, Gromaire-Mertz *et al.* (1999) found that runoff waters from roofs generally determine greater loads of heavy metals compared to loads from yards or streets. This is because in Paris streets and yards are generally clean twice or more times per week with special machines which wash and suck the dust. The detected metals were generally present in the particulate form, that is, metals were bound to suspended solids. This was particularly true for lead, while zinc was found predominantly in the soluble phase. With further concern to the surface runoff effect and to the temporal variation of the heavy metals occurrence in WWTPs, a paper by Villar *et al* (2006) studied a possible correlation between heavy metals and polycyclic aromatic hydrocarbons influent to the municipal WWTP of Jerez de la Frontera (Spain), trying to demonstrate that the origin of these compounds is the same. They found out that heavy metals were mainly coming from industrial sources, while the rain runoff played a minor role. However, heavy metals were dragged into the WWTP by winter rains, rather than summer rains. Data concerning heavy metals influent to large WWTPs for the treatment of municipal and industrial wastewater has been presented by Karvelas *et al* (2003) and Chipasa (2003), respectively for the cities of Thessaloniki (Greece) and Gdansk (Poland). Authors found out abundances of metals much higher than those from purely domestic wastewater (compare table 5.4 and 5.2).

Table 5.4. Metals concentrations influent into large WWTPs

		Karvelas, 2003		**Chipasa, 2003**
		Average	**St.Dev.**	**Range**
Cd	μg/L	3.3	1.1	5÷70
Cr	μg/L	40	12	n.a.
Cu	μg/L	79	35	70÷270
Pb	μg/L	39	9.4	30÷150
Hg	μg/L	n.a.	n.a.	n.a.
Ni	μg/L	770	220	n.a.
Zn	μg/L	470	140	250÷800
Fe	μg/L	480	87	n.a.

Table 5.4 proves that large systems for wastewater treatment are likely coping with higher metals concentrations, because the larger is the plant the higher is the probability that industrial discharges

are present in the catchments area. To confirm this evidence, Balmer (2001) reported that some 5% of heavy metals load in Goteborg WWTPs (Sweden) was due to large industries discharging, except for Cd and Hg, which loads were determined by industries for 7% and 16%, respectively. Concerning the global influent load of metals to a WWTP, it is interesting to note the results described by Balmer (2001): in his work he reported the data of Rya WWTP in Sweden; here the sum of the different contributions in terms of heavy metals load were compared with the total load found in the influent stream of the WWTP (tab. 5.5).

Table 5.5. Heavy metals loads in Rya WWTP (Sweden) in 1999. Data in kg per year

Source	**Cd**	**Cr**	**Cu**	**Pb**	**Hg**	**Ni**	**Zn**
Households	15	200	2000	250	10	200	6000
Industries and landfills	4	46	131	29	4.1	100	850
Small industries	0.1	20	30	40	0.5	2	50
Water not accounted for(*)	2.7	46	131	45	1.8	36	1080
Water works sludge	1.4	19	50	54	0.4	16	190
Drainage water	6.5	340	530	50	0.1	390	2300
Storm water	5	30	1270	450	0.9	70	2550
Sum of sources	35	700	4100	930	18	810	13000
Influent load	34	870	7800	960	22	1300	13400

(*) Wastewater from schools and offices

So, we can say that data from table 5.1 and 5.2 are the minimal, “unavoidable” loads of metals reaching the WWTPs. Moreover, considering also catchments areas with combined sewers the metal levels will be increased according to the rainfall runoff events (table 5.3). Finally, levels of table 5.4 can be reached when particular industrial discharges are present in the catchments area.

The presence of heavy metals is not only of great environmental concern, but also strongly reduces the microbial activity. Heavy metals are reported to inhibit nitrification and denitrification processes (Braam and Klapwijk, 1981; Waara, 1992) and reduced microbial oxidation of organic compounds (Ajmal *et al.*, 1982, 1983; Madoni *et al*, 1996). However, it has to be noted that inhibitory effects are likely expected on activated sludge processes only at concentrations that are not usual in the treatment of municipal wastewater (see table 5.6).

Table 5.6. Metals of importance for inhibitory effects on activated sludge processes

Metal		**Concentration threshold of inhibitory effect on heterotrophic organisms**	**Concentration threshold of inhibitory effect on autotrophic nitrification**
As	µg/L	50	-
Cd	µg/L	1000	-
Cr	µg/L	1000÷10000	250
Cu	µg/L	1000	100
Pb	µg/L	100	-
Hg	µg/L	100	-
Ni	µg/L	1000	250
Zn	µg/L	1000	-

Adapted from Metcalf & Eddy (2003)

In the light of the thresholds of table 5.6 and the typical metal occurrence shown in 5.1-4, the inhibition of biomasses inhibition can be considered of minor importance.

2 The Italian scenario

A recent survey, published in September 2005 by the Italian Environmental Protection Agency (APAT), reports that at the moment in Italy the municipal wastewater treatment is carried out by about 15000 WWTPs with treatment capacity below 2000 PE for some 80%. However, the major part of the overall pollutant loadings are influent to plants larger than 10000 PE. As far as concern the collection systems, most of these plants are fed by combined sewers which collect municipal wastewater, rainfall runoff and, in several cases, a fraction of industrial wastewaters that meet the regulations about the discharge in public sewers (see table 5.7)

Table 5.7. Italian limits for discharge in municipal sewers systems

Metal		**Law limit for discharge in the municipal sewers system**
Al	mg/L	2,0
As	mg/L	0,5
Cd	mg/L	0,02
Cr	mg/L	4
Fe	mg/L	4
Hg	mg/L	0,005
Ni	mg/L	4
Pb	mg/L	0,3
Cu	mg/L	0,4
Zn	mg/L	1,0

As a consequence, the levels of metals influent to municipal WWTPs are very diverse case by case. Moreover, a clear scenario could not be outlined on the basis of the published data. So, it was necessary to have awareness of the *size of the problem* before the investigation for its possible solution. Therefore, a detailed characterization of a number of selected metals and organic persistent compounds (later discussed in the chapter VI) influent to italian municipal WWTPs was carried out preliminarily and is following illustrated and commented.

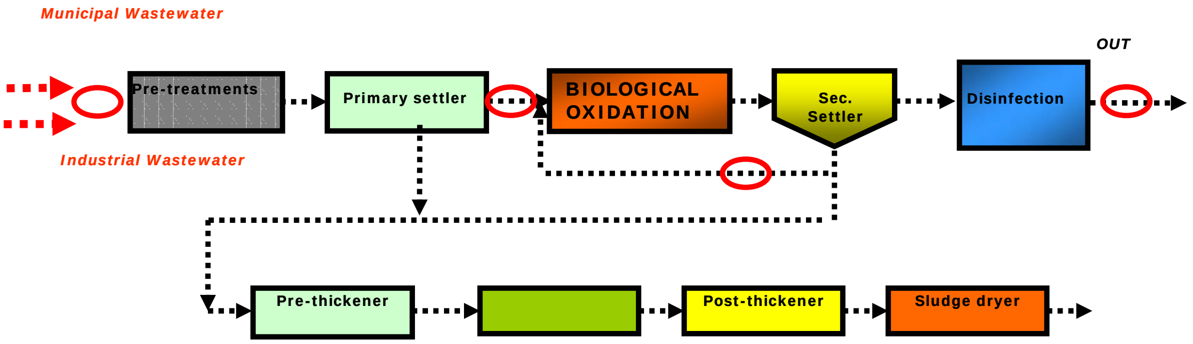
Five WWTPs were opportunely selected and monitored on the basis of the following criteria: (a) the origin of wastewaters collected by the sewers system (pure municipal or mixed industrial/municipal); (b) the treatment capacity; (c) the possible infiltration into the collection systems from high groundwater; (d) the scheme adopted for the biological process. Following these selection criteria, the WWTPs monitored for the study were characterized by: municipal wastewater from 30 to 100% on the total inflow; influent flowrates, calculated as daily average over one year monitoring, from 15000 to 118000 m^3 d^{-1}; infiltration factors from 1 to 3; block flow diagram shown in figure 5.1.a-b-c-d-e. Table 5.8 summarizes the main features concerning the inflows to each WWTP.

Table 5.8 Main features of the wastewaters to the five WWTPs

Plant	Influent flow (m3/d)	Municipal rate (%)	Industrial rate (%)	f
A	25000	~30	~70	1,3
B	15000	~100	~0	3,00
C	4900	~100	~0	1,20
D	118000	~63	~37	1,39
E	21000	~94	~6	1,03

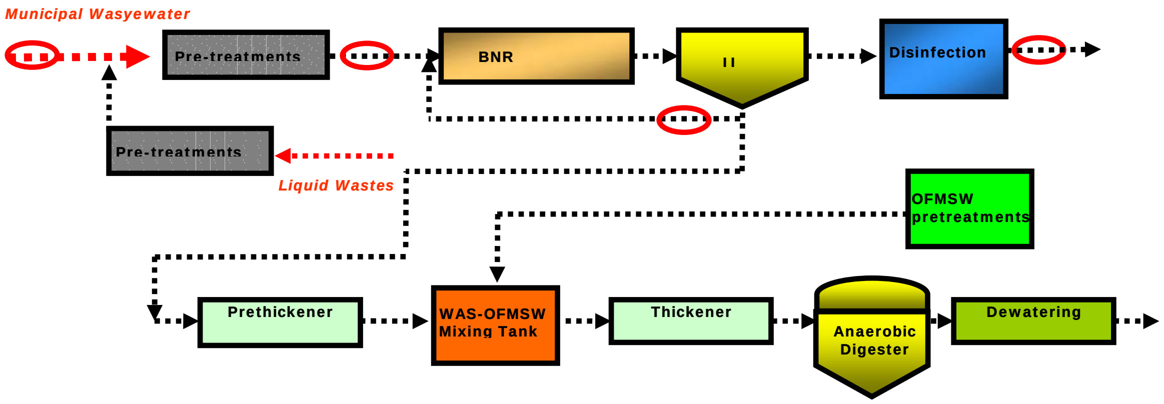
The plants were different also for the flow-scheme operated as reported in the schemes below which are followed also by the sequence of the operation units. Here are also indicated the sampling points within the treatment flow-scheme.

Plant A



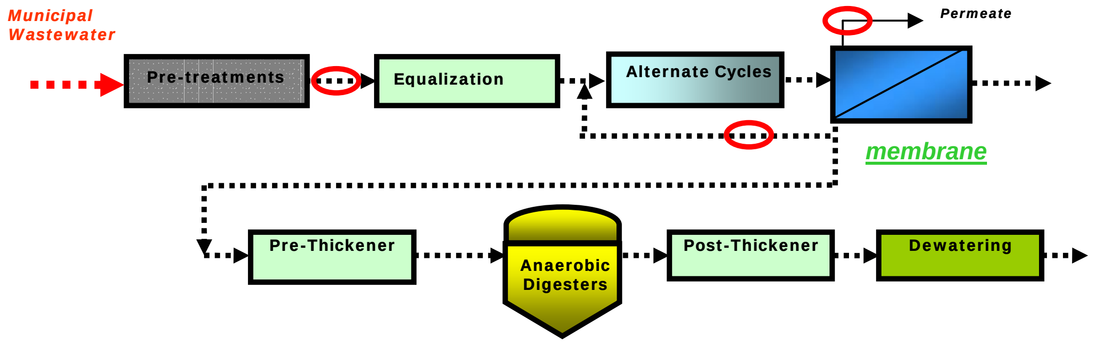
Plant A: (1) Bar screen; (2) Fine sieve; (3) Aerated degritter; (3) Primary settler; (4) aerobic activated sludge bioreactor; (4) secondary clarifier; (5) disinfection by chloride compounds

Plant B

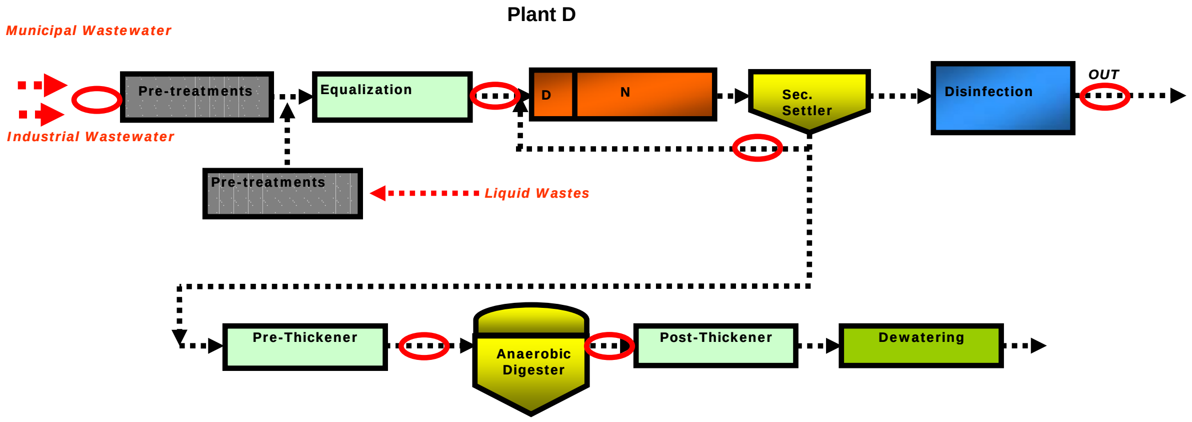


Plant B: (1) Bar screen; (2) Fine sieve; (3) Gravity degritter; (4) bioreactor with biological nutrients removal (A2O with Johannesburg modification); (5) secondary clarifier; (6) disinfection by chloride compounds

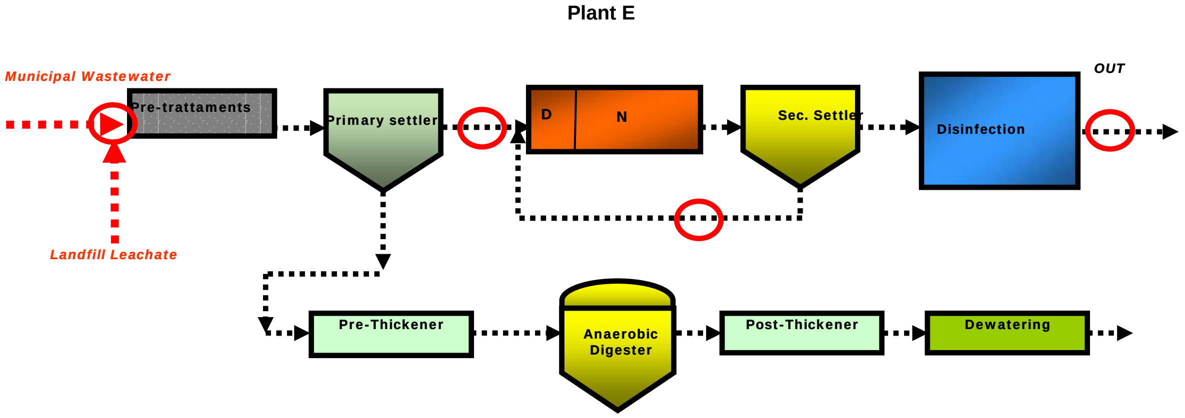
Plant C



Plant C: (1) Bar screen; (2) Fine sieve; (3) Degritting in a vortex chamber; (4) Alternate Cycles-Membrane Bioreactor



Plant D: (1) Bar screen; (2) Fine sieve; (3) Aerated degritter; (4) In-line equalization; (5) biological process according to the predenitrification-nitrification scheme; (4) secondary clarifier; (5) disinfection by peracetic acid



Plant E: (1) bar screen; (2) fine sieve; (3) aerated degritter; (5) bioreactor according to the predenitrification-nitrification scheme; (4) secondary clarifier; (5) disinfection by peracetic acid.
A substantial difference in the sources of wastewater involved different levels of conventional pollutants as inferred from the yearly averages shown in table 5.9.

Table 5.9. Conventional pollutants in the influent wastewaters (average over one year monitoring)

Plant	**TSS (mg/L)**	**COD (mg/L)**	**TN (mg/L)**	**TP (mg/L)**
A	101	371	12	2
B	129	160	13	2
C	262	645	37	5
D	247	346	33	5
E	327	464	44	6

Basically the cases studied ranged from diluted wastewater, in case of relevant infiltration from groundwater and combined collection system, to medium-high strength wastewater, in case of mostly separated collection system and low infiltration factors.
The fraction of industrial wastewater in plant A is very considerable and comes mainly from a chemical-pharmaceutical district. However, also a beer factory is present in the catchments area and increase the organic loading.
The sewers system associated to the plant B serves mainly domestic dwellings located in an area with high groundwater table. As a result high leakage into the collection system is observed.
Also plant C receives mostly municipal wastewater from domestic dwellings, but in this case the sewers system is separated and the infiltration of groundwater is low. As a result, higher abundances of conventional pollutants were observed to the treatment system.

Plant D treats a mix of municipal and industrial wastewater coming from a combined collection system. In this case, the industrial source is represented by a famous petrochemical district.

Plant E receives above all municipal wastewater. However, during the year of investigations there were also frequent but random discharges of leachate from local municipal landfills. Although this practice should be anomalous, to date it can be really observed for the italian real treatment systems, therefore the cases selected are representative for the Italian scenario.

2.1 Sampling and analyses procedures

Metals influent to the wastewater treatment systems are related to be mostly to the suspended particulate, especially street particles (Lau S.L. and Stenstrom M.K., 2005; Villar P. *et al.*, 2006), and knowing the liquid/solid partition can be interesting to study the most suitable treatment operation units of the flow-scheme. The sampling and analyses campaign was carried out over an overall period of 18 months. The samples were taken always in the same sections, noting always about the weather conditions (dry or rainy) to evaluate the possible rainfall runoff impact. In order to distinguish, already in the influent, the metals that can pass through the membrane material from those retained, the sampling was carried out according to a special protocol appropriately set up.

In particular, a simultaneous sampling was carried out by means of two automatic samplers: the first, traditional, (figure 5.1) to collect daily composite samples; the second (figures 5.2 and 5.3), properly engineered for the experimentation and equipped with submerged ultrafiltration membrane, to collect suspended particulate influent to the plant over 24 hours. This last device is able to filtrate 350÷450 L per day of wastewater. The suspended particulate is retained into the vessel over 24 hours sampling thanks to the sieving effect of the UF membrane, a reliable and significant composite daily averaged sample is finally withdrawn and analyzed for the micropollutants on the dry content. As far as the membrane O&M, the filtration cycle can be set by a timer, and the usual values were: permeation (60 seconds)/strong backwashing (15 seconds). Since the membrane underwent to quick initial conditioning fouling, the possible organic layer over the whole sampling period was considered almost stable as well as the effective molecular weight cut off (eMWCO) of the system, that marked the border line between what was considered liquid and particulate phase. At the end of each sampling operation, the membrane was cleaned using both hypochlorite solution (500÷700 mgCl/L) and citric acid (800 mg$C_6H_8O_7$/L) so to re-establish the original conditions.

Figure 5.1. Classical portable automatic sampler

Figure 5.2 Special automatic sampler used to separate liquid from solid phase

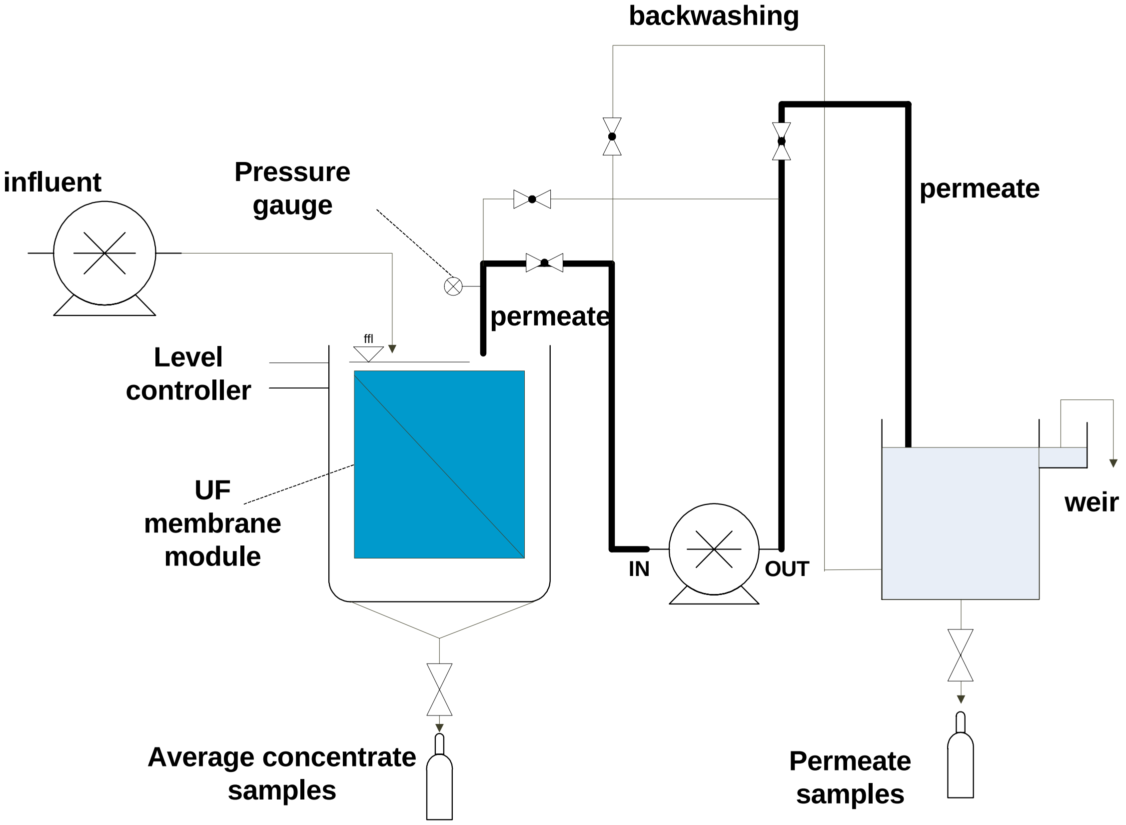


Figure 5.3. Special automatic sampler

Once in the lab, samples were analyzed for metals content according to the EPA methods. Nitric acid (1 ml at 98% w/w) was added to one litre of wastewater sample and a microwaves working station (CEM) was used to mineralize the sample. Atomic Adsorption Spectrometer Varian SpectrAA 220 was used for As and Hg, while Inductively Coupled Plasma Atomic Emission Spectrometry Varian Liberty 110 for Cd, Cr, Ni, Pb, Cu, Fe, Zn and Al.

2.2 Metals abundances and solid/liquid partition

Thanks to the particular sampling procedure adopted, it was possible to know the metals content in: (a) the overall raw wastewater (expressed as weight to volume); (b) the particulate phase (expressed as weight to weight volume); (c) the liquid phase (calculated according to equ. 5.1).

$$\left(\frac{\mu gMetal}{L}\right)_{liq.phase} = \left(\frac{\mu gMetal}{L}\right)_{total} - \left[\left(\frac{\mu gMetal}{gSS}\right) * \left(\frac{gSS}{L}\right)\right] \qquad \text{Equ. 5.1}$$

First of all the global occurrence of metals is discussed in terms of concentrations and variability of the substance. Given the definition of the frequency of occurrence (f.o.) as:

$$f.o. = 100 * \left(\frac{n.samples.with.metal.content \geq d.l.}{n.samples.with.metal.content < d.l.}\right) \qquad \text{Equ. 5.2}$$

where *d.l.* is the detection limit attainable by the analytical method used, tables 5.9 and 5.10 show the frequency of occurrence referred respectively to the overall raw wastewater and the suspended particulate phase.

Table 5.10 Metals in the raw wastewater - frequency of occurrence

	Detection Limit (d.l.)	Frequency of Occurrence (f.o.)				
		A	B	C	D	E
	$\mu g\ L^{-1}$	%	%	%	%	%
As	<1	20	50	0	75	29
Hg	<0,2	80	67	25	75	0
Cu	<2,5	100	67	100	100	100
Pb	<2,5	75	34	100	75	71
Cd	<0,25	20	0	50	50	29
Ni	<0,5	100	100	100	75	100
Cr	<2,5	100	67	100	100	100
Zn	<50	100	100	100	100	100
Fe	<50	100	100	100	100	100
Al	<50	100	100	100	100	100

Table 5.11 Metals in the suspended particulate phase - frequency of occurrence

	Detection Limit (d.l.)	Frequency of Occurence (f.o.)				
		A	B	C	D	E
	$mg\ kgSS^{-1}$	%	%	%	%	%
As	<2,5	100	50	75	100	50
Hg	<0,5	100	100	100	75	100
Cu	<0,5	100	100	100	100	100
Pb	<0,5	100	100	100	75	100
Cd	<0,05	100	100	100	75	100
Ni	<0,1	100	100	100	75	100
Cr	<0,5	100	100	100	75	100
Zn	<10	100	100	75	75	100
Fe	<10	100	100	100	75	100
Al	<10	100	50	100	100	100

From table 5.11 one can observe that the frequency of occurrence of metals in the solid phase was close to the 100%, on the contrary the detection of metals in the raw wastewater was less frequent nothwithstanding the detection limit often < 1 $\mu g\ L^{-1}$.

Table 5.13 show the abundances of metals found out in the samples of raw wastewaters, collected by the traditional automatic sampler, and in the suspended particulate, collected by the special automatic sampler. Since the origin of the wastewaters was rather diverse, attention should be paid both to the overall concentrations and to the variation coefficient, calculated according to equ. 5.2.

Variation Coefficient = 100(Standard Deviation/Average)* Equ. 5.2

Table 5.12. Metals in the raw wastewaters

	Average(µg/l) (±Var.Coeff. (%))	Average(µg/l) (±Var.Coeff. (%))	Average(µg/l) (±Var.Coeff. (%))	Average(µg/l) (±Var.Coeff. (%))	Average(µg/l) (±Var.Coeff. (%))
As	8,8*	4*	n.a.	2,7(±68%)	6(±33%)
Hg	3,8(±49%)	1,5(±58%)	0,7(±8%)	1,8(±40%)	n.a.
Cu	32,2(±19%)	9,9(±56%)	9,8(±44%)	38(±61%)	60,9(±39%)
Pb	6,5(±29%)	8(±	8,6*	2(±60%)	10,5(±27%)
Cd	0,4*	n.a.	8,7(±13%)	27,8(±62%)	0,6(±34%)
Ni	17(±75%)	3,5(±31%)	16,6(±23%)	61,7(±4%)	21,6(±60%)
Cr	26,2(±68%)	8,1(±11%)	56,4(±24%)	56,4(±37%)	59,2(±99%)
Zn	254(±42%)	348(±31%)	1233(±20%)	2411(±29%)	227(±37%)
Fe	696(±20%)	515(±29%)	361(±10%)	531(±30%)	2391(±81%)
Al	399(±23%)	786(±46%)	1940(±8%)	2489(±40%)	2531(±54%)

*only one sample higher than the detection limit

Table 5.13. Metals in the suspended particulate

	A	B	C	D	E
	Average(mg/kgSS) (±Var.Coeff. (%))	Average(mg/kgSS) (±Var.Coeff. (%))	Average(mg/kgSS) (±Var.Coeff.(%))	Average(mg/kgSS) (±Var.Coeff. (%))	Average(mg/kgSS) (±Var.Coeff. (%))
As	7(±6%)	5,6(±52%)	n.a.	2,7(±16,8)	n.a.
Hg	6,9(±51%)	2,7(±48%)	7,7(±25)	1,8(±12,2)	n.a.
Cu	1241(±2%)	117,0(±46%)	43,9(±13)	38(±6,1)	213,54±*
Pb	67,3(±16%)	34,8(±25%)	n.a.	20(±15,5)	37,71±*
Cd	3,7(±4%)	1(±74%)	13,5(±26)	27,8(±20,1)	0,6±*
Ni	124(±7%)	15,1(±27%)	23, 4(±20)	61,7(±21,1)	23,34±*
Cr	694(±9%)	21,9(±39%)	23,9(±44)	56,4(±44,7)	95,07±*
Zn	7326(±56%)	780(±48%)	19,5(±26)	2411(±66,6)	395±*
Fe	25103(±14%)	4040(±36%)	10,4(±22)	531(±16,8)	6386±*
Al	9153(±14%)	8973(±25%)	8,1(±10)	2489(±23,7)	8875±*

*only one sample higher than the detection limit

The abundance of the metals found in the raw wastewater samples followed the general order: Cd<Pb<Cu<Zn<Fe<Al for the total raw wastewaters and Cd<Pb<Cu<Zn<Al for the solid phase. Similar relative abundances and concentration levels of metals have also been reported by other authors (Karvelas *et al.*, 2003; Chipasa *et al.*, 2003).

Furthermore, while the frequencies of occurrence are useful to select the compounds that should be focused in municipal applications, the variation coefficients indicate how steady the occurrence of a substance is. According to the variation coefficient, the descent order of the analyzed compounds is As>Cu>Ni>Hg>Pb>Cd>Cr>Al>Fe>Zn for the overall raw wastewaters, while the order Zn>Cr>Hg>Cd>As>Fe>Ni>Al>Pb>Cu is found for the suspended particulate phase.

Moving toward calculations on the specific per capita loading of metals, the treatment capacity has been calculated on the basis of the COD concentration according to equ. 5.3.

$$Trearment.Capacity_{COD}\,(PE_{COD}) = \frac{Loading_{COD}\,(kgCOD / day)}{ULF_{COD}\,(0{,}120 kgCOD / PE * day)} \qquad \text{Equ. 5.3}$$

Where ULF_{COD} (Unit Loading Factor on COD basis) is the COD theoretically discharged per capita per day due from domestic dwellings.

Table 5.14 Per capita loadings of heavy metals

Effective influent loads (percentage of industrial rate)						
Parameter		A (70%)*	B (0%)*	C (0%)*	D (37%)*	E (6%)**
As	mg/PE day	1,2	4,3		2,1	4,8
Hg	mg/PE day	2,9	1,2	0,7	1,4	
Cu	mg/PE day	10,6	8,8	9,8	29,9	48,7
Pb	mg/PE day	2,1	8,6	8,6	1,6	8,4
Cd	mg/PE day	0,1	n.a.	8,7	21,8	0,5
Ni	mg/PE day	5,6	3,8	16,6	48,6	17,3
Cr	mg/PE day	8,6	8,7	56,4	44,3	47,3
Zn	mg/PE day	83,4	373	1233	1896,7	181,3
Fe	mg/PE day	228,1	552,3	361,3	417,5	1912,5
Al	mg/PE day	130,8	842,1	1940	1958,2	2024,9

*fraction of raw wastewater from domestic source

**fraction of organic loads from municipal landfill leachate

With concern to the partitioning of the metals between particulate and liquid phase of the sewages, figure 5.4 a,b reports the fractions found out in almost municipal and mixed municipal/industrial wastewaters, respectively.

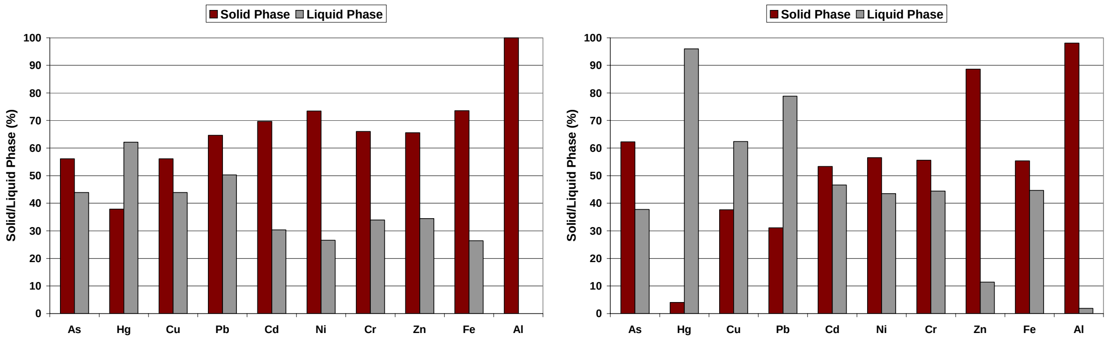


Figure 5.4 a,b. Solid/liquid partition of the metals in (a) almost municipal and (b) mixed municipal/industrial wastewaters

Generally, in almost municipal wastewater metals the major part of the metals is associated to the suspended particulate while this behaviour is less evident for a mix of municipal and industrial sources. However, more indications about the characteristics of the suspended particulate are given in the following pages of this chapter.

After the definition of the general occurrence of metals into italian municipal WWTPs, data have been processed in order to find out possible correlations that can allow to discern whether metals are coming also from industrial source. Therefore following both the “solid phase approach” and the “statistical approach” are described and discussed.

2.3 Searching for the source of the metals: solid phase and statistical approaches

Correlations among metals concentration and distribution (i.e., liquid or particulate phase) and other wastewater parameters, like pH, alkalinity, COD, and ionic strength were not found out as already pointed out by Huang *et al.* (2001). In this study the data were processed also to outline a method that could give information about the probable source of metals into the wastewaters (only municipal or a mix of municipal and industrial). Two possible approaches, named “solid phase” and “statistical” are following discussed.

2.3.1 The solid phase approach

This method is based on the study of metal content into the suspended particulate. The following figures 5.5-a,b,c,d,e show the relationships between the metals associated to the suspended particulate and the same TSS levels.

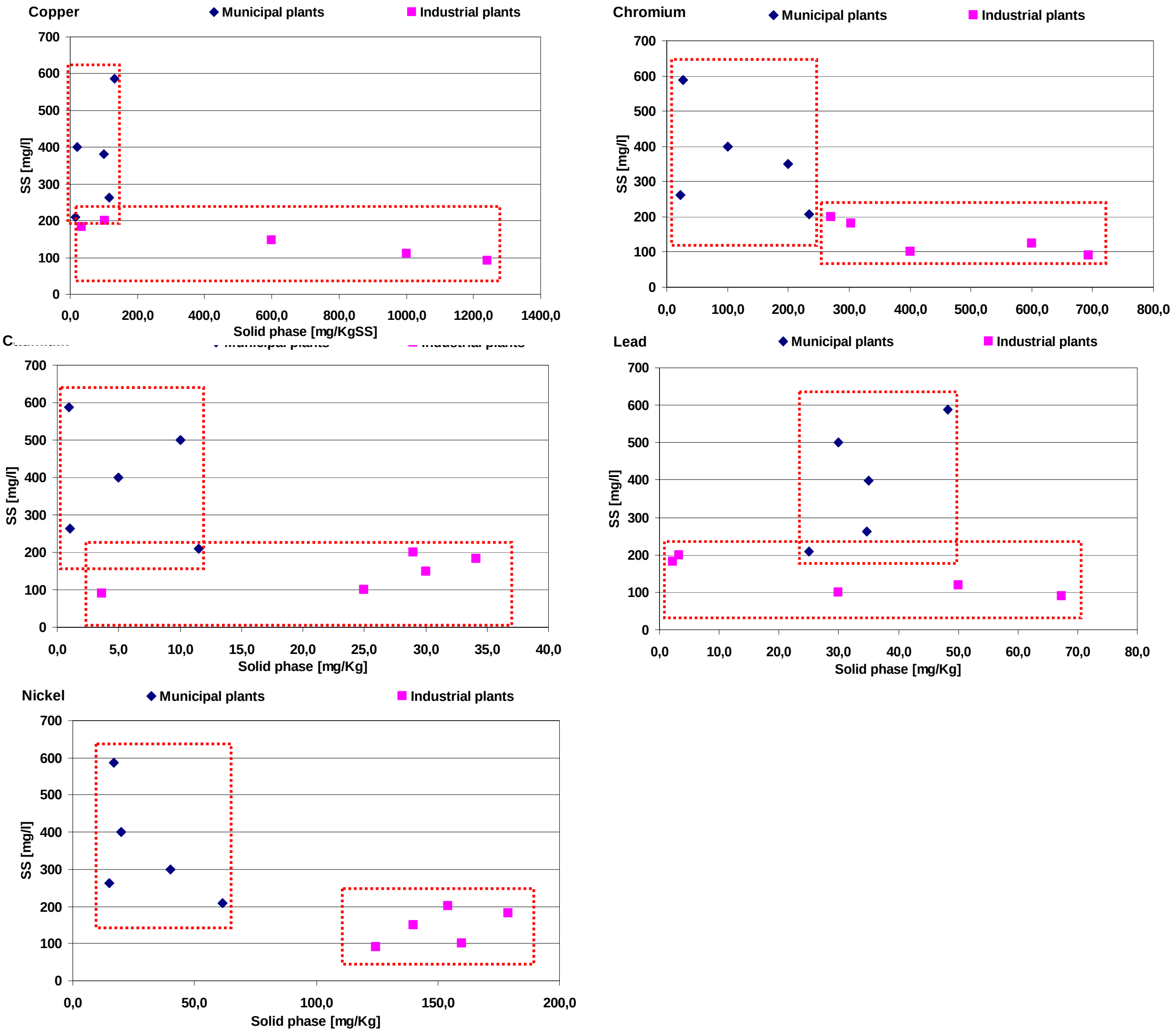


Figure 5.5 –a,b,c,d,e. Tendency of particulate phase vs. TSS in municipal and industrial WWTPs

From figures 5.5 one can observe that metal contents associated to the suspended particulate has vertical trend if the wastewater is almost municipal, while the trend is horizontal if certain industries are present in the catchments area. This evidence can mean that metals from urban sources are already associated to suspended particulate before the discharge into the sewers system, therefore the characteristics of the solid phase are almost constant and do not depend on the solid content. On the contrary, the presence of industrial wastewater corresponded to horizontal trends. This can mean that metals are discharged from industries mostly in liquid form and adhere to the particulate matter during the path in the sewers pipelines. Furthermore, metals sorption onto particulate suspended matter does not seem to reach the equilibrium conditions. In fact, wide variations of metals into the suspended solids (as mgMetal/kgTSS) do not correspond to different solids content. So, two behaviours can be distinguished and can be used as simple indexes to suppose the possible sources of metals in wastewater: (a) stable TSS content but unstable abundances of metals on dry weight basis, to suppose a combined collection of municipal and industrial discharges; (b) stable metals contents on dry basis also with different TSS concentrations, to suppose almost municipal discharges.

2.3.2 The statistical approach

Possible correlations between metals and TSS contents were investigated by a statistical data processing, so to construct possible correlation arrays. The final aim was to determine the compounds which behaviours are similar or comparable.

In this framework the term *correlation* means that there is a connection between two variables, so that exists a mathematical correlation with certain regularity. It must be taken as a statistical relationship, and not as a cause and effect connection.

Here the correlation degree between two variables is named *correlation coefficient* that is always in the range -1÷1. If the correlation coefficient is equal or close to the bounds of the ranges, the correlation is almost definite (linear dependence), that is direct or inverse respectively for positive and negative values. On the contrary, the more the coefficient is close to zero, the more a correlation between the corresponding compounds cannot be assumed.

Given two compounds X and Y, the correlation coefficients were calculated according to the following equations:

$$\mathrm{cor}(X, Y) = \mathrm{cov}(X, Y) / [\mathrm{sd}(X)\ \mathrm{sd}(Y)].$$

where:

$$\mathrm{cov}(X, Y) = E\{[X - E(X)][Y - E(Y)]\} = \text{ covariance between X and Y}$$

and:

$E(X)$, $E(Y)$, $sd(X)$, $sd(Y)$

are respectively the weighted average (E) and the standard deviation (sd) of X and Y.

Following correlations arrays are divided according to the source of wastewater: municipal or mixed industrial/municipal. Two levels of correlation have been assumed: **strong** in the range 0,9÷1; ***medium*** in the range 0,8÷0,9.

Table 5.15. Correlation array for municipal raw wastewaters

	As	Hg	Cu	Pb	Cd	Ni	Cr	Zn	Fe	Al	TSS
As	**1**	0,452	0,321	0,209	-0,415	-0,406	-0,471	-0,676	0,024	-0,026	-0,352
Hg	0,452	**1**	0,987	0,961	-0,976	0,087	-0,889	-0,676	0,898	0,879	0,225
Cu	0,321	**0,987**	**1**	0,982	-0,982	0,175	-0,890	-0,640	0,940	0,931	0,246
Pb	0,209	**0,961**	**0,982**	**1**	-0,942	0,240	-0,814	-0,523	0,975	0,969	0,344
Cd	-0,415	**-0,976**	**-0,982**	**-0,942**	**1**	-0,055	0,947	0,769	-0,884	-0,863	-0,206
Ni	-0,406	0,087	0,175	0,240	-0,055	**1**	0,175	0,459	0,234	0,340	-0,358
Cr	-0,471	***-0,889***	***-0,890***	***-0,814***	**0,947**	0,175	**1**	0,887	-0,766	-0,724	-0,231
Zn	-0,676	-0,676	-0,640	-0,523	0,769	0,459	***0,887***	**1**	-0,430	-0,368	-0,041
Fe	0,024	***0,898***	**0,940**	**0,975**	***-0,884***	0,234	-0,766	-0,430	**1**	0,993	0,494
Al	-0,026	***0,879***	**0,931**	**0,969**	***-0,863***	0,340	-0,724	-0,368	**0,993**	**1**	0,431
TSS	-0,352	0,225	0,246	0,344	-0,206	-0,358	-0,231	-0,041	0,494	0,431	**1**

A general remark from table 5.15, Hg, Cu, Pb and Cd can be correlated with other compounds, while it is difficult to predict Cr, As and Ni on the basis of other metals.

The number of the correlated compounds is expected to decrease when the influent heterogeneity increases. Therefore, this is a behaviour expected when industries are present in the catchments area of the collection system. Table 5.16 shows the correlation array for municipal/industrial plants.

Table 5.16. Correlation array for combined municipal/industrial raw wastewaters

	As	Hg	Cu	Pb	Cd	Ni	Cr	Zn	Fe	Al	TSS
As	**1**	0,379	-0,230	0,529	-0,566	-0,559	-0,857	-0,852	-0,385	-0,922	-0,834
Hg	0,379	**1**	0,052	0,002	0,116	-0,124	-0,566	-0,396	-0,322	-0,412	-0,312
Cu	-0,230	0,052	**1**	-0,267	0,498	0,248	0,333	0,636	0,851	0,417	-0,021
Pb	0,529	0,002	-0,267	**1**	-0,525	-0,321	-0,664	-0,545	-0,415	-0,620	-0,394
Cd	-0,566	0,116	0,498	-0,525	**1**	0,767	0,471	0,634	0,310	0,676	0,485
Ni	-0,559	-0,124	0,248	-0,321	0,767	**1**	0,378	0,590	0,202	0,720	0,710
Cr	***-0,857***	-0,566	0,333	-0,664	0,471	0,378	**1**	0,817	0,592	0,840	0,533
Zn	***-0,852***	-0,396	0,636	-0,545	0,634	0,590	***0,817***	**1**	0,772	0,953	0,682
Fe	-0,385	-0,322	***0,851***	-0,415	0,310	0,202	0,592	0,772	**1**	0,584	0,118
Al	**-0,922**	-0,412	0,417	-0,620	0,676	0,720	***0,840***	**0,953**	0,584	**1**	0,834
TSS	**-0,834**	-0,312	-0,021	-0,394	0,485	0,710	0,533	0,682	0,118	0,834	**1**

As expected, minor correlations between the compounds were found for municipal/industrial plants. In conclusion the statistical data processing has pointed out the impossibility to apply reliable predictive methods based on the abundances of the different metals. Further, the more is the heterogeneity of the sources of metals the more the prediction on the frequency or amount of the pollutants is not feasible.

2.4 The fate of heavy metals in municipal wastewater treatment plants

2.4.1 Fundamentals of metals removal by activated sludge systems

In recent years the research for the heavy metals removal has focused on new technologies rather than traditional methods such as ion exchange, chemical precipitation, solvent extraction which are expensive and inefficient, especially for low strength wastewaters. These drawbacks of traditional metal removal techniques have led the researchers to the investigation of the use of microbial biomass as biosorbent for heavy metals removal. Many studies have shown that activated sludge processes can remove substantial quantities of soluble metals in influent wastewater (Su *et al.*, 1995). The interaction of living organisms with metal ions in aquatic systems can be divided into two main mechanisms. The first mechanism, biosorption, represents the sum of all passive interactions of the cell wall with metal ions. These are adsorption reactions, ion exchange reactions with functional groups at the cell surface and surface complexation reactions. Binding sites for metal ions are carboxylic, hydroxylic, phosphate and sulfonate groups of the lipids, proteins and polysaccharides localized at the cell surface.

In contrast to the biosorption the second mechanism, bioaccumulation, is an active one. This interaction leads to an enrichment of metal ions in the interior of the cell. Often active mechanisms are either defensive tools of the cell to avoid poisoning or they serve to accumulate essential elements present at trace level concentrations. They must be accumulated against a concentration gradient. The formation of special metal-binding substances like thiones and metal-precipitating substances such as hydrogen peroxide contributes t this group of interaction mechanisms. In contrast to biosorption these reactions are supposed to be irreversible. This shows a further effect on the rate of the reaction. While biosorption processes take place within a time scale of minutes, bioaccumulation is being performed on a longer time scale. This is the reason why the major process acting in activated sludge is biosorption.

Biosorption

Biosorption may be defined as the removal of metal or metalloid species, compounds and particulates from solution by biological matter. This technology has been recognized as a potential alternative to existing technologies for removing heavy metals from industrial wastewaters since it can concentrate metals several thousand fold.

Factors which may influence this process include:

- pH;
- the concentration of metal present in the wastewater;
- the composition and characteristics of wastewater and sludge.

Heavy metal removal or uptake by sludge is a consequence of the interaction between metals in the aqueous solution phase and the bacterial cell surface.

The complexity of the microorganisms structure implies that there are many ways for the metal to be captured by the cell. Biosorption mechanisms are therefore various and in some cases they are still not very well understood. They may be classified by the following different criteria:

- according to the dependence on the cells metabolism, biosorption mechanisms can be divided into:

    - metabolism dependent;
    - non-metabolism dependent.

- according to the location where the metal removed from the solution is found, biosorption may be classified as:

    - extracellular accumulation/precipitation;
    - cell surface sorption/precipitation;
    - intracellular accumulation.

Fig.5.6 shows schematically the various biosorption mechanisms.

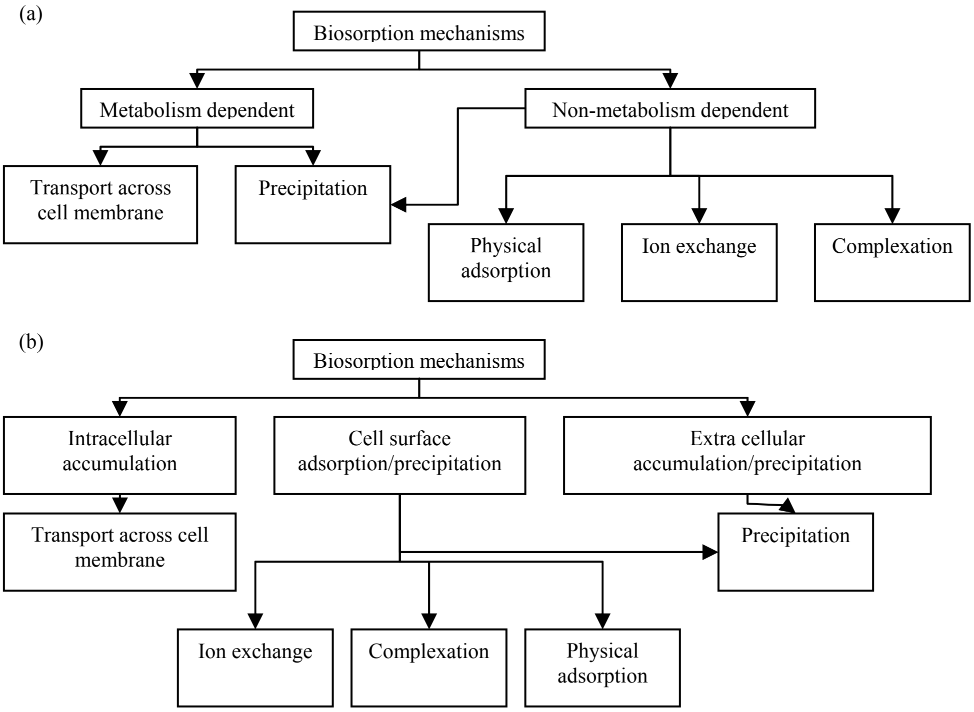


Figure 5.6 Biosorption mechanisms. (a) classified according to the dependence on the cell metabolism; (b) classified according to the location where the metal removed is found.

Transport of the metal across the cell membrane yields intracellular accumulation, which is dependent on the cell metabolism. This implies that this kind of biosorption may take place only with viable cells. It is often associated with an active defence system of microorganisms which react in the presence of a toxic metal. Obviously, in this case biosorption is not immediate since it requires the time for the reaction of the microorganism.

In the case of physicochemical interaction between the metal and functional groups of the cell surface, based on physical adsorption, in exchange and complexation, we have cell surface sorption which is not dependent on the metabolism. Cell walls of microbial biomass, mainly composed of polysaccharides, proteins and lipids, offer particularly abundant metal-binding functional groups, such as carboxylate, hydroxyl, sulphate, phosphate and amino groups. This physicochemical phenomenon of metal biosorption non-metabolism dependent is relatively rapid and can be reversible. In the presence of such a mechanism, which fortunately is the most common, biomass has all the chemical characteristics of an ion exchange resin or of an activated carbon, implying many advantages in the industrial application of biosorption.

In the case of precipitation, the classification is not unique. In fact, the precipitation of the metal may take place both in solution and on the cell surface. Furthermore it may be dependent on the cells metabolism if, in the presence of toxic metals, the microorganism produces compounds which favour the precipitation process. On the other hand, precipitation may not be dependent on the cells metabolism, occurring after a chemical interaction between the metal and the cell surface.

Biosorption by free cells

A distinctive feature of the activated sludge morphology in systems that are characterized by spatial substrate gradients is the presence of large amorphous colonies that can be easily separated from the liquid phase by gravity or, as in our case, filtration. The term “free cells” indicates non-immobilised microorganisms which are free in aqueous solutions. Contacting large volumes of metal-bearing aqueous solutions with microbial biomass in conventional unit operations is not practical, largely due to solid/liquid separation problems. Thus, the smaller the volumetric load to the biomass the better the process of biosorption is enhanced.

In general, the literature suggests the following about the influence of operating conditions on the equilibrium of the biosorption process:

1. temperature seems not to influence biosorption performances in the range 20 – 35°C (Aksu et al., 1992);
2. pH seems to be the most important factor in the biosorptive process since it affects the solution chemistry of the metals, the activity of functional groups in the biomass and the competition of metallic ions (Vegliò & Beolchini, 1997);
3. biomass concentration in solution seems to influence the specific uptake: for lower values of biomass concentration there is an increase in the specific uptake. Gadd et al. (1988) (in Vegliò & Beolchini, 1997) suggested that an increase in biomass concentration leads to interference between binding sites.
4. biosorption is in some cases selective: biosorption is mainly applied to treat waste containing metal ions and the removal of one metal may be influenced by the presence of other metals
5. extracellular polymeric substances (EPS) of microorganisms have been shown to play a crucial role in metal removal: Geesey *et al.* (1989) (in Su *et al.*, 1995) found that EPS are effective modulators of metal in concentration at the cell surface, scavenging metals from solution when the concentrations are low while serving as impermeable barriers when metal concentrations are at toxic levels in the surrounding environment. In the following paragraph the role of the EPS is further discussed because of the important role of these compounds in membrane fouling.

Key role of the EPS for metals removal

The activated sludge flocs are composed of microorganisms, EPS, colloids, mineral particles and ionic components such as divalent cations. EPS are biopolymers resulting from active bacteria secretion, shedding of cell surface material, cell lysis materials and from adsorption of organics from the environment (Wingender *et al*; 1999). They are composed by a variety of organic substances: carbohydrates and proteins being major constituents with humic substances, uronic acids and nucleic acids in smaller quantities (Liu *et al*, 2002).

Many authors have defined two kinds of EPS in flocs or biofilms: soluble and bound EPS. Bound EPS include microbially produced bound polymers but also lysis and hydrolysis products as well as adsorbed or attached matter. Soluble EPS, also defined as soluble microbial products (SMPs) include microbially produced soluble polymers, hydrolysis products of attached organic matter and organic molecules released by cell lysis. EPS have been found to influence the flocculation, settling and dewatering of activated sludge (Liu and Fang, 2003). With concern to membrane bioreactors operation, EPS are widely considered as major responsible for membrane fouling (Drews *et al*., 2006). However, the importance of these compounds for heavy metals biosorption is so widely recognized (Brown and Lester, 1979) that the engineering of the EPS for this purpose has been proposed (Gutnick and Back, 2000). Barker and Stuckey (1999) in a review paper emphasized the chelating properties of SMP, citing a study from Kuo and Parkin (1996) that found that the amount of SMP produced in a 40 day SRT chemostat could chelate approximately 44 mgNi L^{-1}.

As for the EPS biosorption properties, the affinity for metals has been widely studied, but the results from different authors are almost controversial. As further discussed later, dealing with MBRs is of particular interest to know the affinity of soluble or bound EPS rather than overall amounts. Comte *et al* (2006) studied these phenomena and found out that, while all biosorption showed affinity for metals in descending order $Cu^{2+}>Pb^{2+}>Ni^{2+}>>Cd^{2+}$, Cu^{2+}, Pb^{2+} and Ni^{2+} soluble EPS showed stronger biosorption properties than bound EPS. For Cd^{2+} and Cu^{2+} biosorption properties of the two kinds of EPS were close due to weak affinity of Cd^{2+} for EPS and the different possible binding mechanisms implicated by the speciation of Cu^{2+} at pH 7. Different results were found by Battistoni *et al* (1993) that, studying the heavy metal shock load in activated sludge uptake, found out the affinity for the entire biosorption in the descending order Hg>Cd>Ni. Furthermore, in the same study Battistoni found that the favourite binding sites were the cell walls for Hg, cell walls and bound EPS for Ni and soluble EPS for Cd.

However, to date most of the published data about biosorption of heavy metals investigated the concentrations of mgMetal L^{-1}, that can be reliable for some industrial wastewaters, but may be not transportable to concentrations really encountered in municipal systems (µg L^{-1}).

2.4.2 The fate of heavy metals in full scale WWTPs: italian case studies

The fate of heavy metals in full scale municipal WWTPs has been studied and today it is of great topicality because of the open debate on the most appropriate final destiny of the waste activated sludge. In fact, heavy metals present in influent wastewater stream become concentrated in the sludge and disposal of heavy metal-laden sludge can represent an environmental hazard.

Recent studies by Chipasa *et al.* (2003) reported that heavy metals removal occurs both in primary treatment, where a portion of metals associated to the particulate matter is removed, and in secondary biological treatment. Over two years monitoring, the authors found the overall removal in the range 15÷85% in the order Cd<Pb<Cu<Zn and the metal contents in the effluent in the order Cd<Pd<Cu<Zn. The contents of metals in primary and secondary sludge were very fluctuating, in spite of similar operating conditions, and the anaerobic digestion increased these values based on dry weight in the order Zn<Cu<Pb<Cd. The final metal contents in the digested sludge were in the range 10÷200 mgMetal $kgSS^{-1}$ for Cd<Pb<Cu and about 1000 mgMetal $kgSS^{-1}$ that was not suitable for land application. Karvelas *et al* (2003) examined a large WWTPs that treats municipal wastewater in the range 120000÷150000 m^3 day^{-1}. The authors found out overall removals of about 60% for Cr, Ni, Pb, Fe and Cd, while Cu and Mn were removed in the range 20÷30%.

The Italian scenario has been analyzed on the basis of the same selected full scale systems A-E described in the previous paragraph. Dealing with the total treatment systems, all the influent streams were considered. In fact, to date in Italy it is rather common to use municipal WWTP also to treat non-hazardous liquid wastes, such as leachate from municipal solid waste landfill, liquors from septic tanks, residuals from road drains, liquid agro-wastes from small factories, etc. Of course, this practice is engaged only when the treatment capacity of the plant is large enough. However, possible residual treatment capacities of the WWTPs is often calculated only based on macropollutants, while micropollutants are considered only for possible inhibitory effects on the biological process.

Of course the liquid wastes have different impacts on the influent loadings depending on the sources of wastewater. The proportional increases of metal contents are reported in table 5.17 and are related to the case of pure municipal and low loaded wastewater (plant B) and the mixed municipal/industrial wastewater (plant D).

Table 5.17. Proportional increases of metals due to the liquid wastes inloadings

Proportional increases (%)=100*($\text{Metal}_{wastewater+liquidwaste}$-$\text{Metal}_{wastewater}$)/($\text{Metal}_{wastewater}$)		
	Plant B	**Plant D**
As	25	0
Hg	187	0
Cu	811	52
Ob	409	55
Cd	n.a.	4
Ni	414	0
Cr	100	0
Zn	138	13
Fe	712	19
Al	837	0

Further to the inflow of the liquid wastes, the overall abundances of heavy metals are reported in table 5.18.

Table 5.18. Overall contents of metals influent to the five WWTPs analyzed

		A	**B_{total}**	**C**	**D_{total}**	**E**
As	**µg/L**	3,8	5	n.a.	0,8	6
Hg	**µg/L**	8,8	4,3	0,7	0,6	n.d.
Cu	**µg/L**	32,2	90,2	9,8	57,7	60,9
Pb	**µg/L**	6,5	40,7	8,6	3,1	10,5
Cd	**µg/L**	0,4	1	8,7	11,1	0,6
Ni	**µg/L**	17	18	16,6	54	21,6
Cr	**µg/L**	26,2	16,2	56,4	47,9	59,2
Zn	**µg/L**	254,4	828,1	1233	2725,1	226,6
Fe	**µg/L**	696	4185,3	361,3	631,4	2391
Al	**µg/L**	399	7366	1940	2326	2531

Considering insignificant the fraction of metals that is removed within the biogas in the anaerobic digestion, these substances can be released via the treated effluent or via the sewage sludge. The concentrations into the treated effluents and the different release of heavy metals are reported respectively in table 5.19 and figures xx.

Table 5.19. Metals contents in the treated effluent

		A	B	C	D	E
As	µg/L	2,7	2,0	n.d.	1,6	4,9
Hg	µg/L	2	0,6	0,7	1,35	7,68
Cu	µg/L	20,8	13,5	5,59	15,2	15,6
Pb	µg/L	2,5	9,5	4,4	16,4	4,95
Cd	µg/L	0,25	n.d.	n.d.	0,1	n.d.
Ni	µg/L	11,7	3,9	2,41	7,15	1,93
Cr	µg/L	8,6	6,9	2,70	14,0	19,8
Zn	µg/L	223	82,8	63	325	164
Fe	µg/L	251	283	130	533	320
Al	µg/L	328	413	209	557	512

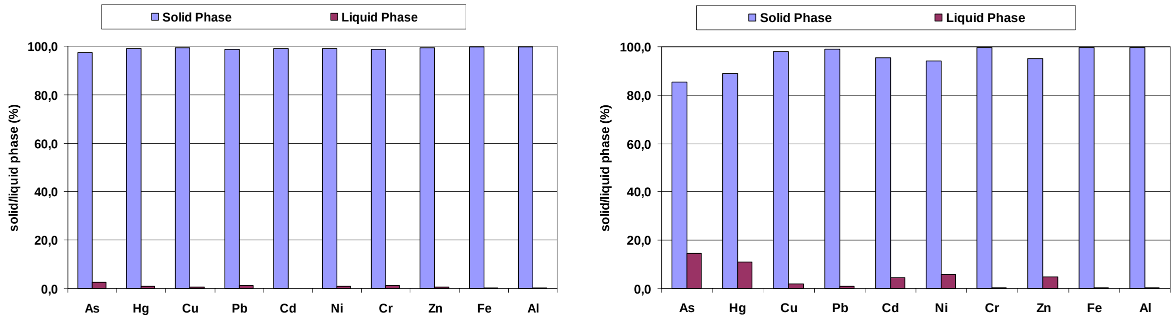


Figure 5.7 – a,b. Metals fractionations in the treated effluents (a) almost municipal and (b) mixed municipal/industrial wastewaters

The metals contents into the sewage sludge are of particular interest for the possible application on land for agriculture. Table 5.20 reports the metals in the sewage sludge and the limits for application in agriculture, according both to the EU Directive 86/278/EEC and to the limits expected by 2015.

Table 5.20. Metals contents in the waste activated sludge – before the anaerobic digestion

		A	B	C	D	E	Land Application**	Land Application***
As	mg/kgSS	3±*	7±*	n.d.	15±(42%)	4±(35%)	-	-
Hg	mg/kgSS	3±(52%)	5±(96%)	n.d.	35,9±*	2±(81%)	16÷25	5
Cu	mg/kgSS	192±(12%)	165±(18%)	264±*	239±(61%)	348±(8%)	1000÷1750	800
Pb	mg/kgSS	46±(6%)	72±(30%)	78±*	135±(50%)	61±(18%)	750÷1200	500
Cd	mg/kgSS	1±(7,5%)	1±(57%)	1±*	3±(50%)	1±(49%)	20÷40	5
Ni	mg/kgSS	35±(8%)	31±(40%)	34±*	35±(67%)	107±(45%)	300÷400	200
Cr	mg/kgSS	560±(9%)	46±(56%)	17±*	118±(56%)	525±*	-	800
Zn	mg/kgSS	840±(4%)	1408±(74%)	716±*	2341±(98%)	433±(27%)	2500÷4000	2000
Fe	mg/kgSS	11833±(6%)	6267±(74)	4399±*	14511±(93%)	9335±(39%)	-	-
Al	mg/kgSS	14069±(4%)	13047±(13%)	11065±*	26447±(15%)	15605±(27%)	-	-

* only sample greater than the detection limit
**EU Directive 86/278/EEC ***Standard pursued by 2015 in the Veneto Region (ARPAV Internal Document)

The levels of metals in the five waste activated sludge met the limit for agriculture application for all the treatment systems analyzed. However, further metals concentrations is performed in the anaerobic digestion due to the removal of a fraction of volatile suspended solids. Table 5.21 reports the concentrations of sludge after the anaerobic digestion for the plants B-C.

Table 5.21. Metals contents in the sewage sludge – after the anaerobic digestion

		B	C	Land Application*	Land Application**
As	mg/kgSS	-	12	-	-
Hg	mg/kgSS	-	5,1	16÷25	5
Cu	mg/kgSS	196	317	1000÷1750	800
Pb	mg/kgSS	56	64,5	750÷1200	500
Cd	mg/kgSS	1	1,6	20÷40	5
Ni	mg/kgSS	36	25,5	300÷400	200
Cr	mg/kgSS	40	30	-	800
Zn	mg/kgSS	8900	946	2500÷4000	2000
Fe	mg/kgSS	1264	5980	-	-
Al	mg/kgSS	22362	13360	-	-

3. Membrane systems and metals removal

3.1 Gross comparative evaluation

How the membrane system can enhance the metals removal from the treated effluent has been pointed out by different authors. However, dealing with municipal wastewater, where micropollutants are present at very low concentrations or in trace, the debate about the real benefits achievable by the membrane treatment systems is still opened. In other words, stated that the membrane systems allow for improved process performances when a mix of municipal and industrial wastewaters from certain industrial sectors (i.e. galvanic, pharmaceutical, organic chemistry, etc.) are treated, the sustainability of the technology for a widespread application to the whole wastewater treatment field is still to be demonstrated. To date, the studies focused on metals, MBRs and real municipal wastewaters do not give information about an optimal strategy to manage the treatment systems. Innocenti et al (2002) studied the effect of sludge age on metals removal in a MBR operating as sequencing batch reactor for the treatment of real wastewater. The authors found that increasing sludge age from 10 to more than 200 days the degree of removals was generally increasing, except for As, Pb, Se, B that did not shown significant changes. More recently Fatone *et al* (2005; 2006) proved that a demonstrative MBR was able to achieve better removals of metals than a conventional process. However, the mechanisms that enhanced the removals were not clear to the researchers.

In this study the approach was manifold and arose result by result.

First of all a demonstration MBR, operating in parallel with conventional full scale plant, allowed for important and reliable comparisons of the removal performances (table 5.22).

Table 5.22. Metals removal in MBR and CASP

		MBR_1	$CASP_1$	$CASP_{range}$
As	%	48,4	8,5	–
Hg	%	93,7	97,5	57÷92
Cu	%	94,9	79,2	54÷82
Pb	%	74	61,5	68÷100
Cd	%	>27,1	>12	25÷74
Ni	%	85,9	79,4	43÷95
Cr	%	75,0	66,2	68÷85
Zn	%	94,4	65,5	87÷88
Fe	%	97,2	85,0	67÷90
Al	%	97,5	95,0	70÷80

Once known the operating parameters, the removals of table 5.22 are very explicative as better discussed below.

The two parallel plants involved in the case 1 are: the demonstration MBR and the full scale WWTP C. As discussed in the chapter dedicated to the nutrients removal, the demonstration MBR was seeded with sludge coming from the full scale WWTP C and fed with the same real wastewater over all the experimental runs. The operating parameters were rather different for the two parallel systems: while the full scale plant operated a SRT in the range 12÷20 days and MLSS between 4 and 6 g L^{-1}, the MBR was managed according to the parameters described in the chapter IV of this dissertation. However, both higher sludge concentrations and longer SRTs did not give the expected benefits in terms of metals removal from the treated effluent, which were always close to the average values of table 5.21.

In conclusion, the MBR is more effective than CASP for metals removal. However, working within the ranges typical of municipal applications different operating parameters did not lead to significant enhancement of biosorption and/or bioaccumulation phenomena. Therefore, biosorption was supposed to be the main removal mechanisms and the membrane exerts the sieving effect respect to the bound metals.

However, several further clarifications had to be studied to have a better knowledge of the membrane effect and to understand the operating parameters that can optimize the removal.

3.2 Membrane effect: towards a better understanding

In this study the first approach was aimed to find the best plant configuration between tertiary filtration (TF) or membrane bioreactor (MBR). Then, the effect of the membrane fouling and/or cake layer was studied under different boundary conditions (biomass concentration and hydrodynamic environment).

The study was carried out by means of a large pilot plant, described in the chapter II of this digression, installed inside a full scale municipal wastewater treatment plant (WWTP) with treatment capacity of 85.000 population equivalent (PE).

The 3D drawing of the full scale municipal WWTP is reported in figure 5.8.

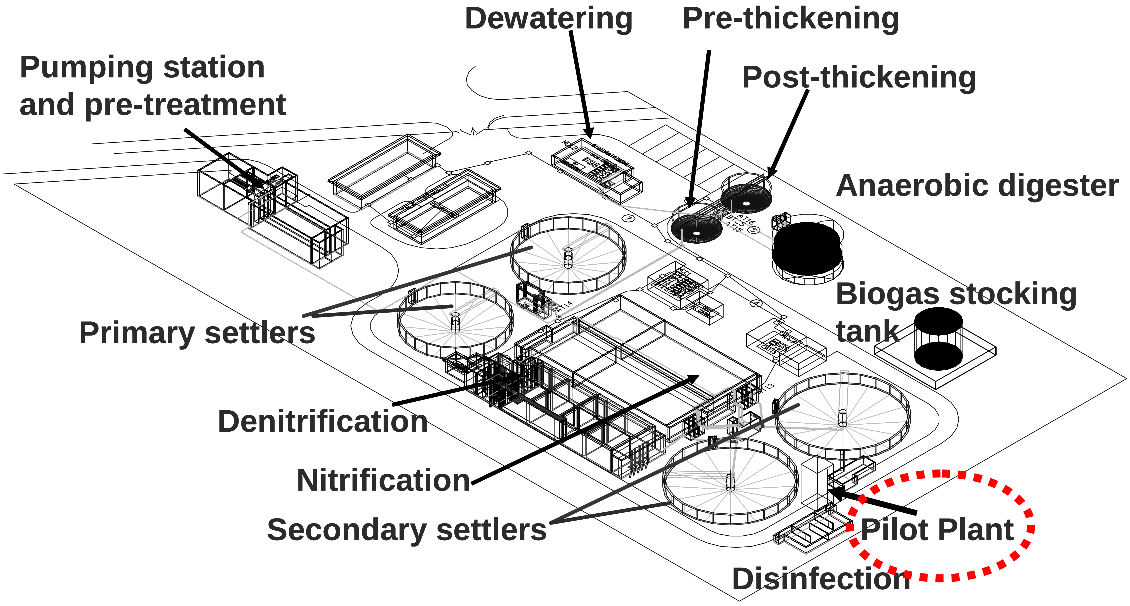


Figure 5.8. 3D drawing of the full scale municipal WWTP that hosts the membrane pilot plant

The main operation unit of the full scale WWTP are: (1) bar screen; (2) fine screen; (3) aerated grit chamber; (4) primary sedimentation; (5) activated sludge process according to the predenitrification-nitrification configuration; (5) secondary clarification; (6) disinfection in a contact tank by chlorine compounds. The waste activated sludge (WAS) and the primary sludge are thickened together and then stabilized in an anaerobic digester. Finally the effluent from the digested sludge is thickened and dewatered by a centrifuge machine.

The membrane pilot plant was located between secondary clarifier and disinfection contact tank (see figure 5.8). This choice allowed: (a) to feed the membrane system with the effluent from the secondary clarifier; (b) to use the NaClO already available for the full scale disinfection contact tank for the periodic cleanings of the UF membrane.

3.2.1 Membrane pilot system: TF and MBR configuration

As before mentioned, the pilot experimentations were carried out according to two configurations: TF (Figure 5.9) and MBR (Figure 5.10). During the TF test, the feeding was continuously taken from the secondary effluent of the full scale plant. As for the MBR configuration, a specification about the methodology is needed. In fact, the aim of the experimentation was to find out the pure effect of the membrane system, under different MLSS concentration, on micropollutants removal. Hence, at the beginning of each test the reactor was filled with new activated sludge taken from the full scale plant and the test lasted 5 days at most. According to this approach, the characteristics of the activated sludge into the MBR were always similar to those of the conventional full scale plant, in other words the modifications of the biomass that can occur in MBRs were always avoided.

Figure 5.9 Configuration of the pilot plant operating as TF

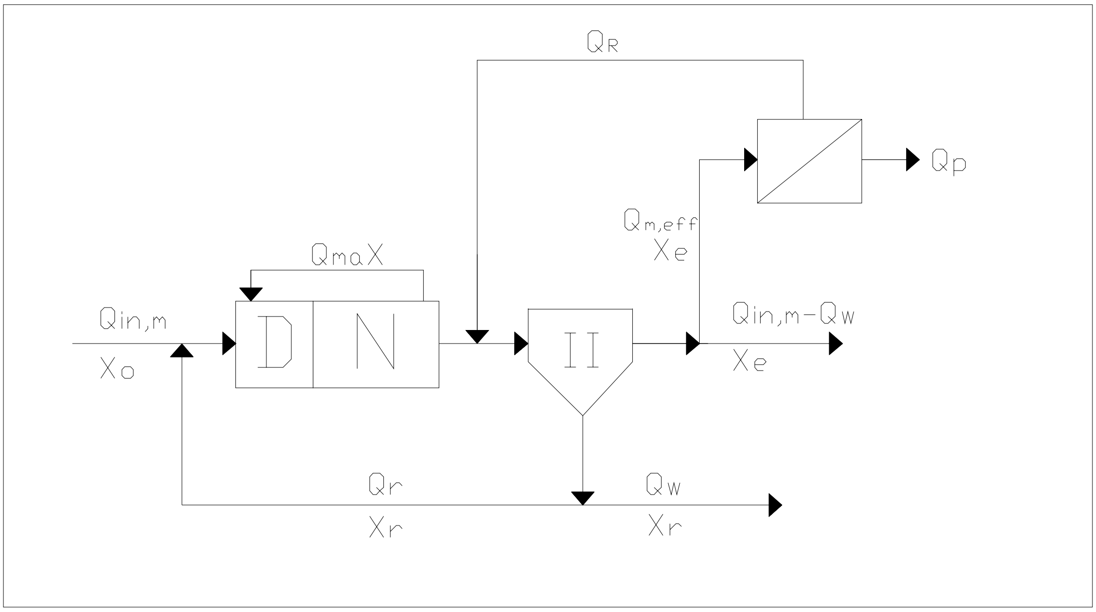
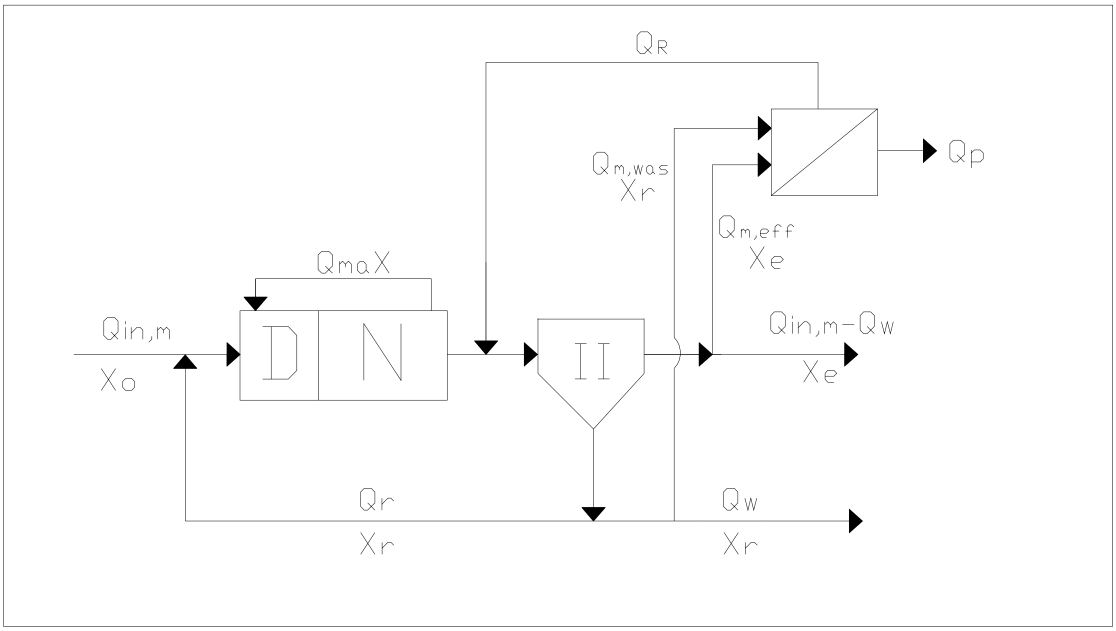


Figure 5.10 Configuration of the pilot plant operating as MBR



In order to quantify how the membrane can directly enhance the removals of conventional processes, the selected metals have been firstly traced within the existing full scale plant and then after the membrane system (table 5.22).

Table 5.23 Micropollutants ranges in the main streams of the full scale WWTP

Samples taken from:	Influent raw wastewater	Primary effluent	Secondary effluent	UF permeate
	Concentration Range (µg L^{-1})			
Metals**	18.00÷265.00	9.00÷112.00	7.70÷93.60	4.70÷56.00

*** Cu, Cd, Hg, Cr, Ni, Pb, As*

Heavy metals and metalloids (Cu, Cd, Hg, Cr, Ni, Pb, As) observed in the influent raw wastewater consisted almost in Cu (13÷94 µg L^{-1}); Cr (7÷45 µg L^{-1}); Ni (4÷51 µg L^{-1}); Pb (5÷15 µg L^{-1}); while As, Hg and Cd usually showed a minor occurrence. The physical primary treatments involved a first important removal also for the heavy metals. This fact was partially in agreement with the partitioning between liquid and solid phase, in fact the maximum soluble fraction (about 90%) was observed for Ni and the minimum (less than 4%) for Hg. The biological conventional process had a major effect on the removal of heavy metals, mainly because of the biosorption on the biomass and/or on the extracellular polymeric substances (EPS). This behaviour has been widely observed and is reported in literature. However, given the range of residual suspended solids escaping from the secondary effluent (5 ÷ 27 mg L^{-1}) with a roughly over-estimated content of heavy metal about 1.0 gMetal kgSS^{-1}, at most a concentration of 5÷27 µg L^{-1} is expected to be associated to the suspended solids in the secondary effluent. Therefore, the heavy metals in the secondary effluent from the full scale conventional WWTP are supposed to be either dissolved cations or linked to the EPS or, more generally, complexes of other forms. To have a better concern about the discharged heavy metals, it should be pointed out that the most persistent are Cr$_{tot}$, Ni and Cu, while Pb is present in minor amount.

As far as the total effect of the membrane system, a further removal of about 40÷50% was observed. This can be attributed both to the membrane sieving effect, and also to other phenomena which are better discussed in the following part of the paper.

3.2.2 Enhancement of heavy metals retention: MBR or TF configuration?

Once estimated the macroscopic effect of the UF membrane on the removal of priority pollutants, the role of UF membrane operating as MBR and TF configuration are described and discussed in this section. Following this purpose, heavy metals were monitored operating the plant according to the configuration showed in Figure 5.8 and Figure 5.9.

However, it must be pointed out that during TF tests the concentration of suspended solids into the membrane tank reached values around 1.5 g L^{-1}, while in the MBR modality the concentrations were in the range 2.5÷ 10 g L^{-1}, almost stable test by test. Furthermore, it is not worth to point out again that, according to the methodology of the test before described, the “MBR tests” simulated only the impact of different biomass concentration on the membrane role. In fact the characteristics of the activated sludge, both physical-chemical and microbiological, were typical of the conventional system, from where the biomass came from.

Twelve experimental tests were carried out in different times, but always treating the real liquor effluent from the secondary clarifiers. Table 5.24 shows the concentrations of heavy metals influent to membrane filtration and the average removals obtained in MBR and TF configuration.

Table 5.24. Removal of metals from the liquid phase: MBR-TT modality

		MBR	TF
Metal	range (μg L^{-1})	Removal %	Removal %
Cu	5.6÷75.0	81	50
Pb	3.5÷11.0	74	34
Cd	0.4÷7.7	64	17
Ni	3.4÷90.0	41	33
Cr	2.8÷40.0	85	73
TSS	range (mg L^{-1})	2500÷10000	5÷1500

TF configuration showed satisfactory metals removals (17÷70%), but always lower than the MBR. This particular behaviour cannot be attributed to the only sieving effect of the membrane, but it suggests that the fouling and/or cake layer on the membrane area plays a role on the removal of metals in the liquid phase. Furthermore, given that the hydrodynamic environment (i.e.: permeate flux, filtration cycle) imposed to the membrane system was almost unvaried, the higher removal performances (increases in the range 8÷47%) of the MBR configuration indicated that different biomass concentrations enhance the *layer effect*. This fact suggested that can exist a new equilibrium, different from that existing in the full scale conventional bioreactor, between metal cations and the rest of the mixed liquor. This is likely obtained upon or close to the membrane surface, where a higher concentration of heavy metal can exist as effect of concentration-polarization phenomena and fouling and/or cake layer.

In order to confirm the previous results and to better investigate the sieving and the layer effect, comparative and contemporary investigations were performed (table 5.24). Also in these cases, the real secondary effluent from the full scale WWTP was used to feed a TF membrane system (that was the membrane automatic sampler of Figure 5.4) and the large pilot plant operating in MBR configuration (test 1). After the test 1, two further comparative and contemporary tests were performed using a 0.45 μm cellulose filter instead of the UF membrane (tests 2 and 3). In other words, the TF was performed by filtering the sample trough a 0,45 μm membrane, while contemporary the large pilot plant operated in MBR configuration (solids content of 5 gMLSS L^{-1}). The analyzed samples were collected always as average over 24 hours.

The comparison between the different configurations of the membrane systems is reported as proportional values, so simply calculated according to equation 5.1.

$$(C_e-C_p)/C_e * 100 \qquad \text{Equ. 5.1}$$

Where: C_e= concentration of metal in the effluent from the TF
C_p= concentration of metal in the effluent from the MBR

Table 5.25. Metals removal: comparison between MBR and TF modality

	Test 1		Tests 2, 3	
METAL	CONC, (range) μg L^{-1}	$(C_e- C_p)/C_e*100$	CONC, (range) μg L^{-1}	$(C_e- C_p)/C_e*100$
As	<2		<2	
Hg	<2		<2	
Cu	16 ÷ 52	69	5.6÷10.6	60
Pb	5 ÷ 7	20	<2.5	
Cd	<0.25		<0.25	
Ni	20 ÷ 29	18	3.4÷9.5	24
Cr	9 ÷11	32	<2.5	

Basically, table 5.25 confirms that the MBR modality is more effective than the TF. Furthermore, even though considerations are possible only for Cu and Ni which were over the detection limits, the benefits of the MBR modality respect to the TF are comparable in the three tests performed: (1) TF adopting a UF membrane (nominal pore size 0,04 μm) in the test 1; (2) TF adopting a cellulose membrane filter (nominale pore size 0,45 μm) in the test 2 and 3. These experimental evidence indicate the major effect of the layer on the role of the membrane system, which do not seem dependent nor on the membrane material nor on the pore size.

3.2.3 Focusing on the layer effect: the hybrid tests

Biosorption processes realized by confining the biomass in a membrane reactor have been widely considered. However, membranes have been used to confine biomass, often free cells, into a reactor where the biosorption has been used to treat wastewater with high heavy metals concentration (Barba *et al*, 2001; Pagnanelli *et al*, 2001; 2003). On the contrary, there is a lack of information about the role of membrane systems for municipal applications and about the operating parameters that can enhance the metals removal in these systems. After having known the real importance of the membrane effect from the previous paragraph, experimental tests were carried out to investigate the effect of different operating parameters such as the filtration cycle and the biomass concentration.

First of all, the potential of the activated sludge as biosorbent was evaluated by bench scale batch tests. In particular, tests at different MLSS concentration allowed to find out the biosorption isotherms which followed the Freundlich equation. However, in order to have a good calibration of the biosorption potential, it was necessary to have concentration well detectable. Therefore, the initial metals concentrations in the reactor were kept at 5 mgMetal L^{-1}. The isotherms relations found with the activated sludge for the biosorption of Ni and Cd are reported in equations 5.2 and 5.3, respectively.

$$\frac{X}{M} = 4{,}0685 \cdot C_e^{0{,}958} \quad (R^2=0{,}9964) \qquad \text{Equ. 5.2}$$

$$\frac{X}{M} = 3{,}0988 \cdot C_e^{1{,}1} \quad (R^2=0{,}9985) \qquad \text{Equ. 5.3}$$

Operating with ionic dissolved metals and concentrations at magnitudes of some milligrams per litre, good empirical isotherms were found out. However, the problems were much more complicated passing to real sewages or lower metal levels up to make not possible reasonable empirical isotherm curves.

Further to the pure biosorption, the role of the membrane was investigated under different operating conditions.

To date the preliminary results are available and they concern the study on the removal of Cd and Ni. These two metals were selected because of the different affinity to biosorption on activated sludge, intended as a mix of biomass, EPS and the rest of the possible biosorbents. The large pilot plant was filled with liquors, secondary effluent or activated sludge according to the specific test, coming from the parallel full scale WWTP. A solution of $Ni(NO_3)_2$ and $Cd(NO_3)_2$ was prepared and dosed into the influent at a constant content of 2 mgCd L^{-1} and 2 mgNi L^{-1}. Samples were taken from the permeate and the retentate, which was filtered through a cellulose membrane (pore size 0,45 μm) and then analyzed for Cd and Ni. This approach allowed to make hypothesis on the final form of the metals: (a) biosorbed on the cell wall or bioaccumulated; (b) biosorbed on the soluble EPS or bound to molecules smaller than 0,45 μm; (c) remained in dissolved cations or bound to molecules that can pass through the UF membrane.

To date the initial experimental grid is not completed and further work is needed. Table 5.26 reports the tests carried out until now and lets understand the work still to be done.

Table 5.26 Experimental grid, to date still to be completed

	9 LMH	18 LMH	27 LMH
0÷0.2 gMLSS L^{-1}	2[a]	0	1
~5 gMLSS L^{-1}	6[a]	0	0
~8 gMLSS L^{-1}	2[a]	0	1

[a]tests with different filtration cycles and temperature

At the moment the mechanisms are still not clear and needs further deep investigations, however general important considerations dealing with the behaviour of the two different metals are possible. In particular, figures 5.11 and 5.12 report the curves typically observed for Ni and Cd during the filtration test. Here, the letter "s" indicates the compound in the mixed liquor after filtration at 0.45 μm, while "p" indicates the metal content in the permeate.

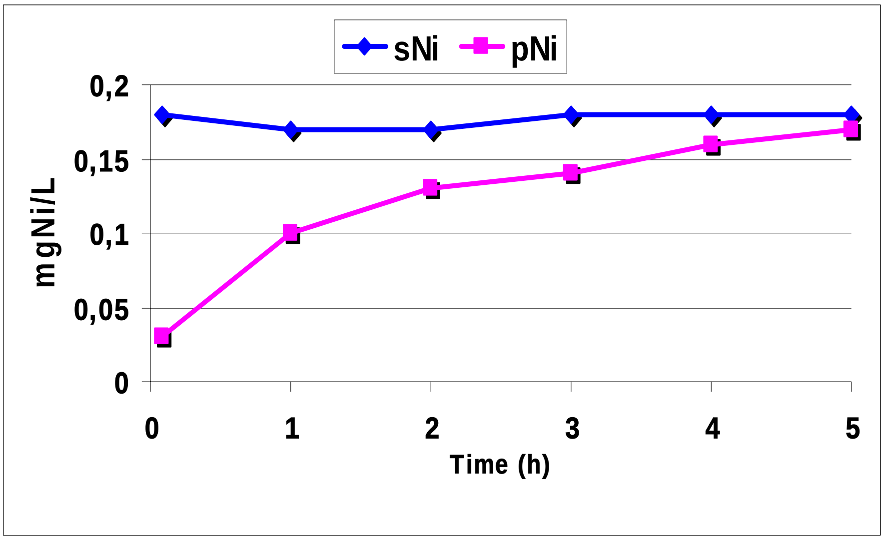


Figure 5.11. Nickel plots during the hybrid test

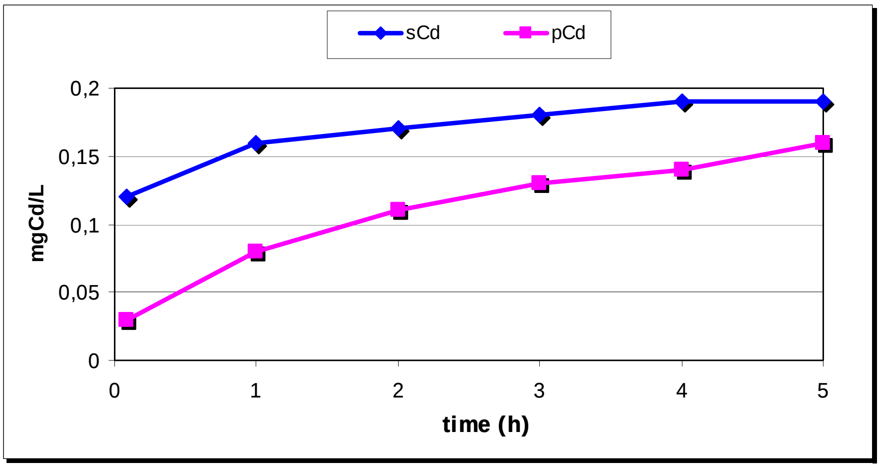


Figure 5.12. Cadmium plots during the hybrid test

The additional effect of the membrane is clearly visible for both the metals investigated. In fact, the metals contents are different in the permeate and in the mixed liquor. Moreover, the trends of the Cd are different from the Ni. The membrane effect, in fact, disappears for the Nickel after 5 hours; otherwise the effect on the Cd removal is almost constant over the filtration time. At the moment, this different behaviour has been attributed either to the biosorption of the metals onto molecules later sieved by the membrane or to the role of the fouling/cake layer on the membrane surface. This latter, in five hours, may reach a saturation for the Cd. However, it is important to point out that the membrane effect weighs upon the overall metals removal for a very small part, while the main effect is attributed to the biosorption on molecules larger than 0,45 µm. Figures 5.13 and 5.14 shows the partition of the metals in the permeate (permMetal), in the liquid phase not sieved (solMetal) and sieved (partMetal) at 0.45 µm.

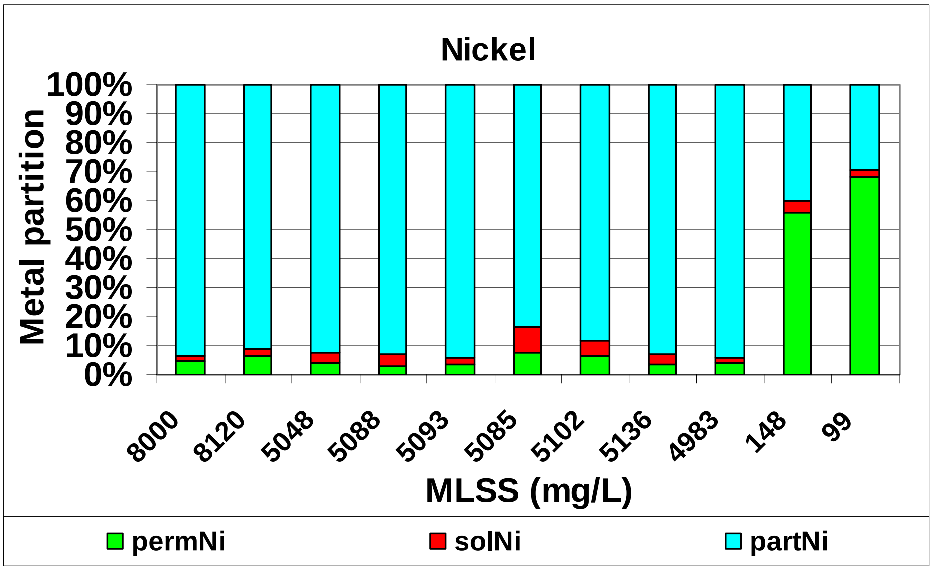


Figure 5.13 Nickel partition in the hybrid tests

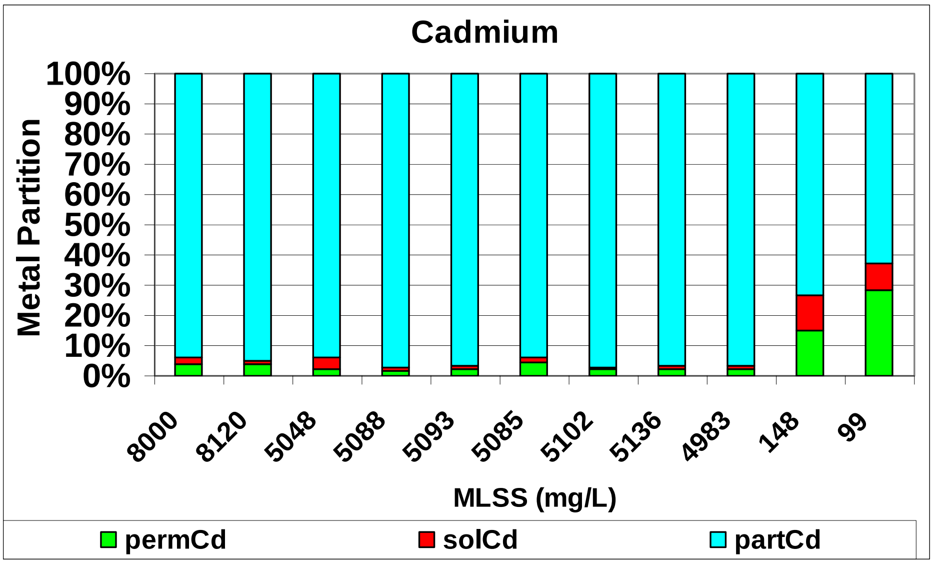


Figure 5.14 Cadmium partition in the hybrid tests

The phenomena were not sensitive to the filtration cycles: filtration/backwashing, filtration/relaxation and continuous filtration gave comparable results. The results for the TF tests were of particular interest. In these tests, in fact, the retention of the Cd was more significant (60÷80%) than the Ni (30÷45). This is partially in agreement with the continuous effect of the membrane showed in figure 5.12 and seems to emphasized the role of the EPS as important biosorbent mean. However, much further experimental work is actually needed to well understand the mechanisms involved.

4. Conclusions

The occurrence and removal of metals in municipal wastewater systems has been investigated in details. The results regard both the definition of the target metals, which should be of major concern when treating municipal sewage, and the destiny of metals in conventional and advanced treatment systems.

As for the occurrence of metals, the main remarks could be resumed as follows:

- As, Hg, Pb, Cd are present in the raw influent to italian municipal wastewater treatment system in a range of 0,1÷10 µg/L; Cu, Ni, Cr are in the range 10÷70 µg/L;
- a remarkable part of the influent metal is associated to suspended particulate and can be removed already in the physical headworks of conventional WWTPs. Therefore, also the street particles play a role in transporting metals into municipal sewers system;
- the secondary effluent from conventional systems were almost in the liquid phase. The overall concentration were in the following ranges: As (0,1÷5 µg/L); Hg (0,7÷7,7); Cu (5,6÷20,8); Pb (2,5÷9,5); Cd (0,1÷0,3); Ni (2,4÷11,7); Cr (2,7÷19,8);
- the statistical approach did not reveal any remarkable link between the abundances of the different metals analyzed. On the other hand, the detailed knowledge of the metal contents in the solid phase could be of help in the identification of the source (industrial or municipal) of metals in the wastewater;
- As for the effect of the membrane systems:
- even working at similar operating parameters, membrane bioreactors were more effective than conventional wastewater treatment plants for metal removal. These better performances were attributed not only to the sieving effect of the membrane but also to a mere effect of the fouling/cake layer which is under current investigations.

References – Chapter V

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Chapter VI. Organic micropollutants: occurrence and removal

In the field of industrial productions, a growing number a hazardous organic compounds is discharged into the environment. Removal of xenobiotic compounds does not concern only high-specialized industrial wastewaters. Indeed, xenobiotic chemicals may also enter municipal treatment plants either as a part of an industrial discharge or as a component of urban run-off or drainage into a sewerage system. The phenomena concerning the xenobiotics in the urban water cycle are of great topicality and the scientifical and technological debate is open on different fronts such as the mitigation of the sources, the treatment methods, the toxic effects, the analytical methods (COST action 636; 2005-2008). For instance, the researchers are discussing about the target compounds, included between the thousands man-made, which are really of major concern for amounts, toxicity and, therefore, must be regulated by strict normative laws. Recently a number of researchers have dealt with the distribution and fate of xenobiotic compounds in conventional wastewater treatment plants (Clark et al., 1995; Byrns, 2001; Katsoyiannis and Samara, 2004). The wastewater treatment plant is no longer viewed as the end-of-pipe structure, but it is considered a complex system for the environmental protection. With particular concern to the best available technologies, membrane bioreactors are supposed to have the potentiality to enhance the removal of organic xenobiotics thanks to the particular operating conditions (especially the high sludge age) which can improve both biotic and abiotic phenomena. However, there is a lack of information about the real applications of these systems and the removal of organic xenobiotics from wastewater. This chapter deals at first with the occurrence and removal of groups of organic micropollutants (PAHs, Volatile Organic Compounds, Halogenated Volatile Organic Compounds, and Chlorobenzenes) in the italian wastewater treatment systems. The aim is twofold: from one side, to select the target compounds which should be focused because really present in the influent sewages; from the other side, to determine the actual removals in existing full scale treatment systems taking care of the very low concentrations involved. Then, the efficiency of the membrane systems will be outlined just by comparing the MBRs with the conventional parallel full scale systems. Final remarks will be outlined on the target compounds, which occurrence is really relevant in the italian sewages, and on the potential of membrane technology for the improvement of the present systems for wastewater treatment.

1. Occurrence of organic micropollutants in the wastewater systems – literature review

Organic micropollutants are generally present in wastewaters at trace levels. Measured concentrations are generally low and rarely exceed discharge limits (when existing), aquatic-life criteria or drinking-water guidelines and health advisories. Unfortunately, despite the low concentrations, these compounds can express a high toxicity potential. Only some organic compounds, i.e. detergents, oils and greases, are present at mg/l levels in wastewaters. The provenience of organic pollutants can be very different: e.g., pesticides are intentionally released in measured applications, industrial by-products are released through regulated and unregulated industrial discharges to water and air resources, other compounds come from household where they are used as chemicals for cleaning and disinfection (Kolpin et al., 2002). Another preferential way for organic micropollutants diffusion is storm-water runoff, particularly in urban and industrial areas: Smith et al. (2000) showed that a gas station site produced a total poly-cyclic aromatic hydrocarbons (PAH) loading in runoff water of some 2.24 $g/m^2\cdot$year, while parking areas and motorways ranged between $3\cdot10^{-2}$ and $5\cdot10^{-2}$ $g/m^2\cdot$year. These runoff waters then reach sewers systems and finally the wastewater treatment plants.

General studies about organic compounds occurrence are lacking, while specific studies concerning specific classes of compounds are more frequent in literature.

Kolpin et al. (2002), reported the levels of some organic contaminants in wastewaters from 139 streams across 30 USA States during 1999 and 2000. They found that some polycyclic aromatic hydrocarbons were generally present. In particular, benzo[a]pyrene, fluoranthene, naphthalene, phenanthrene and pyrene ranged between 0.02 and 0.04 μg/l, respectively, while anthracene averaged 0.07 μg/l. They also found the presence of different insecticides (carbaryl, cis-chlordane, chlorpyrifos and diazinon) in the range 0.02-0.07 μg/l, while dieldrin reached 18 μg/l. Moreover, a number of non-ionic detergent metabolites, like 4-nonylphenol, a product of alkylphenol polyethoxylate detergents degradation, were present, up to 1 μg/l. In general, metabolites and plasticizers (phatalates) were the most abundant and represented the 50% of the total amount of organic compounds.

Durell and Lizotte (1998), monitored 26 WWTPs in New Jersey and New York States, looking for PCBs presence and variations in influent flowrate. They found that the total concentration for PCB in wastewater ranged between 26 and 1096 pg/l for normal flow influent and between 44 and 773 pg/l for high flow influent.

Janssens et al. (1997) reported pesticides levels in the range 0.14-2.58 μg/l in Dutch waters and emphasised that the maximum admissible concentration (MAC) for EC Directive 80/778/EEC was 0.1 μg/l for every single pesticide and 0.5 μg/l for the sum of all the pesticides. Other compounds show also lower concentration: tributyltin was found with concentrations in the range 60-220 ng/l in wastewaters of Swiss WWTPs. It was mainly associated with suspended solids (Fent, 1996).

However, other compounds, like linear alkylbenzene sulphonates (LAS) are present in high concentrations, up to some mg/l in wastewaters (Rogers, 1996).

Table 6.1 shows typical concentrations in municipal wastewaters of some organic pollutants reported in recent literature.

Table 6.1 Organic compounds concentrations in wastewaters reported in literature

Compounds	Concentration	Reference
Dieldrin (pesticide), μg/l	0.18	Kolpin et al., 2002
Lindane (pesticide), μg/l	0.02	Kolpin et al., 2002
PAH (total), μg/l	0.02 – 0.07	Kolpin et al., 2002
Tri-butyl-tin, ng/l	60 - 220	Fent, 1996
PCB, pg/l	26 – 1096	Durell and Lizote, 1998

Despite this low presence, organic compounds are responsible for abnormal physiological processes and reproductive impairment, increased incidences of cancer, development of antibiotic-resistant bacteria, potential increased toxicity of chemical mixtures (Kolpin et al., 2002).

Moreover, one should consider that, even though present at low concentrations in treated wastewater, these compounds are easily accumulated in sludge, so wasted sludge generally present high concentrations of these compounds and is not more suitable for land application or composting (Eljarrat et al., 1997). Table 6.2 summarises the concentrations of these compounds in sewage sludge reported in several studies. In order to restrict the use of sludge in agricultural soils, new laws regarding limits of organic compounds in sludge are going to be introduced in European Union in next years (European Union Working Document on Sludge 3rd Draft ENV.E.3/LM, 2000), so table 6.2 also shows the proposed limits for sludge application on land.

Table 6.2 EU proposed limits for sludge application on land and typical concentrations in sludge for some organic micropollutants

Compunds	**EU limits**	**Concentrations**	**References**
Non ionic detergents, mg/kg	50	13 – 51.4	Innocenti (2003)
PAH (total), mg/kg	6	2 – 20	Rogers, 1996
PCB, μg/kg	0.8	1.6 – 5.4	Morris and Lester, 1994
Dioxins and furans, ngTE/kg	100	200	Disse et al., 1995

Because of this situation, recent laws are going towards the “zero discharge” concept (Decision No 2455/2001/EC), therefore also these trace compounds should be removed from treated wastewaters. So, it is clear the necessity to adopt advanced wastewater treatment processes which enable the possibility to “totally” remove these compounds. This also allows the possibility to easily reuse the treated water.

2. Fate and removal mechanisms of organic micropollutants in wastewater treatment processes

The fate of organic pollutants in sewage treatment has been illustrated in literature and some modelling explications have been attempted.

The different processes competing for final fate of organic pollutants can be here summarised as:

- *Sorption*. Chemical organic compounds are generally hydrophobic, therefore they tend to react with the sludge surface and be adsorbed onto biomass flocs. This phenomenon is generally described through the octanol/water partition constant K_{ow}. Moreover, they can be associated with oils and greases, which are present in high concentrations in domestic wastewaters. The fraction of pollutants bound to sludge and not interested by biodegradation will be discharged with the excess sludge;
- *Volatilisation*. Compounds with relatively high Henry’s law constants may volatilise into the atmosphere, especially when forced by aeration of the bioreactor;
- *Biodegradation*. This is probably the most important process for the removal of organic compounds, but also the less known. Organic pollutants are at least partially degraded, and

sometimes mineralised to CO_2 and water. Bioconversion is the term probably more correct to describe the removal of organic micropollutants in wastewater treatment processes. Biodegradation can be limited by the low concentration of pollutants and the difficulty of contact (bio-availability) between the organic compounds and the microorganisms. Moreover, the degradation rates can be slow compared to the residence time provided by the treatment technology. About this topic it is necessary to emphasise that the adoption of high solid retention times (SRT), like in MBR systems, can advantage the biodegradation of these organic substances in the solids phase.

- *Advection*. Compounds that do not completely biodegrade, volatilise or adsorb on solids will exit the bioreactor in the effluent liquid stream to be discharged into surface waters.

So, according to these mechanisms it is clear that the chemical-physical properties of these compounds are of fundamental importance to determine their fate within the wastewater treatment process. According to Rogers (1996), the sorption potential can be considered more or less important according to the following guidelines:

- log $K_{ow} < 2.5$	low sorption potential
- log $K_{ow} < 2.5$ and > 4	medium sorption potential
- log $K_{ow} > 4$	high sorption potential

On the other hand, considering volatilisation, the Henry constant and the partition octanol/water constant (K_{ow}) are both important. An empirical classification for these compounds can be considered:

- $Hc > 10^{-4}$ and $Hc/K_{ow} > 10^{-9}$	high volatilisation potential
- $Hc < 10^{-4}$ and $Hc/K_{ow} < 10^{-9}$	low volatilisation potential

So, beside their biodegradability, the final fate of the organic micropollutants is almost enterely determined by their chemical-physical properties and by the applied operational conditions in the wastewater treatment process (air flowrate for volatile compounds, HRT for biodegradation in soluble phase and SRT for slowly biodegradable compounds).

However, a general summary of the fate of organic compounds can be attempted considering different classes of substances:

Mineral oils

Mineral oils are present in high concentrations in wastewaters. They arise from industrial discharges, streets runoff and illicit disposal from houses, garages or small factories. Rogers (1996) reported that high concentrations of these compounds are present in sludge, up to some mg/l and that are only partially biodegradable. Scholz and Fuchs (2000) showed that a MBR was able to remove the 92-99% of oily water. The biodegradation rate was in the range 0.26-0.54 ghydrocarbons/gMLVSS·day, with a maximum rate of 0.82 ghydrocarbons/gMLVSS·day. Other tests showed that alkanes, which is 50% of oily water, in the range C10-C24 were equally degraded.

Detergents

The linear alkylbenzene sulphonates (LAS) are widely used as surfactants, both for industrial and domestic use. These surfactants are mixture of components with alkyl chains of C_{10}-C_{15}, with C_{11}-C_{13}, being predominant, and the sulphonic group at the end of the chain. High concentrations of up to 12 g/kg have been detected in digested sludge. They are only partially biodegradable, probably because the phases interaction is difficult and bacteria have no access to this molecules.

Volatile Aromatic Compounds

Benzene, toluene and xylene (BTEX) are among the most diffused compounds in industrial chemistry, therefore, they are generally found in wastewaters. Benzene is reported to be easily biodegradable and the same is for phenols and cresols. The same is for toluene. These compounds are removed by biodegradation for 75-90% in wastewater treatment process (Sayles and Suidan, 1993). Volatilisation accounted for the rest and the global removal was 100%.

Chlorobenzenes

Chlorobenzenes, in particular, the dichloro- and trichloro- are in widespread use in industry and in some domestic products. They are used as solvents, cleaners, heat transfer medium. These compounds are generally present at trace level in wastewater but are found in sludge, were they accumulate. Reported concentrations up to 0.05 mg/kg are present in literature. Hexachlorobenzene account for some 6-125 μg/kg. However, American studies reported concentrations up to 1600 mg/kg for dichlorobenzenes (in Rogers, 1996). More realistic figures report concentration ranging between 0.01 and 40 mg/kg, with median values always < 10 mg/kg for the different dichlorobenzenes. Generally, pentachlorbenzene was not found in sludge samples. However, some evidences concerning biodegradation are reported: in particular aerobic degradation is reported to be more effective than anaerobic degradation (in Rogers, 1996).

Organo-phosphorus compounds

Organo-phosphorus compounds were introduced to substitute the organochlorine pesticides. Malathion, parathion and diazinon are well known commercial names for these compounds. These compounds can be generally degraded in aerobic conditions in wastewater treatment processes and are not detectable in sludge.

Organo-tin compounds

Organo-tin compounds is the most important class of organometallic compounds in industry and agriculture. They are used as stabilisers in productions of industrial organic compounds (PVC, polyethylene, cellulose acetate etc…), or as biocides in anti-fouling. Mono-, di-, tri-butyl-tin were detected in Swiss wastewaters in the range 140-560 ng/l, 130-1030 ng/l, 60-220 ng/l, respectively (Fent, 1996). The most toxic compound is the tri-butyl-tin. In excess sludge in UK WWTPs were found concentrations in the range 0.1-1.3 mg/kg, with an average of 0.4 mg/kg. These compounds are supposed to be not biodegradable in wastewater treatment processes.

Organochlorine pesticides and chlorophenols

These compounds were introduced in 1950-1960s and were soon recognised as very hazardous because of their persistence. Since they are hydrophobic, they are generally associated with suspended solids in wastewaters and tend to accumulate in sludge. These compounds generally show low concentration in wastewaters but are then found in sludge: aldrin, dieldrin, heptachlor and lindane are found in concentrations in the range 0.1-0.5 μg/g.

These compounds are supposed to be biodegradable in anaerobic environment through the reductive dehalogenation pathway (Rogers, 1996), but only partially biodegradable in aerobic environment. Nyholm et al. (1992) and Monteith et al. (1995), reported the partial biodegradation of lindane in bench scale experiments with activated sludge also in aerobic conditions. The adaptation of biomass to this substrate took place after 30-40 days and biodegradation efficiency was higher for high F/M ratios. This suggested that lindane was degraded by a co-oxidation process.

Chlorophenols are present at trace levels in wastewaters and are generally biodegraded in wastewater treatment processes: anaerobic biodegradation is more effective than the aerobic one (Rogers, 1996). When considering the aerobic biodegradation, it was reported that the higher the number of chlorine atoms, the lower was the biodegradation efficiency. Trichlorophenols and pentachlorophenol significantly sorb to activated sludge and are then biodegraded up to 75-90 % (Nyholm et al., 1992).

Polycyclic Aromatic Hydrocarbons (PAHs)

These compounds are not produced intentionally, but are the products of pyro-synthetic formation during high temperature combustion of organic material, therefore they are ubiquitus. Because their medium-high octanol-water partition coefficient (log K_{ow} in the range 3 - 5) PAH are sorbed on activated sludge in wastewater treatment processes. Their concentration in sludge was found in the range 2-20 mg/kg (Rogers, 1996).

Polychlorinated bi-phenyls (PCBs)

These compounds were commercially manufactured in first years of 1900 and widely used because their thermal stability, high dielectric constant and chemical inertness. Consequently they were used in transformer fluids, electric insulating materials and as plasticisers. They are hydrophobic and thus associated with suspended solids in wastewaters, and in minor part, associated to colloidal material or emulsionated in oils. Therefore, they are generally entrapped into sludge. In UK these compounds were found with an average concentration of 0.3 μg/kg, but the values are greatly variable. In general, the higher chlorinated congeners were found in highest concentrations (Rogers, 1996). Disse et al. (1995) reported values up to 200 μg/kg for German sludge.

Morris and Lester (1994) reported that removals of PCBs in activated sludge processes were generally > 90%. Effluent PCBs were related to suspended solids in the effluent rather than present in soluble phase. A half of the removal was due to primary sedimentation. Bio-sorption on activated sludge was the main removal mechanism and PCBs concentration in sludge was in the range 1.6-5.4 μg/kg. However, these levels were two folds lower than in primary sludge. The partition coefficient, K, determined as the ratio between the PCBs in sludge and the PCBs in soluble phase in the activated sludge process, gave results in the range 15000-35000 l/kg, so bio-sorption efficiency was clear.

Polychlorinated dibenzodioxines (PCDD) and Polychlorinated dibenzofurans (PCDF)

These compounds are generally indicated with the name "dioxins", even though they are a group of some 210 different compounds. The most important compounds of dioxins are the 2,3,7,8, congeners, the tetra-chloro-*para*-dibenzodioxine (TCDD), reported in fig. 7.5, which is particularly toxic. These compounds are not intentionally produced in industry but are produced during combustion processes of organic materials, especially plastics. They have low volatility and high octanol/water partition coefficient. Consequently, they adsorb strongly onto organic solids, and are therefore found in trace levels in sewage sludge of WWTPs (Hong et al., 2000). Concentrations in sludges are greatly variable but the *para*-dibenzodioxine is always the most abundant, with concentrations of some thousands of pg/kg in sludges of WWTPs in Sweden Germany and UK.

So, in conclusion, it is evident that removal efficiency is generally high for organic micropollutants (> 80%), but, biodegradation is only partial or absent. Therefore, the pollutants are just concentrated in sludge and they will exert their toxic potential on a solid phase (e.g., on soils) rather than in water bodies, but the problem is not solved. However, it is important to note that the application of an anaerobic digestion process for sludge stabilisation can reduce the toxic potential of sludge, since a number of compounds, especially chlorinated, can be more easily degraded in anaerobic (reductive) conditions.

3. Experimental

3.1 The italian scenario and membrane effect

The same approach used for the occurrence and removals of metals (see chapter V) has been adopted regarding selected organic micropollutants. In particular, the following groups of compounds were selected for the investigations: Polynuclear Aromatic Hydrocarbons (PAHs), Volatile Organic Compounds (VOCs), Halogenated Volatile Organic Compounds (HVOCs), Chlorobenzenes.
The list of the compounds analyzed is shown in table 6.3 together with the instrumental limit of quantification (LOQ) both on the raw samples and on the solid phase.

PAH					
	LOQ			LOQ	
	µg L^{-1}	mg kg^{-1}		µg L^{-1}	mg kg^{-1}
Naphtalene	0,005	0,5	Benzo(a)anthracene	0,005	0,5
Acenaphtilene	0,005	0,5	Crysene	0,005	0,5
Acenaphtene	0,005	0,5	Benzo(b)fluoranthene	0,005	0,5
Fluorene	0,005	0,5	Benzo(k)fluoranthene	0,005	0,5
Fenantrene	0,005	0,5	Benzo[a]pyrene	0,005	0,5
Anthracene	0,005	0,5	Indeno(1,2,3-cd)pyrene	0,005	0,5
Fluoranthene	0,005	0,5	Dibenzo(a,h)anthracene	0,005	0,5
Pyrene	0,005	0,5	Benzo[ghi]perylene	0,005	0,5

VOC					
	LOQ			LOQ	
	µg L^{-1}	mg kg		µg L^{-1}	mg kg
Benzene	0,01	0,25	1,3,5-Trimethylbenzene	0,01	0,25
Toluene	0,5	0,25	Ter-butylbenzene	0,01	0,25
Chlorobenzene	0,01	0,25	1,2,4-Trimethylbenzene	0,01	0,25
Ethylbenzene	0,01	0,25	1,3-Dichlorobenzene	0,01	0,25
m-Xylene + p-Xylene	0,01	0,25	Sec-buthylbenzene	0,01	0,25
Stirene	0,01	0,25	1,4-Dichlorobenzene	0,01	0,25
o-xylene	0,01	0,25	p-Isopropiltoluene	0,01	0,25
Isopropilbenzene	0,01	0,25	1,2-Dichlorobenzene	0,01	0,25
Bromobenzene	0,01	0,25	n-Butylbenzene	0,01	0,25
2-Chlorotoluene	0,01	0,25	1,2,4-Triclhorobenzene	0,01	0,25
n-Propilbenzene	0,01	0,25	1,2,3-Triclhorobenzene	0,01	0,25
4-Chlorotoluene	0,01	0,25			

HVOC					
	LOQ			LOQ	
	µg L^{-1}	mg kg		µg L^{-1}	mg kg
dichlorodifluoromethane	0,005	0,5	trichloroethylene	0,15	0,5
chloromethane	0,005	0,5	1,2 dichlroropropane	0,02	0,5
bromomethane	0,005	0,5	dibromomethane	0,05	0,5
chloroethane	0,005	0,5	dibromodichloromethane	0,005	0,5
trichloromonofluoromethane	0,005	0,5	1,3 dichloropropilene cis	0,02	0,5
1,1 dichloroethylene	0,02	0,5	1,3 dicloropropilene trans	0,02	0,5
methylene chloride	0,005	0,5	1,1,2 trichloroethane	0,05	0,5
1,2 dichloroetiliene trans	0,02	0,5	tetrachloroetylene	1,5	0,5
1,1 dichloroethane	0,02	0,5	1,3 dichloropropane	0,02	0,5
2,2 dichloroprophane	0,02	0,5	dibromochloromethane	0,02	0,5
1,2 dichloroethylene cis	0,10	0,5	1,2 dibromethane	0,05	0,5
bromochloromethane	0,02	0,5	1,1,1,2 tetrachloroethane	0,02	0,5
trichloromethane	0,63	0,5	tribromomethane	0,05	0,5
1,1,1 trichloroehane	0,005	0,5	1,1,2,2 tetracloroethane	0,05	0,5
carbon tetrachloride	0,005	0,5	1,2,3 trichloropropane	0,05	0,5
1,1 dichloro 1 propene	0,02	0,5	1,2 dibromo 3 chloropropane	0,5	0,5
1,2 dichlroroethane	0,02	0,5	esachloro 1,3 butadiene	0,02	0,5

Chlorobenzenes		
	LOQ	
	µg L^{-1}	mg kg
1,2,4,5-tetrachlorobenzene	0,05	1
Pentachlorobenzene	0,05	1
Esachlorobenzene	0,05	1

3.1.1 Polynuclear Aromatic Hydrocarbons (PAHs)

Basically, the abundances found out in the plants analyzed were in the range of µg L-1, and most of the compounds analyzed were found under the instrumental LOQ. Table 6.3 shows the range of concentrations found in the different analyzed plants.

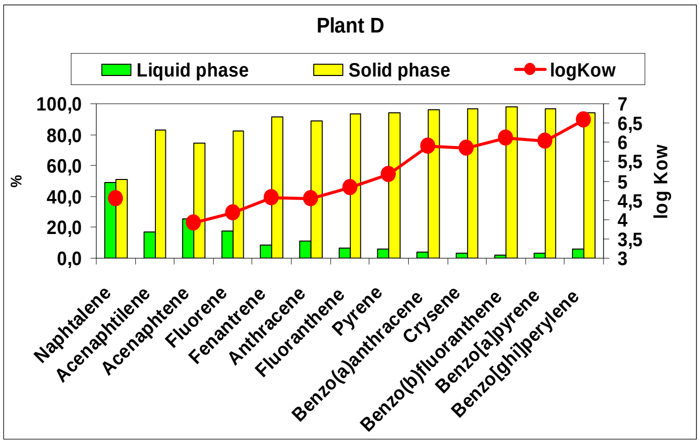
Table 6.3 Abundances of PAHs in the influent sewages to the selectede WWTPs

		A	B	C	D	E	Kolpin et al., 2002
		Influent 30% municipal	Influent 100% municipal	Influent 100% municipal	Influent 60% municipal	Influent 10% municipal	Influent 100% municipal
Naphtalene	µg/L	0,25	0,096	0,113	0,634	0,103	0,02-0,04
Acenaphtilene	µg/L	0,030*	0,017*	<0,005	0,022	0,011	
Acenaphtene	µg/L	0,18	0,084*	0,027*	0,285	0,115	0,02-0,04
Fluorene	µg/L	0,177	0,058	0,008*	0,148	0,043	
Fenanthrene	µg/L	0,084	0,052	0,047	0,188	0,039	0,02-0,04
Anthracene	µg/L	0,014	<0,005	<0,005	0,038	0,013	0,07
Fluoranthene	µg/L	0,028	0,018	<0,005	0,126	0,009	0,02-0,04
Pyrene	µg/L	0,025	0,018	<0,005	0,107	0,01	0,02-0,04
Benzo(a)anthracene	µg/L	0,023	0,02	0,008*	0,025	0,01	
Crysene	µg/L	0,059	<0,005	<0,005	0,025	0,02	
Benzo(b)fluoranthene	µg/L	0,016*	<0,005	<0,005	0,014	0,02	
Benzo(k)fluoranthene	µg/L	0,032*	<0,005	<0,005	<0,005	0,040*	
Benzo[a]pyrene	µg/L	0,016*	<0,005	<0,005	0,014	0,020*	
Indeno(1,2,3-cd)pyrene	µg/L	<0,005	<0,005	<0,005	<0,005	0,020*	
Dibenzo(a,h)anthracene	µg/L	<0,005	<0,005	<0,005	<0,005	0,020*	
Benzo[ghi]perylene	µg/L	0,016*	<0,005	<0,005	0,020*	0,020*	
Total PAHs	*µg/L*	*0,714*	*0,217*	*0,142*	*1,542*	*0,325*	*0,02-0,07*

*only one case higher than the LOQ

From table 6.3 it is important to point out that the PAHs abundances are lower than 2 µg L^{-1} also for a WWTP which includes important petrochemical industries in its catchements area. Moreover, the total concentration of PAHs is mainly composed of naphthalene, which is also very volatile and likely supposed to be stripped already in the physical headworks. The solid/liquid partition of the PAHs is strictly depending on the chemical properties of the compounds. In particular, the PAHs demonstrated to be differently split between liquid and suspended particulate phase according to the Kow (see, for instance, figure 6.1 referred to the plant D).

Figure 6.1. Solid/liquid fractionation and kow in the plant D



As a matter of fact, the influent PAHs were mainly associated to the solid suspended phase and only the naphthalene was found almost equally in liquid and solid phase. To understand which kind of pre-treatments can better remove the PAHs from the influent sewage, it is important to know the size of particles associated to the organic xenobiotics. Literature data have pointed out the contribution of the street particles, that are transported into the sewers systems by the rainfall run-off, on the abundance of metals and PAHs into the sewage influent to the WWTPs (Lau and Stenstrom, 2005; Villar *et al.*, 2006). In particular, Lau and Stenstrom (2005) analysed street particles collected from 18 different city adjacent to five different landuses in the City of Santa Monica (California, USA) finding out that the greater mass of pollutants was associated with particles in the 100-250 µm range. These final remarks let suppose the important role of the physical headworks, such as screening and degritting, in the removal of the adsorbed PAHs. In this experimentation the role of the different operation units in conventional WWTPs was also investigated analysing samples taken from the same points showed in the chapter V. Table 6.4 resumes the removals ranges found out in the examined plants.

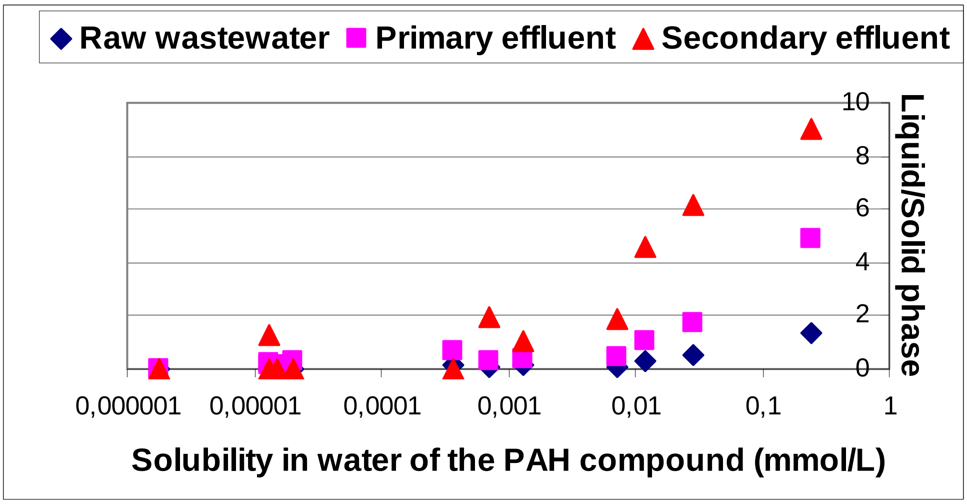
Table 6.4 Removals of the PAHs in conventional plants

	Headworks and primary treatments	Secondary treatments	*Total*
Removal of PAHs (%)	20÷40	20÷50	*63÷90*

From table 6.4 one can observe that the removal of PAHs is relevant already in conventional sytems. The resulting effluent concentrations of total PAHs are in the range 0,01÷0,14, where the main compound is the naphthalene (40÷60%).

The chemical properties of the compounds could be used also to suppose the partition of the PAHs concentrations over the treatment flowscheme. In particular, plotting the solid/liquid partition vs the solubility in water at 25°C, the curves of figure 6.2 were obtained.

Figure 6.2 Solid/liquid partition of the PAHs compounds and solubility in water



As far as the possible impact of the membranes, the removals of parallel MBR and CASP have been compared and are reported in table 6.5.

Table 6.5 Removals of MBR and CASP – data from the Treviso installations (average on 5 samples)

	Removal MBR (%)	Removal CASP (%)
Nafthalene	73	66
Acenafthylene	>81,5	>81,5
Acenafthene	80	82,0
Fluorene	>80,0	>80,0
Fenanthrene	66	63
Anthracene	82	>87
Fluoranthene	65	>95,8
Pyrene	58	76
Chrysene	>78	>78,3

Table 6.5 shows that the removals of PAHs in conventional and MBR systems are comparable when treating purely municipal wastewaters. In other words, if the influent contains abundances of PAHs already very low, the possible advantages of membrane systems are not economically justificable, disregarding what has been found for the metals (see chapter V).

3.1.2 Volatile Organic Compounds

Volatile organic solvents are widely used in small factories, therefore can be found in municipal sewers systems and influent to the WWTPs. Table 6.6 resumes the occurrence of VOCs found out in the examined italian full scale WWTPs.

Table 6.6 Occurrence of VOCs in italian sewage influent to municipal WWTPs

Parameter		A	B	C	D	E
		30% municipal	100% municipal	100% municipal	60% municipal	10% municipal
Benzene	µg/L	0,21	<0,005	0,063	0,239	0,063*
Toluene	µg/L	3,544	4,885	3,008	7,169	3,008
m-Xylene + p-Xylene	µg/L	0,568	0,15	0,193	0,775	0,15
o-xylene	µg/L	0,035	0,192	0,313*	0,351	0,035
Styrene	µg/L	0,148	0,139	0,226	1,116	0,139
Ethylbenzene	µg/L	0,238	0,093	0,132	0,216	0,093
Chlorobenzene	µg/L	0,020*	0,120*	0,031*	0,349*	0,020*
Isopropylbenzene	µg/L	0,530*	0,063*	0,063*	<0,005	0,063*
Bromobenzene	µg/L	<0,005	<0,005	<0,005	<0,005	<0,005
2-Chlorotoluene	µg/L	0,058	0,208*	0,118	<0,005	0,058*
n-Propylbenzene	µg/L	5,567	<0,005	0,110*	0,149	0,110*
4-Chlorotoluene	µg/L	0,05	0,301	0,306	0,22	0,05
1,3,5-Trimetylbenzene	µg/L	0,053	<0,005	<0,005	0,360*	0,053*
1,2,4-Trimetylbenzene	µg/L	0,168	1,018	0,764	0,81	0,168
Ter-butylbenzene	µg/L	0,08	<0,005	<0,005	<0,005	0,080*
1,3-Dichlorobenzene	µg/L	0,04	<0,005	0,090*	<0,005	0,040*
Sec-butylbenzene	µg/L	<0,005	<0,005	<0,005	<0,005	<0,005
1,4-Dichlorobenzene	µg/L	0,03	0,618	1,054	<0,005	0,030*
p-Isopropyltoluene	µg/L	0,02	<0,005	0,098	0,56	0,02
1,2-Dichlorobenzene	µg/L	<0,005	<0,005	<0,005	<0,005	<0,005
n-Butilbenzene	µg/L	0,020*	<0,005	0,156	<0,005	0,020*
1,2,4-Trichlorobenzene	µg/L	<0,005	<0,005	<0,005	<0,005	<0,005

*only one case higher than the LOQ

The volatile organic solvents, such as the BTEX (benzene, toluene and xyxlens) or the trimethylbenzene, were found with a remarkable frequency of occurrence, although no industries were declared to be in the catchments area. As for the concentration, BTEX were in the range 3÷10 μg L^{-1}, and the toluene accounted for the 73÷89%. Moreover, 1,2,4-Trimetylbenzene was in the range 0,1÷1 μg L^{-1}. As far as the other volatile compounds, they were sporadically found and, rather than compounds to be focused on, they could be considered as singular exceptional incomings. The volatile organic compounds were found only in the liquid phase, while the abundances on the suspended particulate were always under the LOQ.

As far as the removals in conventional plants, considering the high volatility of the compounds a first important stripping phenomenon was supposed already in the physical headworks (table 6.7).

Table 6.7 Removals of organic solvents in the conventional treatment stages

	Headworks and primary treatments	Secondary treatments	*Total*
Removal of VOCs (%)	40÷60	10÷50	*60÷99*

Generally, the removals of VOCs were higher than 90% and lower values were singular events due probably to wrong sampling. This class of compounds present both high Henry's law constants, and thus they tend to volatilise, and medium values of the logarithmic partition constant K_{ow}. Therefore, in the bioreactor they can either volatilise or adsorb on sludge, or both. In this study, the concentration of BTEX in sludge was under the detection limit. So, these were quite totally removed from the bioreactor. This is probably due to the fact that these compounds are both biodegradable (Xiao et al., 2000) and volatile. Therefore, they were not found neither in the treated water nor in the wasted sludge.

In this case, the effect of the membrane was not quantifiable with accuracy. However, it can be considered not remarkable and, considering the very low effluent concentrations (often aroung 0,1 µg/L), the adoption of these kind of technologies is not considered economically sustainable.

HVOCs and chlorobenzenes

While the chlorobenzenes were always under the LOQ, different HVOC compounds were found for the different compounds and no reasonable correlation with the origin of the wastewater could be made. To date, further investigations and refining of the analytical methods are needed.

4. Conclusions

Organic xenobiotics occurrence and removal have beed investigated in real wastewater treatment systems. Owing to the number of plants sampled, only four families of compounds were focused. However, also using this approach, more than 80 compounds were analyzed among PAHs, VOCs, HVOCs and chlorobenzenes. This approach allowed to evaluate the occurrence in italian wastewater treatment systems and to select possible target compounds.

As far as the PAHs, abundances lower than 2 µg L^{-1} were observed also in plants located in a petrochemical site. These pollutants inflow to the wastewater treatment plants mainly associated to suspended particulate matter according to the Kow. In particular, the particles that bring PAHs are also in the range of grit. Therefore, a first important removal (20÷40%) is observed already in the physical headworks. Moreover, the biological secondary conventional treatments exert a further removal in the range 20÷50%. As a result, the total PAHs in the treated effluent were in the range 0,1÷0,14 µg L^{-1}. The effect of the membrane systems, evaluated parallely to the conventional plant, was not significant to justify the possible increased costs of the treatment facilities.

The occurrence of VOCs was mainly attributed to organic solvents such as BTEX and trimetylbenzene. The influent abundances were in the range 3÷10 µg L^{-1} for the BTEX, mainly toluene, and 0,1÷1 µg L^{-1} for the trimetylbenzene. The stripping of these compounds was remarkable (40÷60%) already in the physical headworks, moreover the biological conventional processes were effective so far to involve further 10÷50% removal. The effect of the membrane system was not valuable because of the very low influent concentrations.

The chlorobenzenes were always under the limits of quantification, while the HVOC where very variable case by case and did not allow any kind of reasonable consideration. However, the maximal HVOC concentrations were around some µg L^{-1}.

In the view of the investigations carried out, PAHs are already removed from the treated effluents and MBRs operating within the experimented parameters (sludge age in the range 10÷40 days) do not give significant enhancement of the already satisfactory removals of the conventional activated sludge processes.

As far as the VOCs, the organic solvents should be of major concern. The removals are performed already in the physical headworks by stripping. Therefore, in case of relevant influent concentrations, these operation units should be put under suction and the resulting gassous effluents should be treated adequately. However, the municipal systems are considered not in these conditions and the expenses of the treatment for the possible gas emissions would be not justified in the overall environmental balanced.

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Chapter VII. Impact of biomass (bulk) parameters on membrane fouling

Membrane fouling and its consequences in terms of plant maintenance and operating costs are key issues that limit the widespread application of MBRs. A number of factors influence fouling phenomena and the solids content in the mixed liquor is reported to play a major role. In this chapter, firstly the background information about membrane fouling are given, taking as sources a recent review by Le-Clech *et al.* (2006) and “The MBR book” (Judd, 2006). Then the impacts of biomass bulk parameters on the fouling of an industrial module, operating at constant permeate flux, are discussed. Finally, a statistical approach is used to process the experimental data in order to obtain a mathematical model which relates the trans membrane pressure and the biomass bulk parameters.

1. Fouling in membrane bioreactors used in wastewater treatment

1.1 Fouling mechanisms for complex fluids

Significant advances in understanding fouling of individual components such as bacteria, yeast, proteins, and colloids have occurred in microfiltration and ultrafiltration literature (Belfort *et al.*, 1994; Chan *et al.*, 2004; Marshall *et al.*, 1993; Fane and Fell, 1987). Much of this literature has focused on the effect of charge (via pH variation or salt concentration), crossflow, concentration, membrane hydrophilicity, membrane pore size and flux (constant pressure or constant flux). While some broad trends for simple colloids are valid for macromolecules (the most commonly studied of which are proteins), the labile nature of proteins and range of polydispersity of naturally occurring macromolecules such as polysaccharides and humic substances add a particular complexity to the fouling mechanisms. In addition, the interaction between the suspended colloids or those in the deposited “cake” in a mixed species environment has the potential to significantly change the nature of the foulant layer in terms of resistance and reversibility, even for simple model systems.

Le Clech *et al.* (2006) resume the main findings about: (1) the effects of sustainable and critical flux in mixed species environment; (2) the effect of operating modes on performance; (3) the cake structure and the effect of mixed species on cake morphology (figure 7.1 a-b); (4) effect of membrane morphology and surface chemistry on fouling mechanisms

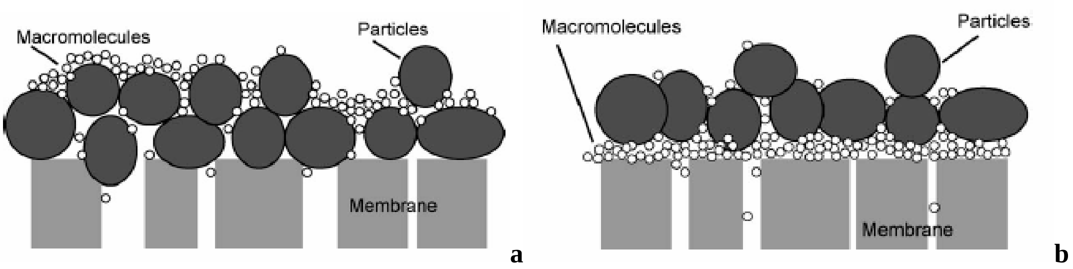


Figure 7.1 a-b. Cake layer as prefilter (a) and composite cake structure (b)

To sum up the authors stated that in complex fluids, the interactions between the macromolecular and particulate components of the feed can result in unexpected and rapid changes in fouling. The kinetics and inventory of macromolecules adsorbing will dictate the initial fouling phase. Progressive closure of pores or membrane surface results in a change in transmission and species convected to the surface and the foulant cake. While the initial low fouling phase at low flux (or “sub-critical” flux) features slow progressive adsorption of macromolecules on the membrane surface, a more rapid fouling phase then occurs. During that period, pore closure results in enhanced rejection of macromolecules and deposition of larger particles (Fig. 7.2). Evolution of this foulant cake and its irreversibility depend on both its composition and the hydrodynamic environment under which it was established. The interaction between particulate and macromolecular fouling needs to be considered with many of the same complexities observed in fouling studies of natural organic matter. Macromolecular fouling can increase particulate adhesion, but particles can affect the transmission and infiltration of macromolecules into the membrane pores. Greater understanding of the foulant structure in mixed specie systems will allow better control measures to prevent foulant build-up or to disengage the foulant layer. The lessons learnt from such studies are important for understanding fouling in MBRs.

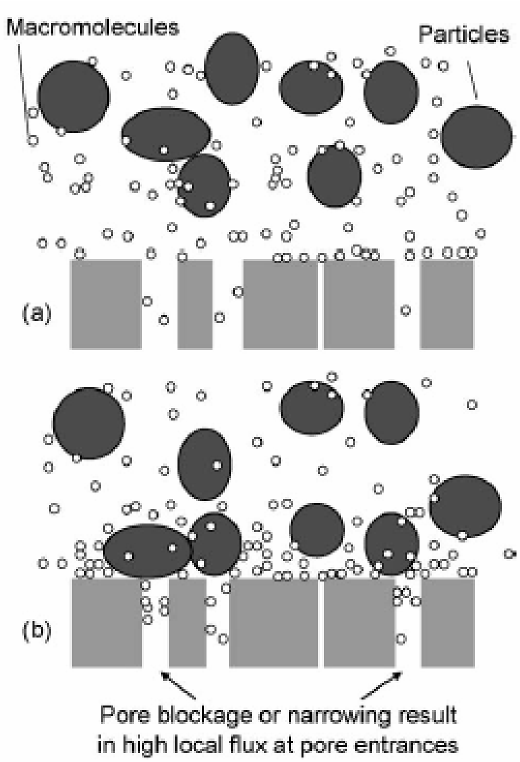


Figure 7.2 Progressive pore blockage leading to rapid TMP increase

1.2 Fouling in MBRs

All the parameters involved in the design and operation of MBR processes have an influence on membrane fouling. Basically, three categories of factors can defined, i.e. membrane and module characteristics, feed and biomass parameters and operating conditions (Fig. 7.3). While some of these parameters have a direct influence on MBR fouling, many others result in subsequent effects on phenomena exacerbating fouling propensity. The complex interactions between these parameters complicate the perception of MBR fouling and it is therefore crucial to fully understand the biological, chemical and physical phenomena occurring in MBRs to assess fouling propensity and mechanisms.

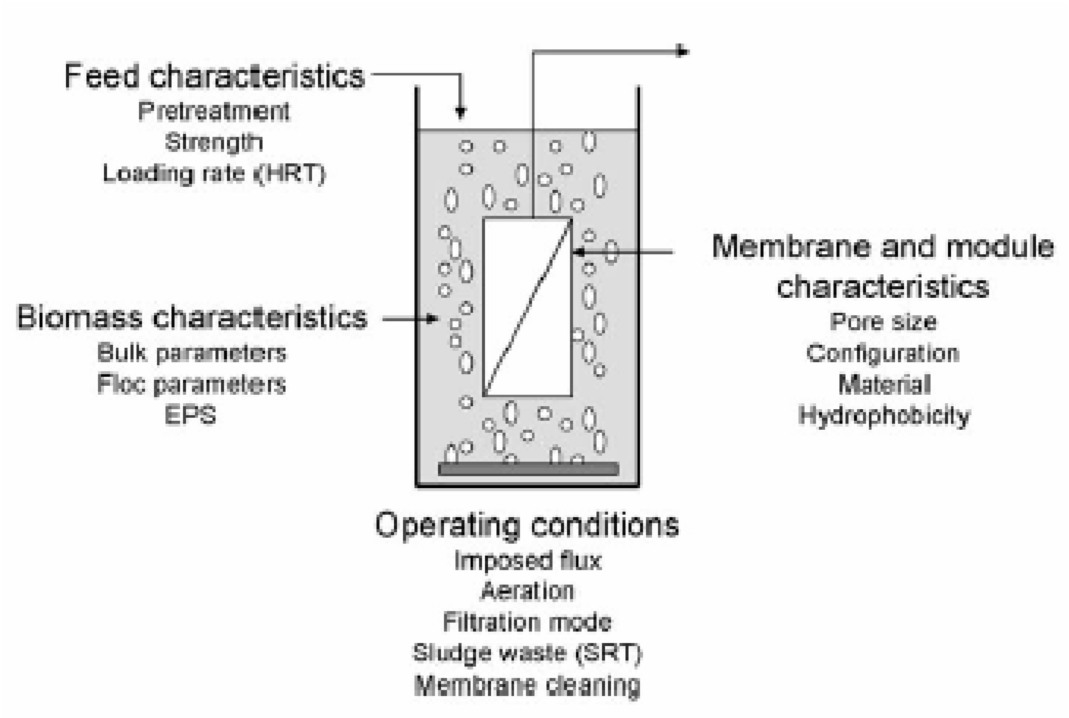


Figure 7.3. Factors affecting fouling in submerged MBRs

With particular concern to the feed-biomass characteristics, Le-Clech *et al.* (2006) pointed out the important role of: (a) nature of feed and concentration; (b) biomass fractionation; (c) biomass bulk parameters (i.e.: MLSS concentration, viscosity, temperature, dissolved oxygen) (d) floc characteristics (floc size, hydrophobicity/surface charge); (e) extracellular polymeric substances (EPS); (f) soluble microbial products (SMP). Among the parameters influencing the fouling phenomena in MBRs, following the attention is focused only on the information which are the background for the experimental results later discussed, while further reading of Le-Clech *et al.* (2006) and Judd (2006) is suggested to an a complete overview on the fouling in MBRs.

1.2.1 Biomass bulk parameters

MLSS concentration

Often considered at first sight as the main foulant parameter, MLSS concentration has indeed a complex interaction with MBR fouling, and controversial findings about the effect of this parameter on membrane filtration have been reported. If the other biomass characteristics are not accounted for, the increase in MLSS concentration seems to have a mostly negative impact (higher TMP or lower flux) on the MBR hydraulic performances (Chang and Kim, 2005; Cicek *et al.*, 1999). However, some authors have reported positive impact (Brookes *et al.*, 2006; Defrance and Jaffrin, 1999), and some observed insignificant impact (Clech *et al.*, 2003, Hong *et al.*, 2002, Lesjean *et al.*,2005). The existence of a threshold above which the MLSS concentration has a negative influence was also reported (at 30 g/l) (Lubbecke *et al.*, 1995).A more detailed fouling trend has been described by Rosenberger et al. (2005). While a rise in MLSS seems to decrease fouling at low MLSS concentration (<6 g/l), more fouling is expected as the MLSS concentration increases above 15 g/l. The level of MLSS does not appear to have significant effect on membrane fouling between 8 and 12 g/l. Another study (WERF, 2006) reviewed the significant effect of MLSS for concentrations lower than 5 g/l, and indicated that hydrodynamics (more than MLSS concentration) control the critical flux (Jc) for greater MLSS levels (WERF, 2006). This is only partially verified by the data reported in Table 7.1.

More subtle studies showed apparent contradictory trends from data obtained in the same study. For example, the cake resistance (R_c) was observed to increase and the specific cake resistance (α_c) to decrease as MLSS increased. Although having similar meaning conceptually R_c and α_c seemed to behave inversely (Chang and Kim, 2005). This can be reconciled by noting:

$$R_c = \alpha_c m_c$$

where m_c is the cake load/area of membrane. The cake load m_c would tend to rise with MLSS concentration. Bin *et al.*(2004) observed the permeate flux to decrease (but at a lower fouling rate) when MLSS increased. This was explained by the creation of a rapid fouling cake layer (potentially protecting the membrane) at high concentration, while progressive pore blocking created by colloids and particles was thought to take place at lower MLSS concentration.

Table 7.1 Influence of shift in MLSS concentration (g/L) on MBR fouling (adapted from Le-Clech *et al.*, 2006)

MLSS shift	Fouling parameters
Fouling increase	
0.09-3-7	Rc: 21 to 54 x 10^{11} m^{-1} and α_c 18.5 to 0.7 x 10^8 m/kg
2.4-9.6	Rp: 9 to 22×10^{11} m^{-1}
7-18	Jc: 47–36 L/m^2 h (for SRT: 30–100 days)
2.1-9.6	Jc: 13–8 L/m^2 h
1-10	Jc: 75–35 L/m^2 h
2-15	Limiting flux: 105–50 L/m^2 h
1.6-22	Stabilized flux: 65–25 L/m^2 h
Fouling decrease	
3.5-10	Jc: <60 to >80 L/m^2 h
No (or little) effect	
9-14	No impact on fouling rate
4.4-11.6	No impact between 4 and 8 g/L, slightly less fouling for 12 g/L
6-18	Similar fouling rates for J<10 L/m^2 h, and slightly lower fouling rates for higher J
4-15.1	Jc decreased from 25 to 22 L/m^2 h
3.6-8.4	-

Since the value of J_c is often determined during short-term experiments, it is expected that J_c indicates the deposition of suspended solids rather than colloidal and soluble materials. As a result, the flux value at which the experiment is carried out, has a significant impact on the determination of the effect of the MLSS concentration. Similarly, the test duration can be a factor. While MBR performances are expected to decrease for higher MLSS (at applied flux superior to J_c), the MLSS concentration may not play a significant role in fouling propensity when the MBR is operated at low fluxes. In that later case, EPS components and concentrations have more effect on the MBR fouling than the MLSS concentration. Contradictory results may also arise from the mode of filtration, i.e. constant flux versus constant TMP. Empirically derived equations predicting flux performance have been proposed in numerous papers (Fang and Shi, 2005; Sato and Ishii, 1991; Krauth and Staab, 1993; Shimizu *et al.*, 1996). However, these equations have limited use as they are generally obtained under very specific conditions and take into account some specific operating parameters and disregard some others.

A mathematical expression linking MLSS concentration, EPS and TMP with cake specific resistance has been proposed by Cho *et al.* (2005). In this study, specific resistance did not change significantly for MLSS ranging from 4 to 10 g/l and when the EPS and TMP were kept constant.

The experimental method used for changing MLSS concentration can also significantly impact upon biomass characteristics since biomass acclimatization periods are not always respected (Cicek *et al.*, 1999). Although the removal performances are generally high for MBR processes, MLSS concentration also plays a significant role in this regard. For example, an optimal MLSS concentration at 6 g/l was obtained based on the highest COD removal (Ren *et al.*, 2005) and on the highest virus removal (Wong *et al.*, 2004).

The lack of a clear correlation between MLSS concentration and any other foulant characteristics indicates that the MLSS concentration (alone) is a poor indicator of biomass fouling propensity (Brookes *et al.*, 2003; Jefferson *et al.*, 2004). These authors recommended the use of fundamental operating parameters like HRT and SRT for prediction of foulant production. This has been supported by the relatively stable foulant characteristics obtained once true steady-state was established in the bioreactor. Current studies tend to consider the non-settleable organic substances (rather than the MLSS concentration) as the main players in the fouling propensity in MBRs.

Viscosity

In the MBR, like in conventional activated sludge processes, biomass viscosity is closely related to its concentration, and has been cited as a foulant parameter (Yeom *et al.*, 2004). A critical MLSS concentration exists under which the viscosity remains low and rises only slowly with the concentration. Above this critical value, suspension viscosity tends to increase exponentially with the solids concentration (Itonaga *et al.*, 2004). This critical value was observed to change from 10 to 17 g MLSS/L for different operating conditions (conventional and hybrid (precoagulation/ sedimentation) MBRs, respectively). Similar observations were reported for the behaviour of the capillary suction time (CST), another parameter closely related to viscosity (Brookes *et al.*, 2003). The importance of MLSS viscosity is that it modifies bubble size and can dampen the movement of hollow fibers in submerged bundles (Wicaksana *et al.*, 2006). The net result of this phenomenon would be a greater rate of fouling. Increased viscosity also reduces the efficiency of mass transfer of oxygen and can therefore effect dissolved oxygen (DO) (Germain and Stephenson, 2005), fouling tends to be worse at low DO (see below). The effect of MLSS concentration on viscosity at different shear rates obtained from a submerged MBR is shown in Fig. 7.4. These results also indicate the pseudo plastic (or “shear-thinning”) property of the sludge obtained in MBR.

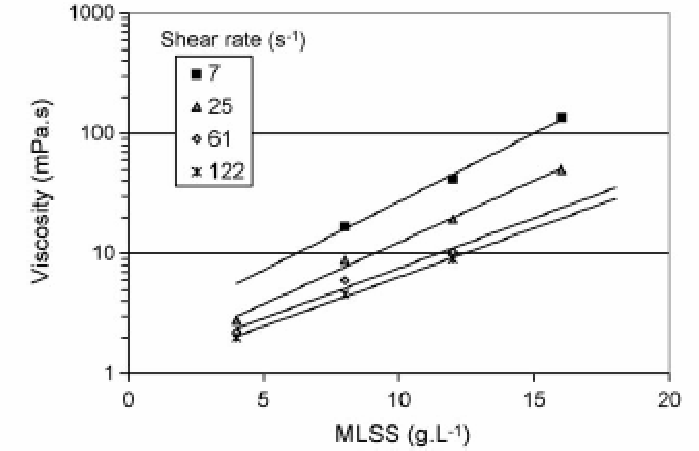


Figure 7.4 Viscosity obtained at different MLSS concentrations and shear rates

Temperature

Temperature impacts on membrane filtration through its influence on the permeate fluid viscosity (Mulder, 2000). The common approach to comparing hydraulic performance obtained at different temperatures is to normalize the operating flux at a reference temperature (generally 25 °C). This could be done by applying a temperature correction factor (Rautenbach and Albrecht, 1989). To avoid the interference of the temperature effects on MBR fouling, non-linear regression between critical flux and temperature was obtained (Fan *et al.*, 2006):

$J_{c,t} = J_{c,20} \times 1.025^{(t-20)}$

Interestingly, experiments carried out at two sets of temperatures (17–18 and 13–14 °C) featured different hydraulic resistances even after the flux had been normalized (Jiang *et al.*, 2005). The greater resistances observed at low temperature were explained by four phenomena occurring in the system: (1) within that temperature range, the sludge viscosity (rather than permeate viscosity) was calculated to increase by 10%, reducing the shear stress generated by coarse bubbles, (2) intensified defloculation tend to occur at low temperature, reducing biomass floc size and releasing EPS to the solution, (3) particle back transport velocity, calculated with the Brownian diffusion coefficient (linearly related to temperature), is less at low temperature, and (4) biodegradation of COD was also reduced at decreased temperature, resulting in a higher concentration of solute and particle COD in the reactor (Jiang *et al.*, 2005). This last phenomenon was also observed by (Fawehinmi *et al.,* 2004) with higher SMP levels measured in an anaerobic MBR operated at 20 °C rather than at 30 °C. All of these factors are directly linked to membrane fouling, so it is expected to observe greater deposition of materials on the membrane surface at lower temperatures (Rosenberger *et al.*, 2006).

Dissolved Oxygen

The average level of DO in the bioreactor is controlled by the aeration rate, which not only provides oxygen to the biomass but also tend to limit fouling formation on the membrane surface. The effects of DO on MBR fouling are therefore multiple and may include changes in biofilm structure, SMP levels, and floc size distribution (Lee *et al.*, 2005). As a general trend, higher DO tends to lead to better filterability, and lower fouling rate. This was explained by the lower specific cake resistance of the fouling layer which featured larger particle sizes and greater porosity (Kim *et al.*, 2006; Kang *et al.*, 2003). As expected, significant differences were observed in microbial communities and resulting biofouling when the MBR was operated under various DO levels (from 6 to less than 0.1 mg/L in Kim *et al.*, 2006). Surprisingly, the COD in biomass suspension (i.e. an indicator for SMP level) decreased from 37 to 27 mg/L for DO of 3.4 and 0.9 mgO_2/L, respectively (Ji and Zhou, 2006) and therefore cannot explained the hydraulic performances obtained in MBR operated at higher DO. Moreover, the contribution of SMP to membrane filterability was found to be a minimum compared to those of the physico-chemical properties of cake layer (i.e. particle size and porosity) (Kang *et al.*, 2003). In a study obtained with anoxic and aerobic sludges (Jang *et al.*, 2005), floc deterioration was observed and used as a possible explanation for the higher fouling rates obtained for the denitrification assay. The effect of oxygen limitation causing a lowering of the cell surface hydrophobicity, and consecutive floc deterioration, was concluded to be the main reason for the worsen MBR fouling for anoxic conditions. In the MBR, fouling may also be due to the creation of a biofilm layer on the membrane surface. As a general definition, bacterial biofilm characterizes the population of microorganisms concentrating, depositing and/or growing at the solid/liquid interface (Yun *et al.*, 2006). As described later in the review, the formation of biofilms is possible through the active role of EPS which surround the microorganisms. Biofilm properties such as adhesion strength (interaction between microorganisms and membrane) and cohesion strength (interaction between microorganisms themselves) can be determined and are directly dependant of the nature of the EPS (Yun *et al.*, 2006). As the thickness of the biological fouling layer increases with extended MBR filtration time, some biofilm regions have been observed to become anaerobic (Zhang *et al.*, 2006). Because of the poor oxygen transfer within the biofilm structure, the fouling sub-layers (on the membrane surface) may become anaerobic, and therefore affect membrane fouling differently. Endogenous decay, similar to that expected within the fouling layer, was simulated and revealed the level of carbohydrate in the extracted EPS (eEPS) to significantly increase. Since the transition between aerobic to anaerobic conditions seems to produce a large amount of EPS, this phenomenon could also be responsible for MBR fouling (Zhang *et al.*, 2006). More details about fouling in anaerobic MBR can be found in (Judd, 2006). The direct impact of air bubbles (as a foulant parameter) on MBR filtration was even investigated by Jang et al. However, it was concluded that the effect of air blocking on the surface can be ignored in MBR processes with high MLSS concentration (as it accounted for less than 1% of total resistance R_t) (Jang *et al.*, 2004). However, under some circumstances, air bubbles my be present or be formed in the lumens of hollow fibers and this can be detrimental. Finally, it is important to keep in mind that the aeration rate controls biological requirements and parameters such as DO, ammonium/nitrate ratio (Kox, 2004).

1.2.2 Constant flux operation

Current trend in MBR design is to operate at constant flux, although few recent studies report the operation of MBR at constant TMP. Following the industrial approach of the research, our experimentations were carried out at constant flux that, therefore, is following introduced.

With the constant flux approach, the convection of foulant does not diminish and fouling phenomena self-accelerates and can eventually create a sharp increase of TMP. With fouling rate, and therefore cleaning frequency, increasing with flux, operation conditions favour the MBR to be run at modest fluxes to limit fouling severity. As a result, numerous studies have reported the fouling behavior for long-term MBR filtration carried out at sub-critical flux. However, these long-term experiments have revealed noticeable fouling for MBRs operated at sub-critical flux. Since its first reference to MBRs in 2001 (Ognier *et al.*), fouling behavior over time is generally characterized by a twostep pattern. During the first period, a very small TMP rise was observed. For trials carried out over extended time periods, a noticeable change in the rate of TMP increase then arises after some critical time period (Fig. 7.5).

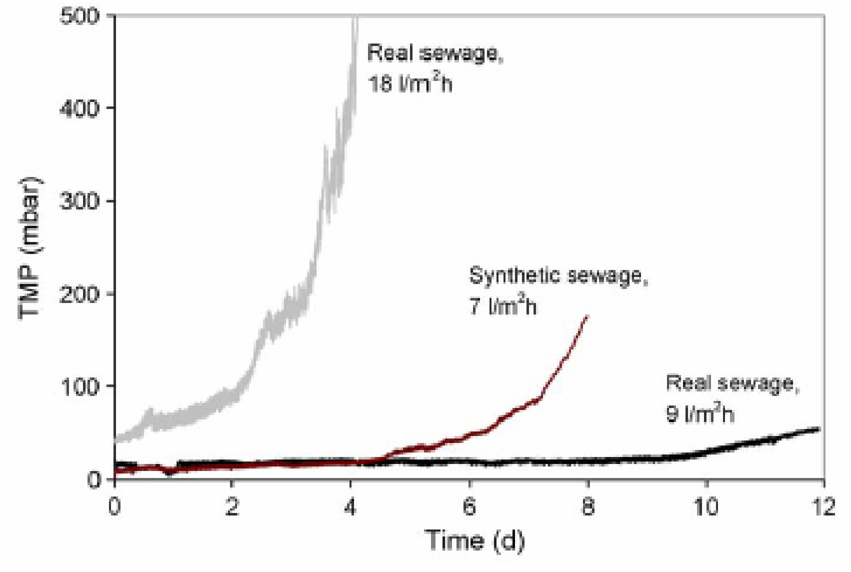


Figure 7.5. Long term filtration for constant flux operation

Pollice *et al.* (2005) reviewed the phenomena and two parameters were introduced as indicators for operation under sub-critical conditions: the critical time over which the prolonged first step is maintained (t_{crit}) and the fouling rate (dTMP/dt) during that step. Table 7.2 reports t_{crit} and dTMP/dt for recent trials and reveals the long periods of filtration (up to 1200 h) for which fouling rate can be maintained at very low values (down to 2×10^{-4} kPa/h).

Table 7.2 Subcritical long term parameters (adapted from Le-Clech *et al.*, 2006)

Flux (LMH)	dTMP/dt (kPa/h)	t_{crit} (h)
17	0.005	>600
22	0.011	1200
25	0.024	300
30	0.072	250
n.a	0.023	350
20	-	600
8	-	350
30	0.036	360
10	0.036	550
8	0.03	72
7	0.006	96
9	0.004	240
18	0.104	48
12	0.0002	300
4	0.013	192
6	0.031	137
8	0.6	74

The fouling rates for the high TMP-rise-period have also been reported previously (Brookes *et al.*, 2006). Prior to these two filtration-steps generally described in the literature, a conditioning period has also been observed (Zhang *et al.*, 2006). This conditioning period (from now called stage 1) has not been observed or described as such until recently, but may be a key aspect of fouling creation in MBRs. The dynamics of the biomass detachment from the membrane in relation to the filtration and aeration turbulence has also been rarely reported, but was recently considered in the formation of a mathematical model (Li and Wang, 2006). Based on the recent work reported by Zhang *et al.* (2006), a detailed analysis of the mechanisms and factors involved in these three fouling stages follows and is summarized in Fig. 7.6.

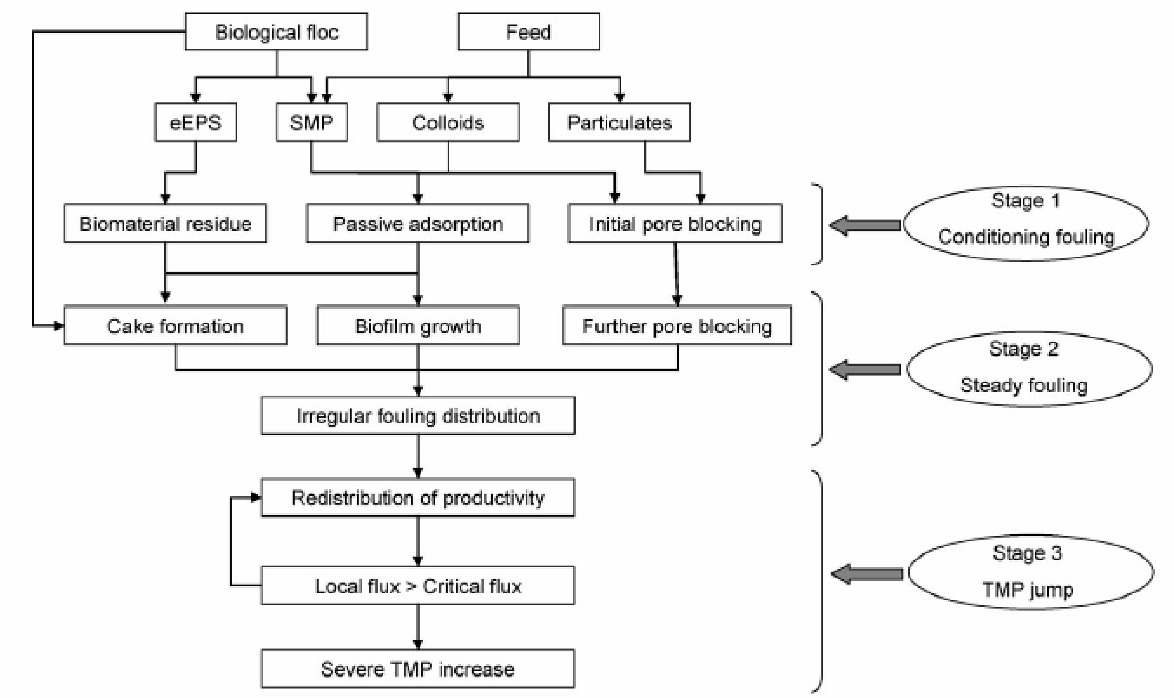


Figure 7.6 Fouling mechanisms for MBR operated at constant flux

Stage 1—conditioning fouling

As in constant TMP operation, strong interactions between the membrane surface and the EPS present in the mixed liquor are probably responsible responsible for the initial stage of fouling during constant flux operation. Ognier *et al*. (2002) described the rapid fouling phenomena inducing irreversible resistance and taking place in the early stage of MBR filtration (in frontal mode, i.e. dead-end operation). Passive adsorption of colloids and organics has been observed even for zero-flux operation, and before any deposition mechanism initiates (Zhang *et al.,* 2006). Another detailed study based on passive adsorption revealed that the hydraulic resistance due to this process was almost independent of tangential shear. In terms of relative hydraulic resistance contribution, the initial adsorption has been reported to account for 20–2000% of the clean membrane resistance (mainly depending on the pore size) (Ognier *et al.*, 2002). In a more recent study, its contribution to the overall resistance was found to become negligible once filtration was conducted (Choi *et al.*, 2005). The adsorption propensity (determined with the modified Freundlich isothermal adsorption equation) was also studied in relation to the filtration modes employed in submerged MBRs (Ma *et al.*, 2005). As a result, colloid adsorption and initial pore blocking (Jiang *et al.*, 2005) of new or cleaned membranes by organics substances is expected in MBRs. The intensity of this effect depends on membrane pore size distribution and surface chemistry (and especially hydrophobicity) (Ognier *et al.*, 2002). In a test cell equipped with direct observation through the membrane (DOTM) technology, and with crossflow but zero flux, floc was visually observed to temporarily land on the membrane (Zhang *et al.,* 2006). This was defined as a random interaction process rather than proper cake formation phenomenon. While some flocs were seen to roll and slide across the membrane, biological aggregates typically detached and left a residual footprint of smaller flocs or EPS material. Biomass approaching the membrane surface was then able to attach more easily to the membrane, colonize the separation surface and contribute to stage 2.

Stage 2—slow (steady) fouling.

Even though MBRs are operated below the critical flux for the biomass, biofloc may randomly land (see above) and contribute to the second fouling stage. After stage 1, the membrane surface is expected to be mostly covered by SMP, leading to the higher attachment propensity of biomass particles and colloids. Because of the low critical flux determined for SMP species, further adsorption and deposition of organics on the membrane surface may also occur during stage 2. Since adsorption may take place not only at the membrane pores but also on the whole surface, biological flocs may initiate cake formation without directly affecting the permeability in this stage. Over time, this phenomenon would worsen. The rate of EPS deposition, and resulting TMP rise, is expected to increase when the operating flux is higher, leading to a shorter stage 2 operation (Table 7.2). The fouling mechanisms described above would prevail even with a good hydrodynamic environment that provides adequate surface shear over the membrane surface. However as maldistributions of flow, shear or flux are generally expected in MBRs, irregular fouling patterns can be anticipated.

Stage 3—TMP jump.

With regions or pores of the membrane more fouled than others, flux is expected to significantly decrease in those specific locations. As a result, the overall permeate productivity redistributes to the less fouled membrane areas or pores, for which local flux increases, exceeding a critical flux (defined as sustainable flux in Section 4.2.2). These phenomena have a self-accelerating nature and severe fouling, characterized by an exponential TMP increase, is generally obtained if the filtration is maintained. The sudden rise in TMP or "jump" is a consequence of constant flux operation and several mechanisms can be postulated for the rapid increase in TMP at a given condition (Zhang *et al.*, 2006):

(i) *The inhomogeneous fouling (area loss) model.*

This model was proposed to explain the observed TMP profiles in nominally sub-critical filtration of upflow anaerobic sludge (Cho and Fane, 2002). The TMP jump appeared to coincide with a measured loss of local permeability at different positions along the membrane, due to slow fouling by EPS. It was argued that the flux redistribution (to maintain the constant average flux) resulted in regions of supra-critical flux and consequently in rapid fouling and TMP rise.

(ii) *The inhomogeneous fouling (pore loss) model.*

Similar TMP transients have been observed for the crossflow MF of a model biopolymer (alginate) (Ye *et al.*, 2005). These trends revealed that the TMP transient can occur with relatively simple feeds. The data obtained have been explained by a model that involves flux redistribution among open pores, allowing for the pore size distribution. Local pore velocities eventually exceed the critical flux of alginate aggregates that rapidly block the pores. This idea was also the basis of the model proposed by Ognier *et al.* (2004). While the “area loss” model considers macroscopic redistribution of flux, the “pore loss” model focuses on microscopic scale. In MBR systems, it is expected that both mechanisms occur simultaneously.

(iii) The critical suction pressure model.

Using a fine colloid, filtered in dead-end mode, onto an immersed hollow fiber, gradual TMP rise followed by a rapid increase in TMP was observed. Both autopsy and modeling suggested a critical suction pressure at which coagulation occurs at the base of the cake (Chang *et al.*, 2005). The very thin dense layer observed next to the membrane confirmed the rapid increase in resistance leading to the TMP jump. Although this model was obtained with dead-end rather than crossflow operation, there is no reason why this mechanism could not apply to sidestream or submerged MBRs. A requirement for that model is that fouling continues to occur over time until the critical suction pressure is reached, and that the deposit compound(s) have the potential to coalesce or collapse. Biofilms and deposit layers in MBRs are likely to have this tendency.

(iv) Percolation theory.

According to percolation theory, the porosity of the fouling layer gradually reduces due to the continuous filtration and material deposition within the deposit layer. At a critical condition, the fouling cake loses connectivity and resistance, and TMP, increase rapidly. This model has been proposed for MBRs (Hermanowicz, 2004), but the model indicates a very rapid change (within minutes), which has not been observed in practice. However, it is plausible that the percolation theory approach, combined with the inhomogeneous fouling (area loss) model, could satisfy the more gradual kinetics of the typical TMP transient. Similarly, fractal theory was successfully applied to describe cake microstructure and properties and to explain the cake compression observed during MBR operation (Meng *et al.*, 2005).

(v) The inhomogeneous fiber bundle model.

Another manifestation of the TMP transient has been observed for model fiber bundles where the flow from individual fibers was monitored (Yeo *et al.*, 2006). The bundle was operated under suction at constant permeate flow, giving constant average flux, and initially this was evenly distributed amongst the fibers. However over time, the flows became less evenly distributed so that the standard deviation of the fluxes of individual fibers started to increase from the initial range of 0.1–0.15 up to 0.4 l/m2 h. Consequently, the TMP rose to maintain the average flux across the fiber bundle, mirroring the increase in the fluxes standard deviation. At some point both TMP and standard deviation showed a rapid rise. This is believed to be due to flow maldistribution within the bundle leading to local blockages between fibers and membrane fouling. It was possible to obtain more steadily TMP and standard deviation profiles when the flow regime around the fibers was more vigorous (higher liquid and/or air intensity). Although this trend was observed for a small model bundle, the phenomena are likely to occur in larger bundles.

The mechanisms (i)–(v) listed above are all self-accelerating and this is a feature of stage 3 fouling. It is probable that more than one of these mechanisms apply simultaneously when an MBR reaches the TMP jump condition.

2. Experimental

2.1 Methodology

The study on the sludge filterability was carried out using the big pilot membrane plant installed in the Falconara municipal WWTP (see part II for the description of the experimental set up). In order to study the mere effect of the biomass bulk parameters, the tests were carried out in a way to keep stable, as far as possible, the other factors influencing fouling. Therefore:

- the filtration cycle was always permeation/backwashing as long as 300 and 30 seconds, respectively;
- at the end of each test an intensive membrane cleaning was performed to start each test with the same permeability. It consisted in submerging the module in the cleaning solution (hypochlorite at 500÷600 mgCl L^{-1}) overnight, while keeping always switched on the aeration to scour the membrane. At the end of the cleaning bath, a sequence of permeation (300 seconds)/backwashing (60 seconds) was carried out along 60 minutes;
- the aeration for membrane scouring was always switched on and the DO in the activated sludge was always close to saturation levels;
- each filtration test lasted 90÷100 hours;

Only the biomass contents and the permeate fluxes were manipulated according to the temporal sequence of the experimental grid shown in table 7.3.

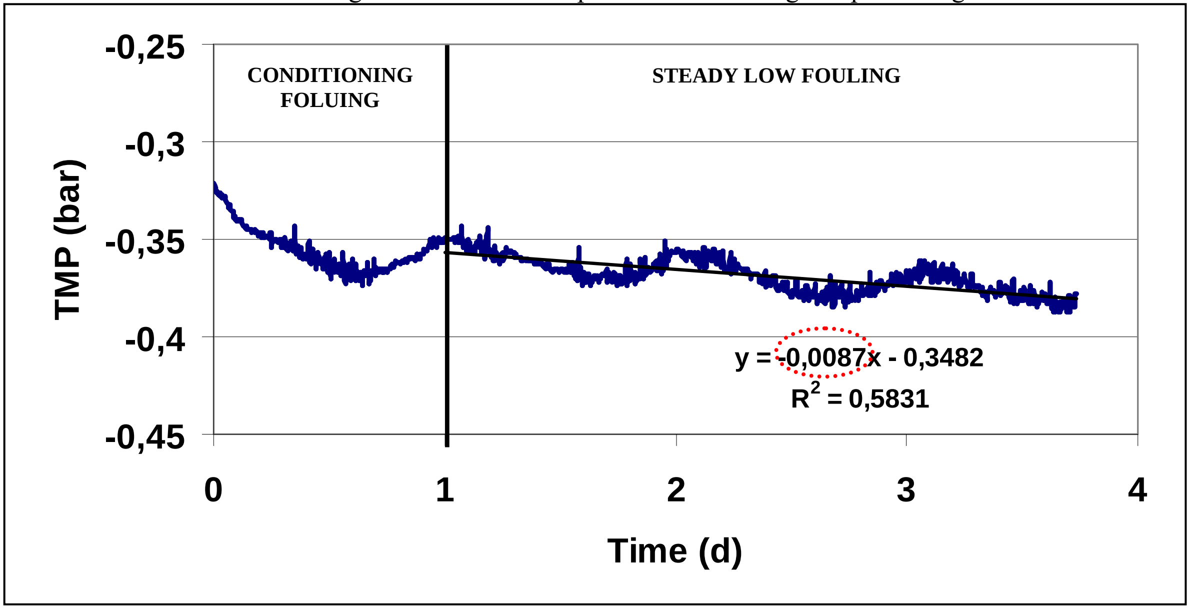
Table 7.3 Experimental grid indicating the temporal sequence of the tests

		Permeate fluxes (LMH)				
		9	**18**	**28**	**37**	**46**
MLSS (g L^{-1})	**0÷0,1**	*1st*	*2nd*	*3rd*	*4th*	*5th*
	1,9÷2,1	*6th*	*7th*	*8th*	*9th*	-
	4,8÷5,2	*10th*	*11th*	*12th*	*13th*	-
	9,7÷10,3	*14th*	*15th*	*16th*	*17th*	-

The experimental grid was repeated four times in order to have totally 64 tests which represents a reliable sample of data to be statistically analysed. As far as the duration of the tests, in order to evaluate the slow steady fouling, each filtration test lasted 4 days.

As for the data screening, the peaks linked to the backwashing were ignored considering the TMPs during certain permeation times. Moreover, the initial conditioning fouling was not considered supposing this phenomenon to be exhausted after 24 hours filtration (see figure 7.7 for the example of data screening).

Figure 7.7 Example of data screening and processing



Except for the final statistical evaluations, when the liquor temperature was considered as variable parameter, the average permeability was adjusted for the temperature according to Mulder (2000). On the other side, the short term TMP variations were not adjusted for purpose of the statistical analyses because the temperature was considered as independent parameter in the modelling. Therefore, the average TMP was considered as the slope of the best fit line from the day second to the day fourth (see figure 7.7).

2.2 Tertiary filtration vs MBR

As far as the real scale issues, the two membrane-based options available to treat sewage for water reuse, tertiary filtration (TF) of the effluent from a conventional activated sludge (CAS) process and an integrated membrane bioreactor (MBR) have been recently explored by Coté *et al* (2004). These options were compared from technical, performance and cost points of view using ZeeWeed ® immersed membranes. The analysis showed that an integrated MBR is less expensive than the CAS-TF option. The total life cycle costs for the treatment of sewage to a quality suitable for irrigation reuse or for feeding reverse osmosis decrease from 0.40\$/m^3 to 0.20\$/m^3 as plant size increases to 75000 m^3/d.

In our study, the TF was studied also as starting point to evaluate the impact of the biomass bulk parameters on the membrane fouling. The main foulants, in fact, are supposed to be in the secondary liquid effluents as much as in the settled sludge. In fact, non settleable compounds like the SMPs are present in similar concentrations inside the secondary clarifier.

2.2.1 Tertiary filtration

According to the scale of the research, the results are presented and discussed in terms of fouling rate magnitude, so to clearly describe the macroscopic fouling phenomena.

The data coming from the TF tests (figure 7.8) were screened and processed according to the methodology before cited and gave the steady fouling rates reported table 7.4.

Figure 7.8 TMPs in the TF tests

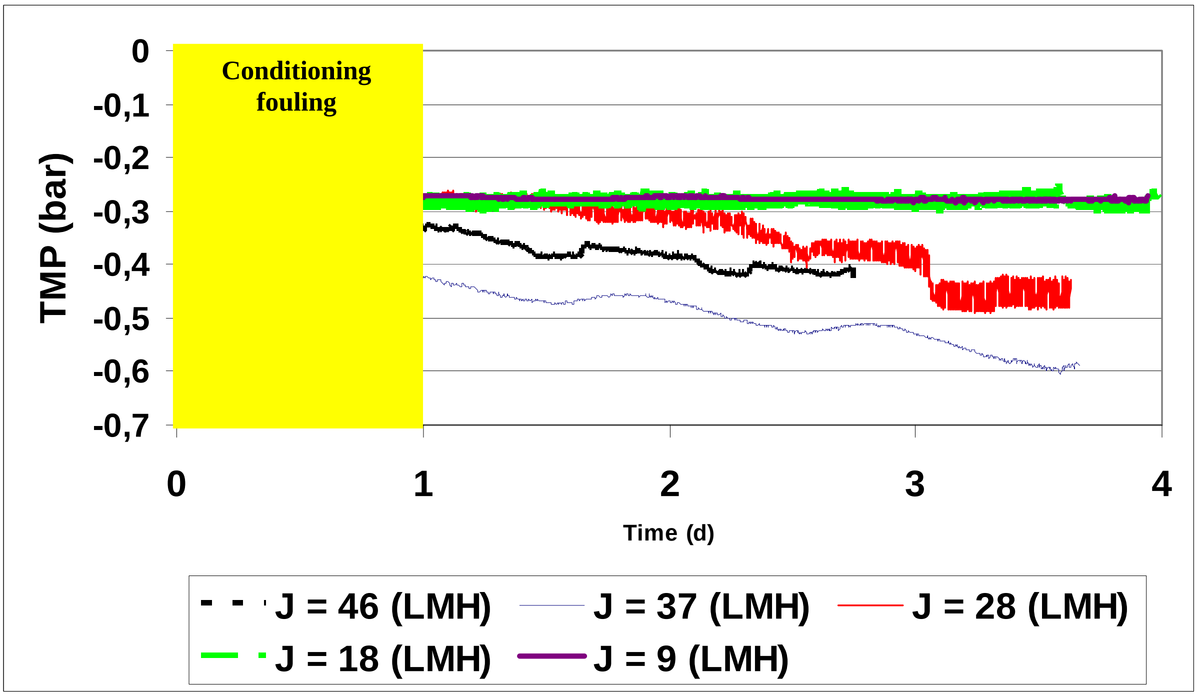


Table 7.4 Results from the TF tests

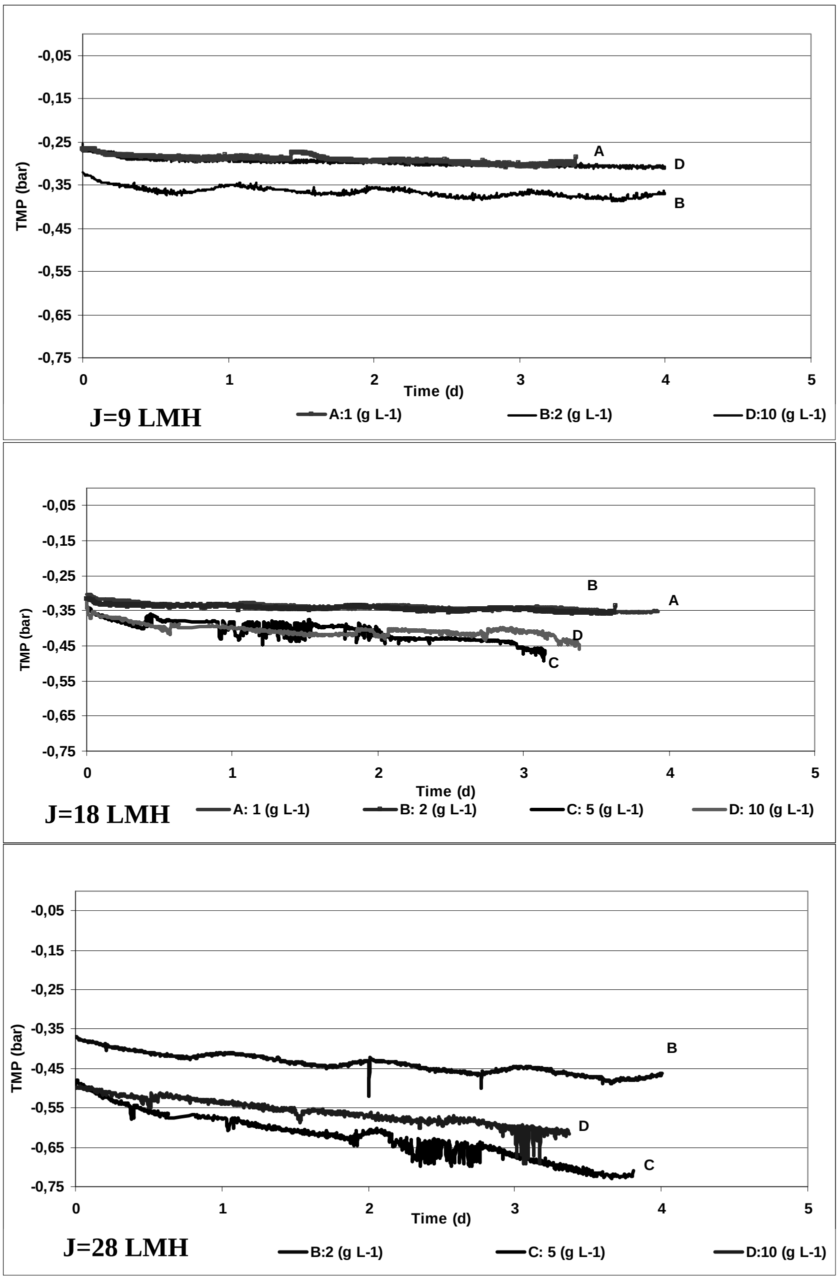
Permeate flux	TMP decline	Magnitude TMP decline	$TSS_{out\ sec}$
(LMH)	(bar day^{-1})	(bar day^{-1})	(mg L^{-1})
9	-0.001	10^{-3}	14
18	-0.001	10^{-3}	17
28	-0.055	10^{-2}	13
37	-0.063	10^{-2}	25
46	-0.028	10^{-2}	30

Considering that the critical flux for this type of membrane was reported to be in the range 17÷30 LMH (Fan *et al.*; 2006), while sub-critical flux, characterized by a low to null fouling rates, was clearly applied in the tests 1 and 2, the tests 3, 4 and 5 seemed to operate under super-critical fluxes. Here, basically, the conditioning fouling lasted the first day, when the TMP decline was less severe, while the steady-state fouling rate was observed from the second day on. As expected, the higher was the permeate flux, the faster the membranes were fouled, but unexpectedly the net flux 46 LMH involved a lower steady TMP decline (0,028 bar day^{-1}).

2.2.2 Mixed liquor filtration

The fluxes between close to the critical conditions are those most interesting to study the behaviour of real systems. Therefore, the results about the filtration of the mixed liquor are following presented and discussed. The TMP trends referred to the tests at fluxes 9; 18; 28 LMH are reported in the figures 7.9 a-b-c, respectively.

Figure 7.9. TMP in the filtration tests of the mixed liquor



As a general and most evident remark, the higher was the permeate flux, the more evident were the impacts of the MLSS content on the fouling rates. However, The three cases of figure 7.9 have peculiarities which deserves more detailed comments.

While no relevant effects of the MLSS contents were found out when the permeate flux was much lower than the critical value (9 LMH, Figure 7.9a), approaching to the critical flux (case of flux 18 LMH, fig. 7.9.b), the membrane was more sensitive to the MLSS concentration. As a result, turning from 2 to 5 gMLSS L^{-1}, the TMP decline worsened from -0.006 to -0.03 bar day^{-1}.

However, no further worsening of the TMP decline was obtained turning from 5 to 10 gMLSS L^{-1} (see curve C and D Figure 7.9b). Therefore, among the MLSS contents typically applied for municipal wastewaters treatment, values close to 5 gMLSS L^{-1} were supposed to mark the border line between weak and severe impact of the biomass concentration. Furthermore, when the permeate flux was supposed to be slightly overcritical (28 LMH, Figure 7.9c), the TMP decline was not remarkably influenced by the MLSS concentration. However, its effect was clearly visible in the initial TMP absolute value, that is the pressure soon after the beginning of the filtration.

The experimental results can be simply summed up plotting the membrane permeability (Js) versus the flux (J), where Js is calculated considering the average TMP over the days 2 to 4 according to the following relation

$$\text{Js (Permeability @ 20°C)} = \text{J (Net flux)}/\text{TMP}_{\text{average-days } 2\div4}$$

Therefore, the mere effect of the MLSS concentration on the sludge filterability is visible from Figure 7.10, where the curves at 2; 5; 10 gMLSS $L^{-1}$are plotted.

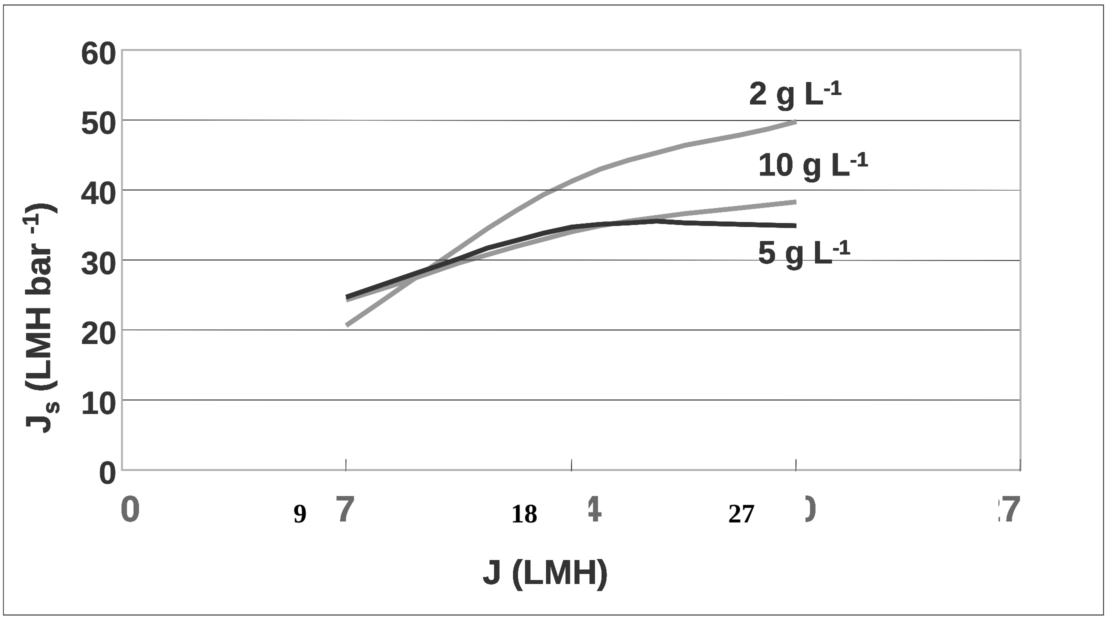


Figure 7.10 Membrane permeability (Js) vs permeate flux (J) at different MLSS contents

Figure 7.10 confirms that the filterability of the sludge is affected by the MLSS content if the concentrations pass from 2 to 5 g L^{-1}, while MLSS from 5 to 10 g L^{-1} has similar impacts on the UF process. In the light of the results just described, the right compromise between biomass concentration and permeate flux must be pursued to achieve the industrial and economical sustainability of the process. As a result, from one side biomass concentration up to 2 gMLSS L^{-1} can increase the membrane permeability, so this strategy can reduce the capital and O&M costs; from the other side, higher biomass concentration can enhance the micropollutants removal (see chapter V). However, in this last case, over-critical conditions are observed and more frequent chemical cleanings of the membranes are required. This fact could not cope with the continuous feeding of the plant and could not allow for the optimization of the membrane life.

As general preliminary consideration, the application of higher fluxes seems to be convenient, but further investigations are needed to better evaluate the membrane life and real impact on the retention capability of the membranes.

2.2.3 Statistical data processing and empirical model

The scale of the experimentations do not allowed for precise and stable boundary conditions in the filtration tests. However, this is likely occurring in real membrane system for municipal wastewater treatment. To make reliable considerations and trying to modelling the impact of biomass bulk parameters on fouling phenomena, the statistical approach was supposed to be the most viable. Following the data statistical analyses are presented and discussed and, finally, a predictive mathematical model is proposed.

Methodology

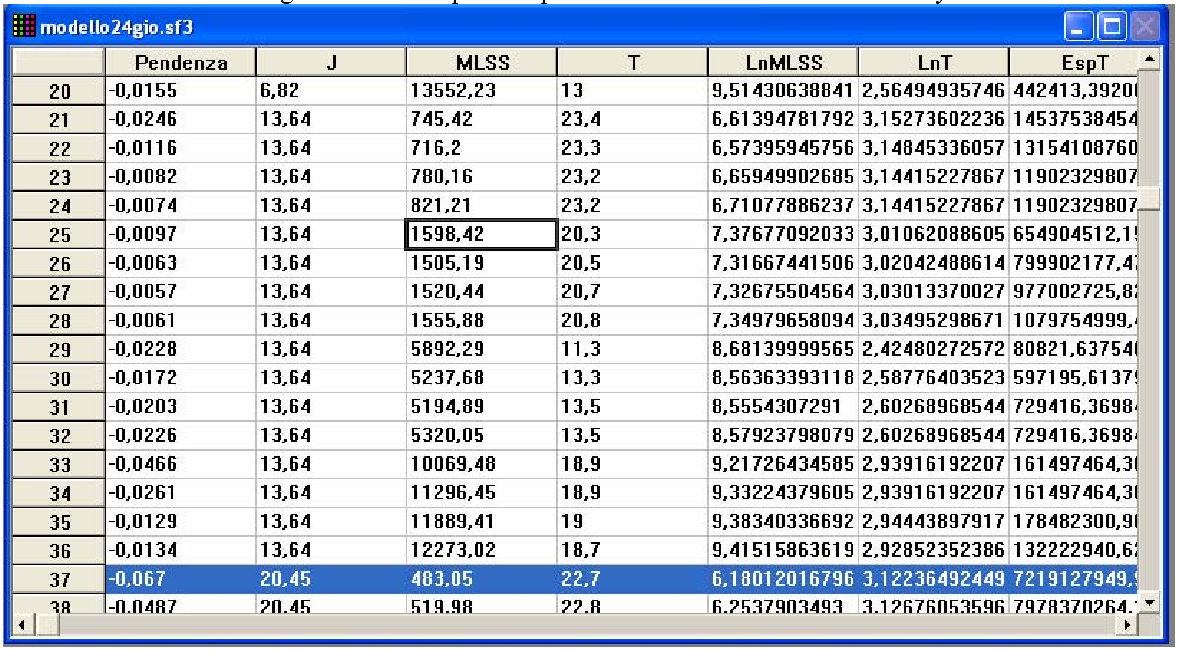
The parameters used to be related with according to the statistical analysis were: (1) TMP; (2) permeate flux (J); (3) MLSS and (4) temperature of the liquor (T).

The software *Statgraphics Plus 3* was used to process the data and find out the empirical expression which best fits the experimental results.

The input matrix was the set of data of TMP decline, MLSS, T and J. according to the linear multiple variable analysis, six steps were covered to reach the final equation:

1. *definition of the dependent and independent variables*. The independent variable are set as absolute values, while the independent can be set both as absolute values and as depending parameters according to different mathematical functions, such as ln, log, exponential of quadratic. Figure 7.11 shows an example of input matrix in the software.

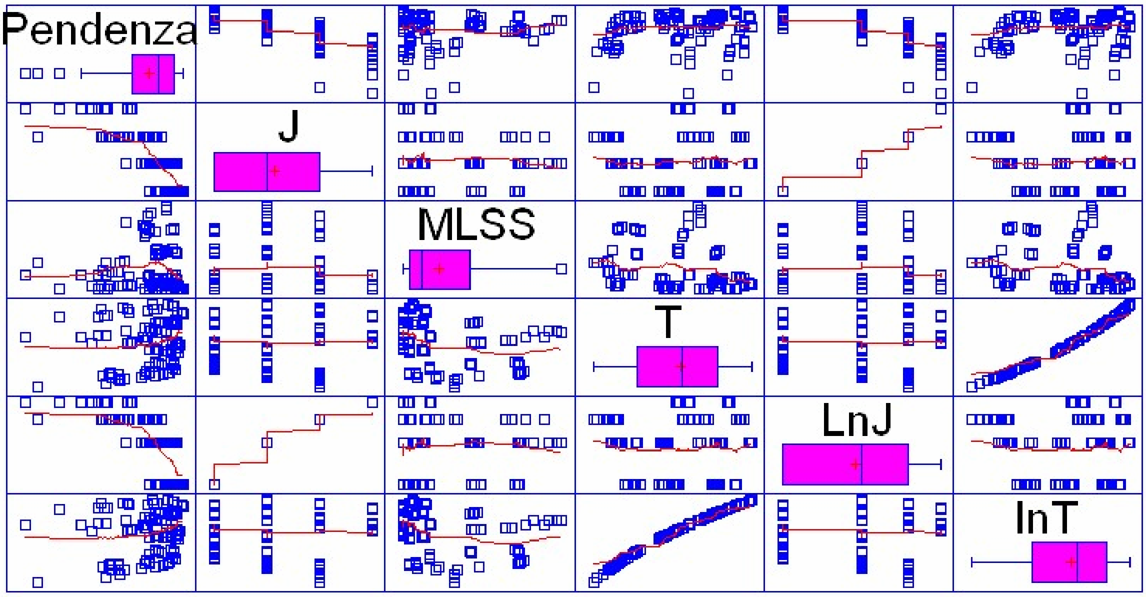
Figure 7.11 Example of input matrix for the multi variable analysis



	Pendenza	J	MLSS	T	LnMLSS	LnT	EspT
20	-0,0155	6,82	13552,23	13	9,51430638841	2,56494935746	442413,3920
21	-0,0246	13,64	745,42	23,4	6,61394781792	3,15273602236	14537538454
22	-0,0116	13,64	716,2	23,3	6,57395945756	3,14845336057	13154108760
23	-0,0082	13,64	780,16	23,2	6,65949902685	3,14415227867	11902329807
24	-0,0074	13,64	821,21	23,2	6,71077886237	3,14415227867	11902329807
25	-0,0097	13,64	1598,42	20,3	7,37677092033	3,01062088605	654904512,1
26	-0,0063	13,64	1505,19	20,5	7,31667441506	3,02042488614	799902177,4
27	-0,0057	13,64	1520,44	20,7	7,32675504564	3,03013370027	977002725,8
28	-0,0061	13,64	1555,88	20,8	7,34979658094	3,03495298671	1079754999,
29	-0,0228	13,64	5892,29	11,3	8,68139999565	2,42480272572	80821,63754
30	-0,0172	13,64	5237,68	13,3	8,56363393118	2,58776403523	597195,6137
31	-0,0203	13,64	5194,89	13,5	8,5554307291	2,60268968544	729416,3698
32	-0,0226	13,64	5320,05	13,5	8,57923798079	2,60268968544	729416,3698
33	-0,0466	13,64	10069,48	18,9	9,21726434585	2,93916192207	161497464,3
34	-0,0261	13,64	11296,45	18,9	9,33224379605	2,93916192207	161497464,3
35	-0,0129	13,64	11889,41	19	9,38340336692	2,94443897917	178482300,9
36	-0,0134	13,64	12273,02	18,7	9,41515863619	2,92852352386	132222940,6
37	-0,067	20,45	483,05	22,7	6,18012016796	3,12236492449	7219127949,
38	-0,0487	20,45	519,98	22,8	6,2537903493	3,12676053596	7978370264.

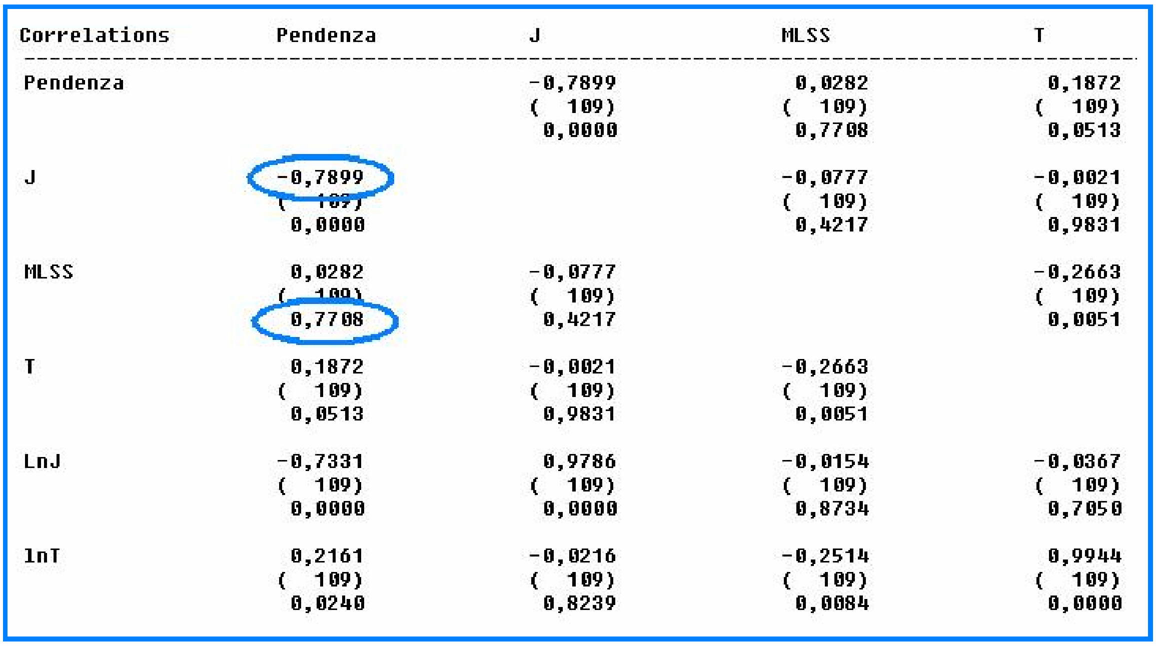
2. using the tool MATRIX PLOT, the software plots the first graphic correlations between the different parameters as shown, for instance, in figure 7.12.

Figure 7.12 Example of first graphic correlations



3. the first phase of the multiple variable analysis is performed according to the *p-value* method. This value is in the range [-1,1] and defines the force of the relations between the parameters. Figure 7.13 shows the window which define the output of the p-value analysis

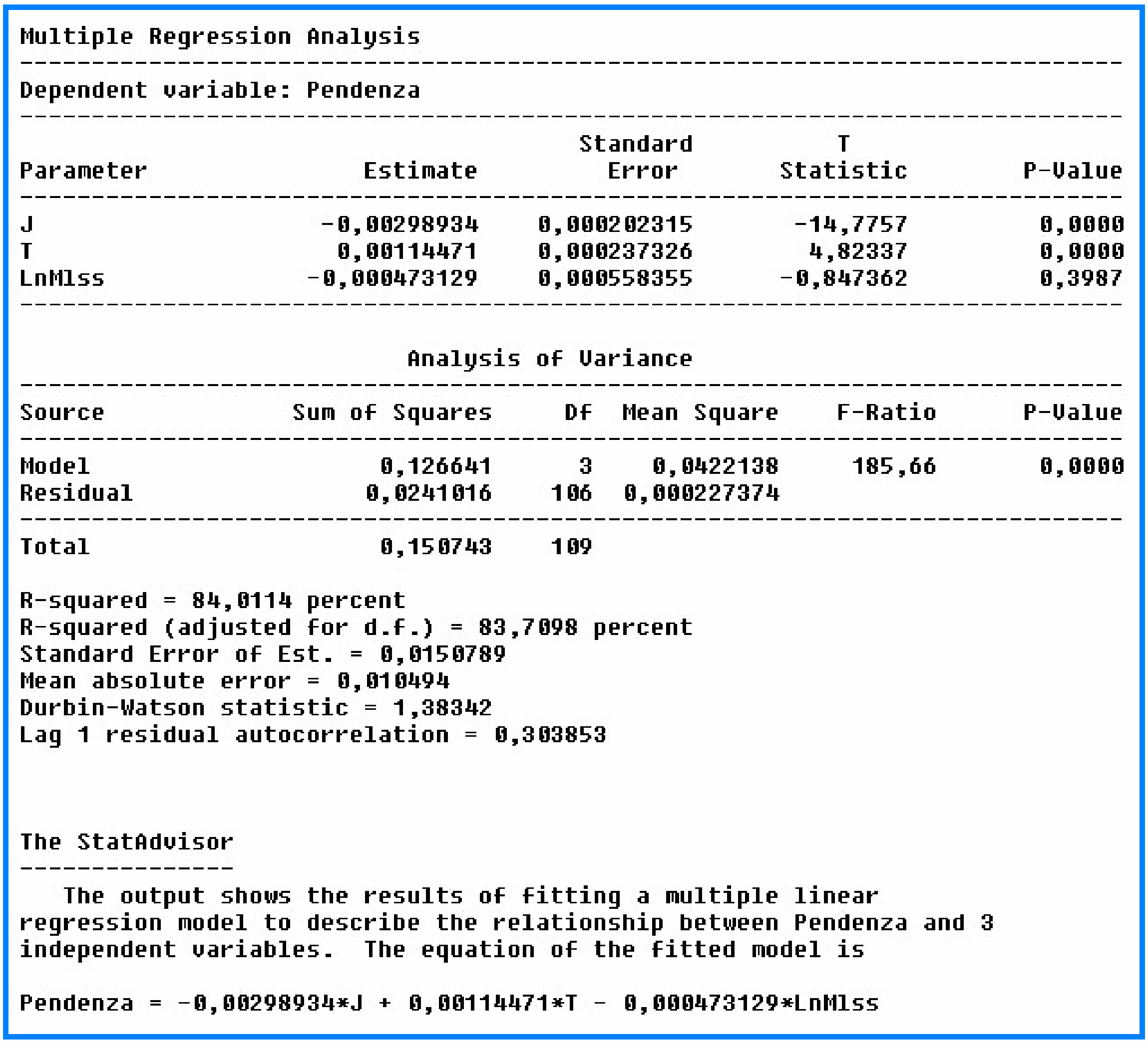
Figure 7.13 Output of the p-value analysis



```
Correlations          Pendenza          J                 MLSS              T
-----------------------------------------------------------------------------------------
Pendenza                                -0,7899            0,0282            0,1872
                                        (   109)           (   109)          (   109)
                                         0,0000            0,7708            0,0513

J                     -0,7899                             -0,0777           -0,0021
                      (   109)                             (   109)          (   109)
                       0,0000                              0,4217            0,9831

MLSS                   0,0282           -0,0777                             -0,2663
                      (   109)          (   109)                             (   109)
                       0,7708            0,4217                              0,0051

T                      0,1872           -0,0021           -0,2663
                      (   109)          (   109)          (   109)
                       0,0513            0,9831            0,0051

LnJ                   -0,7331            0,9786           -0,0154           -0,0367
                      (   109)          (   109)          (   109)          (   109)
                       0,0000            0,0000            0,8734            0,7050

lnT                    0,2161           -0,0216           -0,2514            0,9944
                      (   109)          (   109)          (   109)          (   109)
                       0,0240            0,8239            0,0084            0,0000
```

4. after the multiple variable analysis, a linear multiple regression is carried out obtaining the final expressions and the coefficients (R^2, R^2 adjusted) used to evaluate the statistic reliability of the correlation. Figure 7.14 shows the window referred to the output of the linear multiple regression

Figure 7.14 Output of the linear multiple regression



```
Multiple Regression Analysis
-----------------------------------------------------------------------------
Dependent variable: Pendenza
-----------------------------------------------------------------------------
                                       Standard          T
Parameter               Estimate         Error       Statistic        P-Value
-----------------------------------------------------------------------------
J                     -0,00298934    0,000202315      -14,7757         0,0000
T                      0,00114471    0,000237326       4,82337         0,0000
LnMlss               -0,000473129    0,000558355     -0,847362         0,3987
-----------------------------------------------------------------------------

                           Analysis of Variance
-----------------------------------------------------------------------------
Source             Sum of Squares     Df  Mean Square    F-Ratio      P-Value
-----------------------------------------------------------------------------
Model                    0,126641      3    0,0422138     185,66       0,0000
Residual                0,0241016    106  0,000227374
-----------------------------------------------------------------------------
Total                    0,150743    109

R-squared = 84,0114 percent
R-squared (adjusted for d.f.) = 83,7098 percent
Standard Error of Est. = 0,0150789
Mean absolute error = 0,010494
Durbin-Watson statistic = 1,38342
Lag 1 residual autocorrelation = 0,303853



The StatAdvisor
---------------
   The output shows the results of fitting a multiple linear
regression model to describe the relationship between Pendenza and 3
independent variables.  The equation of the fitted model is

Pendenza = -0,00298934*J + 0,00114471*T - 0,000473129*LnMlss
```

5. After the individuations of different expressions, explorative techniques allow to refine the relations by individuating and neglecting the parameters which involve insignificant variations of the R^2 coefficient. This action can be taken according to two different procedures:

    - *Backward procedure* that starts from the most complicated model and eliminate the useless parameters, simplifying the expression as far as the R^2 coefficient is not worsened too much
    - *Forward procedure* that starts from the most simple model and add the parameters taking into account the values which involves higher improvement of the R^2 coefficient

6. Once defined the most appropriate expression, the residual analysis is the last step to validate the correlation. In case the residuals, that are the standard deviations, meet the evaluation criteria, the expression is considered validated.

In our case a linear multiple variable analysis was done, taking as independent values the *starting absolute TMP* value and the *TMP decline over the filtration time,* according to the following equation:

TMP = $a + b \cdot$ t

Where: a = starting absolute TMP
b = dTMP/dt
t = filtration time

In the equation above, *a* and *b* are supposed to vary depending on *the MLSS contents, the liquor temperatures (T) and the permeate fluxes (J),* which are considered as the independent variables in the statistical analysis.

Global and combined model

Two different approaches were followed and compared:

- *the global model* that considered, as data input, the whole experimental data set and gave one only expression as output;
- *the combined approach* that was based on the concept of the critical flux, which is defined as the flux that, when exceeded, involved a rise of the TMP not corresponding to a rise of permeate flux. Therefore, this type of approach gave a system of equations as output. This took into account the super- and sub- critical conditions as well as the range transient from super- and sub-critical.

Global approach

All the available experimental data were considered as input for the global approach and the resulting equations are reported in table 7.5.

Table 7.5 Results of the statistical analysis – global approach

Factor a	**Factor b**
-0,1334488*ln J -0,0111254*ln MLSS +0,00357041*T	**-0,00298934*J –0,000473129*ln MLSS +0,00114471*T**
R^2=0,9932	R^2= 0,8401 ;
R^2*(adjusted)=0,*9930	R^2*(adjusted)=* 0,8371
Global empirical model	
TMP = -0,1334488*ln J -0,0111254*ln MLSS +0,00357041*T + (-0,00298934*J -0,000473129*ln MLSS +0,00114471*T)*t	

Combined approach

According to the combined approach, the statistical analyses were done with three different input, dividing the filtration tests according to the permeate fluxes:

- $9 \le J$ (LMH) ≤ 18
- $18 \le J$ (LMH) ≤ 28
- $28 \le J$ (LMH) ≤ 37

The results are reported in the table 7.6 a-b-c.

Table 7.6a Results of the statistical analysis – combined approach

Sub-critical fluxes	
Factor a	**Factor b**
-0,115792*ln(J)-0,00773981*ln(MLSS) -0,00224911*ln(T)	-0,00876217*ln(J)-0,00195897*ln(MLSS) +0,00727485*ln(T)
R^2=0,9932	R^2=0,7759
R^2(adjusted)=0,9930	R^2(adjusted)=0,7696
Global sub-critical equation	
TMP= (-0,115792*ln(J) -0,00773981*ln(MLSS) -0,00224911*ln(T)) + ((-0,00876217*ln(J) -0,00195897*ln(MLSS) +0,00727485*ln(T))*t	

Table 7.6b Results of the statistical analysis – combined approach

Transient (sub-super) fluxes	
Factor a	**Factor b**
-0,241259*ln(J)-0,00900319*ln(MLSS)+0,117986*ln(T)	-0,0488664*ln(J)+0,00118612*ln(MLSS) +0,0413028*ln(T)
R^2=0,9982	R^2= 0,8707
R^2(adjusted)=0,9982	R^2(adjusted)=0,8664
Global transient equation	
TMP=(-0,241259*ln(J)-0,00900319*ln(MLSS)+0,117986*ln(T))+((-0,0488664*ln(J)+0,00118612*ln(MLSS)+0,0413028*ln(T))*t	

Table 7.6c Results of the statistical analysis – combined approach

Super-critical fluxes	
Factor a	**Factor b**
-0,143898*ln(J)-0,0215891*ln(MLSS)+0,0575719*ln(T)	-0,0618893*ln(J)+0,00138575*ln(MLSS)+0,0461221*ln(T)
R^2=0,9748	R^2= 0,8823
R^2(adjusted)=0,9733	R^2adjusted= 0,8755
Global super-critical equation	
TMP=(-0,143898*ln(J)-0,0215891*ln(MLSS)+0,0575719*ln(T))+((0,0618893*ln(J)+0,00138575*ln(MLSS)+0,0461221*ln(T))*t	

In the light of the results shown in table 7.6, the final combined mathematical model is:

$TMP = a + b * t$

where
$a = C_1 \ln J + C_2 \ln MLSS + C_3 \ln T$
$b = C_4 \ln J + C_5 \ln MLSS + C_6 \ln T$

Table 7.7 Coefficients of the combined statistical model

a			
	C_1	C_2	C_3
9 < J (LMH) < 18	-0,115792	-0,007740	-0,002249
18 < J (LMH) < 28	-0,241259	-0,009003	0,117986
28 < J (LMH) < 37	-0,143898	-0,021589	0,057572

b			
	C_4	C_5	C_6
9 < J (LMH) < 18	-0,008762	-0,001959	0,007275
18 < J (LMH) < 28	-0,048866	-0,001186	0,041303
28 < J (LMH) < 37	-0,061889	0,001386	0,046122

The validation of the model can be inferred from figure 7.15, where the experimental curves have been plotted together the output of the combined statistical model.

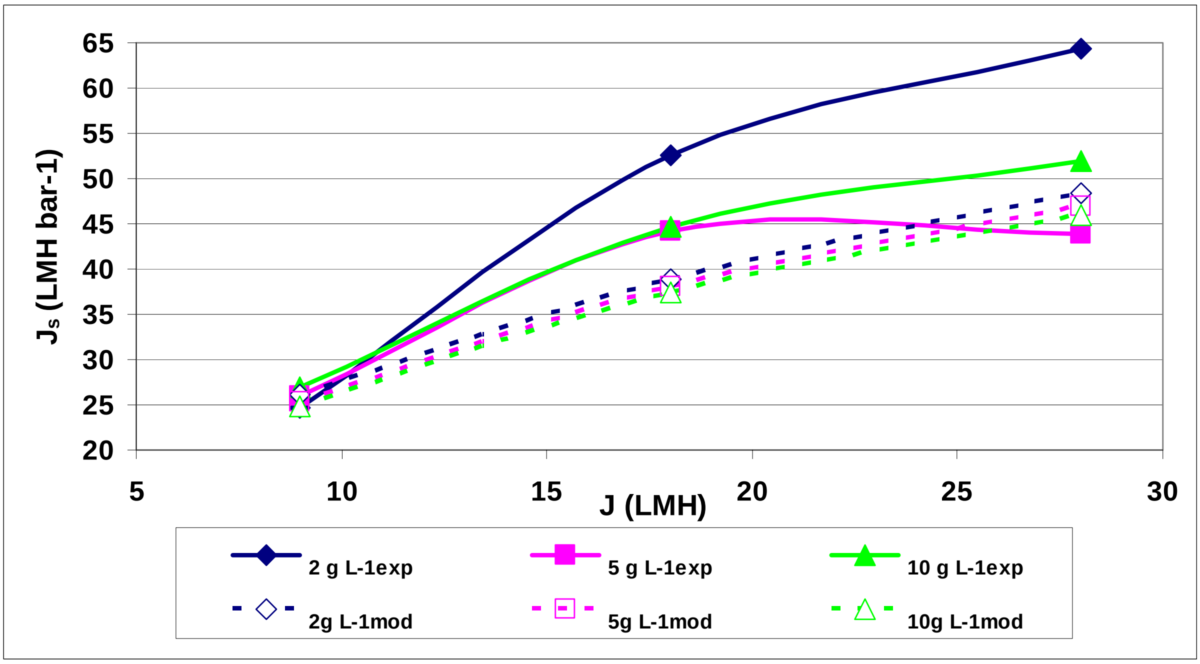


Figure 7.15 Comparison of experimental and output from the statistical combined model

The model can be considered validated operating subcritical fluxes, while remarkable disparities have been found for fluxes close to the critical. As far as the supercritical fluxes, an acceptable validation can be attributed for MLSS 5 and 10 g L^{-1}, while the deviation is not reasonable for the concentration 2 g L^{-1}. A possible explanation for these uncertainties of the model is imputed to the extra cellular polymers which were not taken into account in the statistical analyses. These compounds, in fact, are reported to play a key role in fouling phenomena and their level is important to have a good agreement between theoretical and field values. At the moment the filtration tests are continuing thickening the experimental points (tests at 14 and 23 LMH) in order to improve the reliability of the empirical statistical model in the fluxes commonly operated in full scale MBRs.

3. Conclusions

The chapter VII has dealt with one of the key issues that limit the widespread application of membrane bioreactors: the membrane fouling. In particular, the influence of biomass bulk parameters has been investigated using an industrial module of submerged hollow fiber membranes installed into a full scale wastewater treatment plants. In particular, the impact of the biomass concentration on the sludge filterability has been investigated carrying out a long campaign of filtration tests, over one whole year, at 0-2-5-10 g L^{-1} at 9-18-27-36 LMH. The steady slow fouling rate has been focused performing 4 days long tests.

The results pointed out that the filterability of the sludge is affected by the MLSS content if the concentrations pass from 2 to 5 g L^{-1}, while MLSS from 5 to 10 g L^{-1} has similar impacts on the UF process. In the light of the results just described, the right compromise between biomass concentration and permeate flux must be pursued to achieve the industrial and economical sustainability of the process. As a result, from one side biomass concentration up to 2 gMLSS L^{-1} can increase the membrane permeability, so this strategy can reduce the capital and O&M costs; from the other side, higher biomass concentration can enhance the micropollutants removal (see chapter V). However, in this last case, over-critical conditions are observed and more frequent chemical cleanings of the membranes are required. This fact could not cope with the continuous feeding of the plant and could not allow for the optimization of the membrane life.

As general preliminary consideration, the application of higher fluxes seems to be convenient, but further investigations are needed to better evaluate the membrane life and real impact on the retention capability of the membranes.

After having found the direct remarks about the experimental results, a statistical approach was used to process the data and define a mathematical model which could relate trans membrane pressures, biomass contents, liquor temperatures and permeate fluxes. The statistical approach was supposed the only one appropriated to the scale of the research. However, the comparison of theoretical and experimental results were not fully satisfactory for permeate fluxes in the around of the critical value. Therefore, further tests to thicken the experimental points are needed to validate the model and use it as reliable predictive tool.

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Chapter VIII. Full scale validation of the AC-MBR process

Are membrane bioreactors ready for a widespread application? An exhaustive answer has been given by Daigger *et al*. (2005). In this paper the authors observed that MBR installations now number >1000 in Asia, Europe, and North America. The widespread application demonstrates that MBRs are cost-effective for an increasing number and a growing variety of applications. Three criteria were used to assess whether MBR technology was ready for widespread application in urban water management systems: engineering, equipment, and verification. First, the engineering principles must be understood well enough to allow systems to be successfully implemented in a range of settings. Second, reliable equipment and technological support must be commercially available in sufficient quantities to meet existing and developing demand. Third, enough experience with the technology must exist to enable the verification of successful design and the identification of the factors required for successful design and operation. Basing on those criteria, the authors concluded that MBR technology is ready for widespread application in developed countries, but also that developing countries may have the most to gain from MBR technology because it can address their pressing needs for improved sanitation. The same scenario is emerging from the first chapter of this dissertation, that makes clearness on how the membrane bioreactor can no longer be considered as a novel process and its possible widespread full scale application is actually a topic of major concern. This chapter deals with the full scale validation of the alternate cycles-membrane bioreactor process that is presented as my “happy conclusion” of the doctorate experience. The chapter illustrates and discusses both the plant upgrading and the design strategies and the operation and maintenance of the plant. Finally the real know-how of the AC-MBR process will be clearly depicted.

1. MBRs today: full scale applications and great need of standardizations

Although the precise number of MBR installations worldwide is not known, thousands exist. Most of these installations are small, but they apply to a wide range of wastewaters, including those from municipalities and industry. At the moment the majority of the MBRs for municipal wastewater treatment does not exceed 10000 m^3 d^{-1}, mainly because the investment costs of the MBRs do not scale in the same way of the conventional plants (Churchuose and Wildgoose, 1999). However, even larger MBRs are becoming sustainable thanks to the rapidly declining cost of the membranes. Compared with the early 1990s, the cost of today's micro- and ultra-filtration membrane equipment has dropped by >90%. Several advances contributed to the reduced price, including development of better materials, more cost-effective configuration of membrane facilities, lower production costs as a result of greater economies of scale, more efficient production, and marketplace competition. Likewise, the costs for complete MBR facilities have also been declining. For example, in 2001, the total price of water for unrestricted urban irrigation produced by a 3800-m^3/day (1 million gal/day) MBR was ~\$0.80/m^3 (\$3.05 per 1000 gal) (Grady *et al.*, 1999). Three years later, the price for the same facility declined to ~\$0.48–0.58/m^3 (\$1.80–2.20 per 1000 gal) (DeCarolis *et al.*, 2004). To better understand the present state of the MBR application for municipal wastewater treatment, it is sufficient to think that to date the world's largest MBR (Nordkanal – Germany) (Engelhardt and Linder, 2006) treats the average flowrate of 1880 m^3 h^{-1} and even larger plants are under construction or have been commissioned (Judd, 2006; de Korte, 2006).

In spite of the full scale diffusion of the membrane technology for municipal wastewater treatment, the most appropriate practice to design and operate these systems is not well consolidated. This evidence is also pointed out in a recent book entirely dedicated to MBRs (Judd, 2006), where the author states the difficulty in attempting to generalise with design and operation of these plants. As the technology is installed in larger facilities, the method of implementing MBRs is changing. In the past, MBR manufacturers sold complete treatment units, known as "package plants". The small size of many existing units and the objective to minimize the need for operator attention often led to conservative designs that included very long SRTs of 30–50 days and MLSS concentrations as high as 30 g/L. Many assumed that these conservative operating parameters were necessary for successful MBRs. Subsequent research and experience have demonstrated, however, that designs based on specific process objectives but lower MLSS concentrations (generally <10 g/L) are more cost-effective for larger installations. Researchers evaluated MBR performance with MLSS concentrations ranging from 2 to 20 g/L and found no adverse impacts on effluent quality (Adham and Trussell, 2001). At the same time, MBR design is now entering a new generation. The emphasis is on the economy of scale achieved when membrane manufacturers function solely as equipment suppliers, rather than as providers of complete systems. These concepts are being incorporated into the new, larger facilities being built. Another factor is that MBRs produce high-quality effluents that can be reused. In fact, some versions of the MBR process were specifically developed to allow small-scale reuse of non-potable water. More recently, MBRs that produce effluents with sufficient quality for indirect potable reuse have been demonstrated in larger facilities. In conclusion, although MBRs are being implemented at an increasing rate, technical issues still demand advances. The recent use of lower MLSS concentrations has allowed higher water fluxes, and this factor has improved the cost-effectiveness of MBRs and helped accelerate demand. However, the lifetimes of the membranes operating with higher fluxes will not be established without several years of operating experience. Experience indicates that preliminary treatment can optimize membrane capacity and lifetime. An especially important pretreatment is removing fibrous material, such as hair. Screens with an opening of <2 mm are currently being used. The quantity and noxious nature of the materials removed by such fine screens pose problems for most operations. The proper balance between better screening to prolong membrane life versus the ongoing difficulties that the screenings create has not yet been established. MBRs normally operate with a higher MLSS concentration than do conventional activated sludge processes, and this reduces the size and cost of the bioreactor. However, the trade-offs are increased membrane surface area and costs of oxygen transfer. These trade-offs are understood qualitatively, but more data are needed to quantify them.

As for the Italian scenario, to date the two largest operating MBRs are located in Brescia (1580 m^3 h^{-1}) (Meraviglia et al., 2003) and in Viareggio (250 m^3 h^{-1}) (Battistoni et al., 2006). Both come from the up-grading of existing plants and adopt submerged modules of ultrafiltration (UF) hollow fiber membranes. However, while the first is widely known because has been the largest in the world for few years, the second is more recent and less known, but may be considered very interesting because it is operating the alternate cycles process for the biological treatment.

This chapter describes and discusses in details the design of the upgrading and the first year of operation which was carried out under the direct supervision of my research group.

In particular, after the discussion of the original plant and its following upgrading, the AC-MBR is described in details focusing on the operating strategies that can be taken by the plant managers. Then, the data of one year management are discussed giving, in conclusion, the indication for the suitable operating parameters and the maximal treatment capacity of the system. After the process, the treatment of the subject is focused mainly on the membrane section. In particular, starting from the general consideration that a real municipal treatment system rarely can be considered under nominal steady-state conditions, both ordinary operation and singular short term events have been analyzed in details, so to understand the behaviour of a full scale MBR. Hence, using the parameters routinely determined and measured to monitor the system, both virtually steady and unsteady state operations are described and discussed. As a result it was found out the effect of parameters that: (1) can be directly manipulated by the operators (i.e.: specific aeration demand for membrane scouring, operating net flux, cleaning protocol); (b) depend on the nature of the feed (i.e.: long term seasonal fluctuations and irregular peaks of the inloadings); (c) change consequently to the before mentioned reasons (i.e.: change of sludge sedimentation characteristics). Finally, in order to evaluate the industrial sustainability of the operation and maintenance (O&M) of this type of systems, the real specific costs coming from power requirements and chemicals purchase are calculated.

2. Viareggio WWTP’s history: from 1974 to 2007

The original construction of the Viareggio WWTP is dated back to the 1974. At that time the configurations of the plant was as shown in figure 8.1.

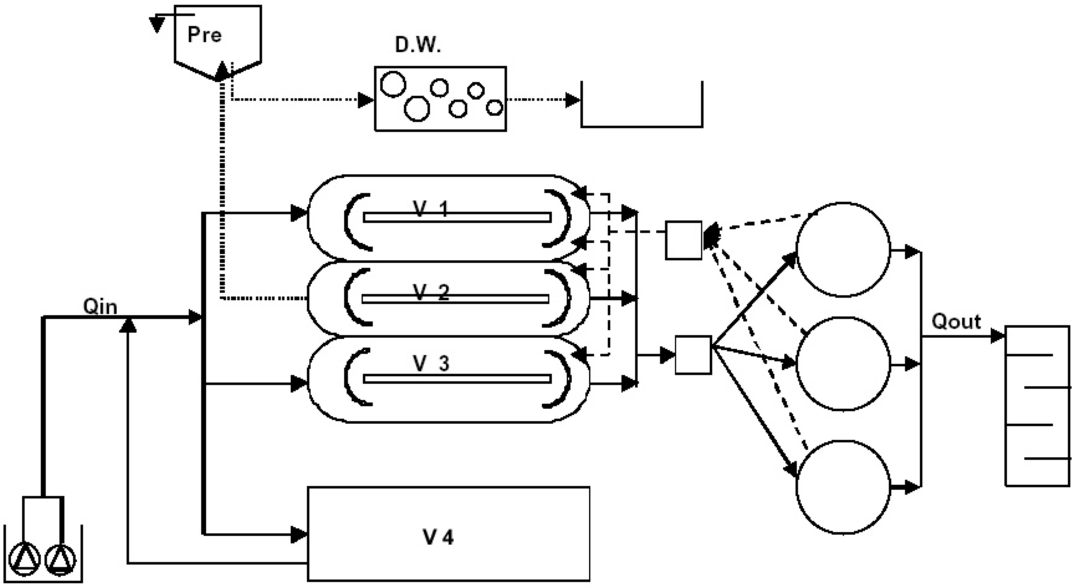
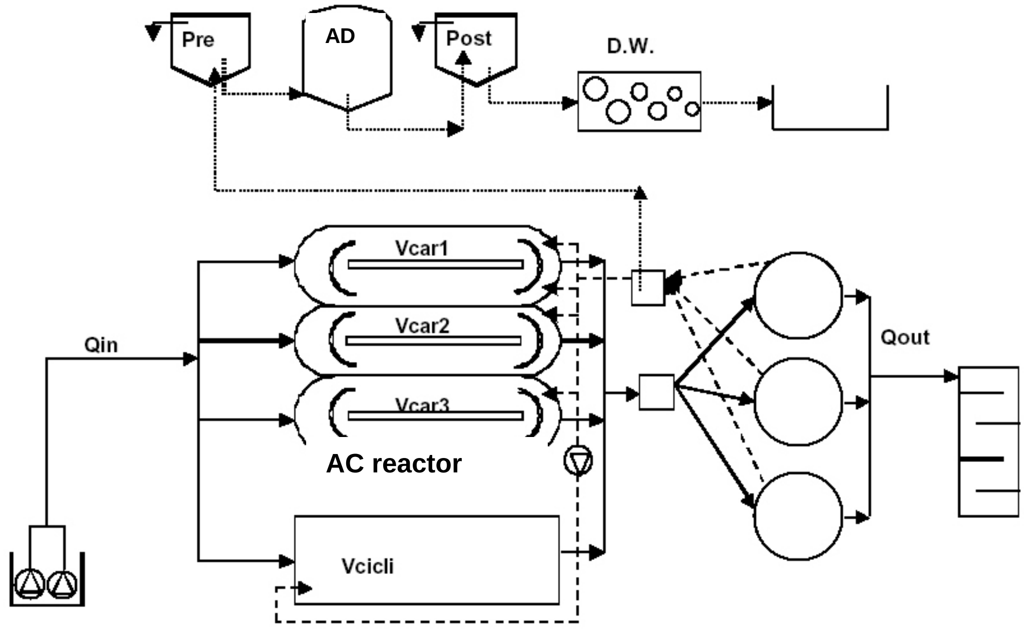


Figure 8.1 Original configuration of the Viareggio WWTP

After the initial pumping station, up to two times the dry weather flows (DWFs) went to the Carousel® biological tanks (V1 and V2). The exceeding flows during wet weather events were diverted to a primary longitudinal clarifier (V4) and pumped back to the biological treatment as soon as the inflow-rate decreased under 2 DWFs. After the biological treatment, the solid/liquid separation was performed in conventional circular secondary clarifiers and the clarified secondary effluent was disinfected with chloride compounds before being discharged in the water body. The waste activated sludge was aerobically stabilized in the tank V2, then statically thickened, dewatered and disposed in the local landfill for municipal solid waste.

The treatment capacity of the original plant amounted to around 70.000 population equivalent (PE), but in the last decade the influent mass loadings were ~80.000 PE (calculated on COD basis considering the unit loading factor of 120 gCOD capita^{-1} day^{-1}) in autumn/winter/spring and ~100.000 PE in summer. Therefore the biological process was severely overloaded in carbon and nitrogen. Moreover, the overflow rate to the final clarifier was as high as 2.2 m^{3} m^{-2} h^{-1}, that frequently led to high solids content in the treated effluent.

So the plant upgrading became a must and was carried out in two steps. In the first step the biological reaction volume was increased realizing the best recovery of the existing structures. In fact: (a) the primary longitudinal settler was converted in alternate cycles tank; (b) the tank V2 (figure 8.1) retrofitted to carry out the biological wastewater treatment together with V1 and V3; (c) two new anaerobic digesters for the stabilisation of the waste activated sludge were constructed, also with the purpose of the future co-digestion with other organic substrates, so to increase the biogas production to burn in a co-generation machine. After the first step of upgrading, the resulting treatment scheme was as shown in figure 8.2



However, the first step upgrading was not sufficient to meet the required quality standard of the effluent. In fact the plant was still critical especially for the small secondary clarification, but also because the activated sludge of AC and Carousel processes were mixed together and did not allow for the adequate natural speciation of the biomasses according to the different biological process performed.

Besides the problems coming from the inadequacy of the plant, the water shortage for the local cultivations, caused from the seepage of the sea-water in the aquifer, suggested the wastewater reuse as the best solution also to satisfy the agricultural requirements. Therefore, the AC reactor was coupled with the ultrafiltration membranes, so to obtain the AC/MBR process. To support the MBR with the suitable headworks, new pre-treatments (fine sieve and degritting in vortex chamber) and an off-line equalization basin were built. Actually, the MBR can treat up to 6000 m^3 d^{-1} and was not designed to cope with 2 dry weather flow, as required from the local wastewater regulation, because it operates at the side of the existing conventional plant which can cope with the excess flowrates in wet periods. Therefore the equalization basin of 450 m^3 was sufficient to equalize the hourly peaks within a day. The overall flow-scheme of the present Viareggio WWTP is reported figure 8.3.

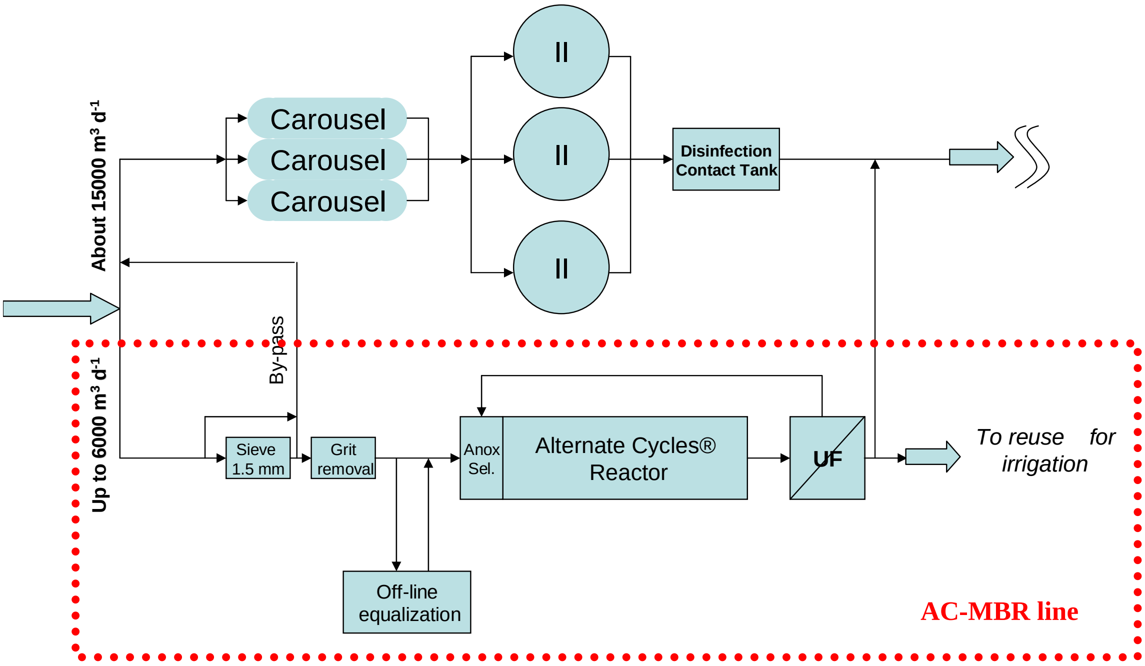
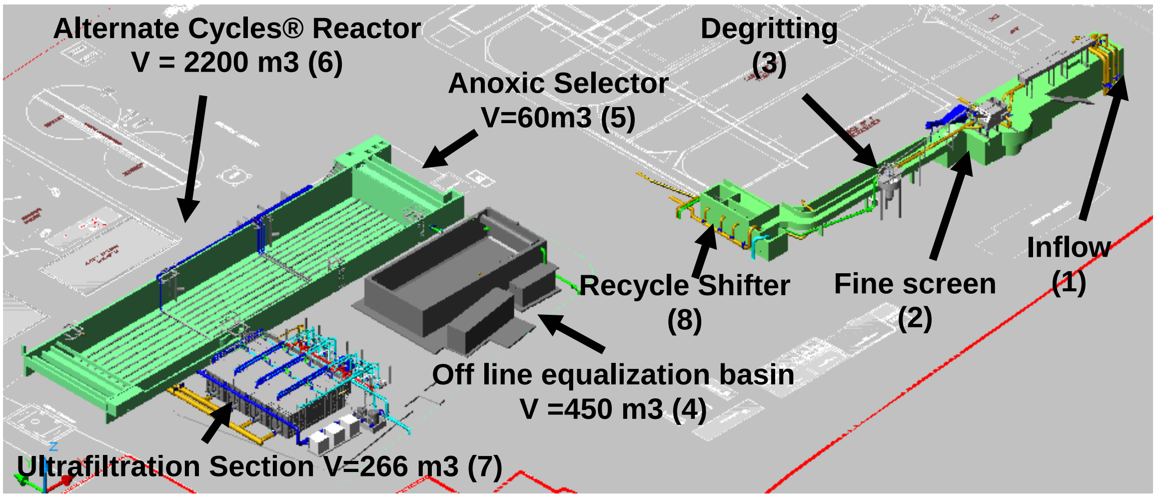


Figure 8.3 Present flowscheme of the Viareggio municipal WWTP

Focusing on the AC-MBR line, the 3D drawing is reported in figure 8.4 where the progressive numbers in brackets indicate the direction of the flows.



3. The design of the operation units for the AC-MBR line

A correct design of a MBR system must couple the needs of biological and filtration processes, taking always into account that the principle of safeguarding the membrane life is also of major importance. Therefore, the design strategies are following explained in details starting from the pre-treatments and equalization, up to the biological filtration processes.

3.1 Flow selection, physical headworks and equalization

First of all, the design of a municipal plant for water reuse must take into account the characteristics of the influent raw wastewater and evaluate whether the reuse standards may be achieved with sustainable treatment costs. In our case study, the wastewater coming from one branch of the sewers system underwent to relevant infiltration of sea-water that increased severely the salinity of the influent. On the other hand, other branches drained catchments areas that did not undergo to this phenomenon. Considering that MBRs are not able to decrease the salinity of the wastewaters to reach the Italian standards for irrigation reuse, it was necessary to provide the plant with an hydraulic system which selected the less saline flows to be sent to the AC-MBR line and contemporary diverted the rest of the incoming wastewater to the existing conventional plant. Therefore, soon after the head pumping station, to feed the MBR a system provided with automatically controlled weirs selected the flows coming from the suitable sewers system (figure 8.5 a-b).

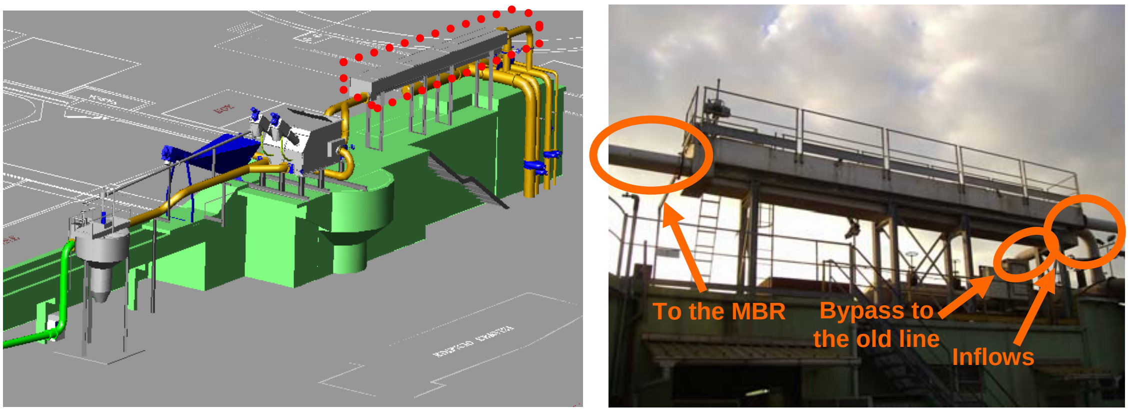


Figure 8.5a-b Drawing (a) and picture (b) of the systems to select the right flow to the MBR

After the flow selection the raw wastewater must be adequately pre-treated before feeding the bioreactor. In fact, adequate pre-treatment including fine screening is essential to the stable, long-term operation of MBRs used to treat municipal wastewater. Trash and fibers into the bioreactor could affect seriously the membrane performances and life. Cotè *et al.* (2006) pointed out that a poor pre-treatment may: (1) build-up of trash, hair and fibrous material on the membrane area, (2) increase the risk of sludge accumulation into the fibers; (3) damage the membranes. In addition, trash in the mixed liquor can plug the coarse bubble aerators used to scour the membranes which have holes ranging in size 5÷10 mm (figure 8.6 a).

As for the suitable pre-treatment of this case study, the membrane manufacturer recommends sieves with geometry punched holes or mesh and openings smaller than 2 mm. In the case study, firstly an inappropriate wedge wire geometry was used, but later a replacement with a fine punched hole sieve with openings of 1.5 mm was done.

After the fine sieve, also the degritting must be very effective. In fact the presence of grit into the membrane tank can plug the aerators for membrane scouring (figure 8.6 a) and also cause phenomena of membrane clogging (figure 8.6 b-c), which can be recovered only by expensive manual operations.

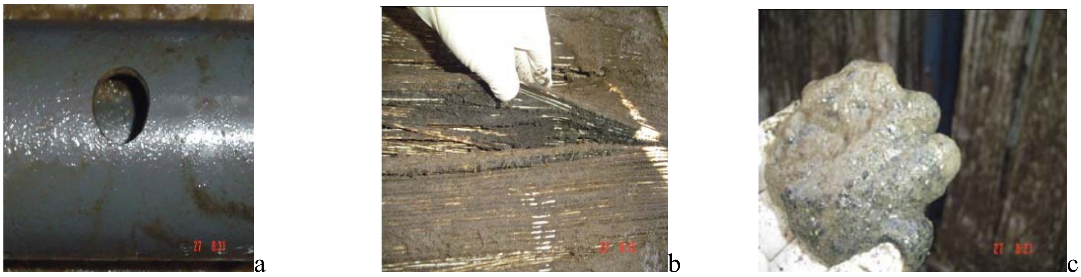


Figure 8.6 a-b-c. Aeration system for membrane scouring (a) and membrane clogging (b, c) caused by excess of grit in the activated sludge

Therefore the degritting was carried out in a vortex chamber adequately oversized.

After the physical headworks, the equalization of the inflow is another key issue to design a membrane system. In fact a municipal MBR, which has to cope with the filtration of all the influent, can be designed according to two strategies: (1) putting a large equalization before the bioreactor which is able to flatten the peaks and assure a constant feeding to the membranes; (2) oversize the membrane area in order to cope with the natural fluctuation of the inflow into municipal wastewater treatment systems, but operating at risky unsteady permeate fluxes. As mentioned before, our particular case study was almost easy because possible high overflows could be diverted to the existing plant. Therefore an off-line equalization basin (V ~ 450 m^3) was sufficient to assure constantly the design flowrate and to make the membrane working at stable permeate fluxes.

3.2 The alternate cycles bioreactor

For the AC bioreactor the previous primary clarifier was retrofitted recovering completely the existing structures. The main actions to prepare the bioreactor were: (1) installation of microbubble systems for the aeration (figure 8.7a) of the activated sludge during the aerobic phases; (2) installations of three submerged mixers (figure 8.7b) to keep suspended the biomass during the anoxic phases; (3) installation of two couples of DO-ORP sensors to control the process in the middle and at the end of the tank; (4) installation of the control device equipped also with a software for the plant wide control. Moreover, a baffle at the beginning of the tank was constructed to obtain a down-up flow anoxic selector. The AC bioreactor operates as two CSTRs in series, just in line with the design guidelines described in the chapter III.

Figure 8.7 a-b. Aerators (a) and mixers (b) in the AC tank

3.3 The ultrafiltration section

3.3.1 The membranes

At the moment the membrane tank is equipped with eight Zenon cassettes (figure 8.9c) disposed in four parallel and separated lines (called “filtration trains”), moreover it has been designed to host four more cassettes in case of future extension of the filtration capacity. The four lines are separated and distinctly fed (figure 8.8 and 8.9a). As far as the design, basically the ultrafiltration (UF) section was engineered according to the usual practice for Zenon hollow fibres membranes, with coarse aeration at the bottom of the modules for the membrane scouring. However, a particular design detail was adopted to face possible severe accumulation of nocardioform foam or floating materials into the tank. In fact, besides the classical vertical pipe that withdraws and send the foams to the waste activated sludge (WAS) treatment line, a particular physical mean, that is similar to that

proposed at pilot scale by Trussell *et al*[14], was adopted. In particular, along the whole tank side opposite to the feeding, a continuous weir was constructed in a way that the possible foam not removed by the vertical pipe falls into the return sludge pipeline (figure 8.8).
The characteristics of the UF membranes are outlined in table 8.1.

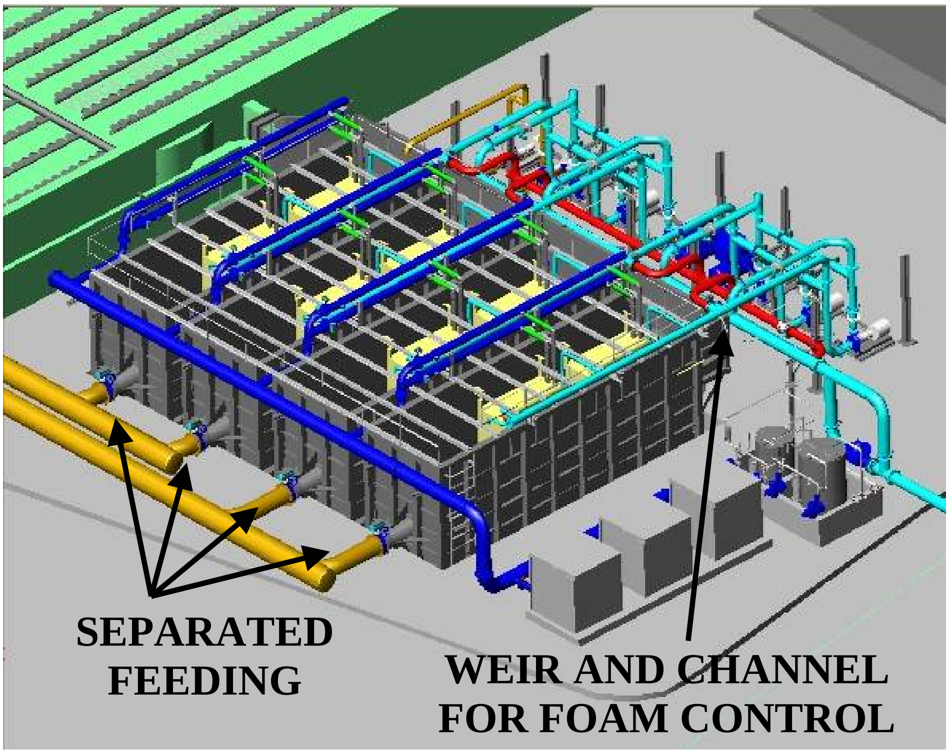


Figure 8.8. 3D drawing of the UF section

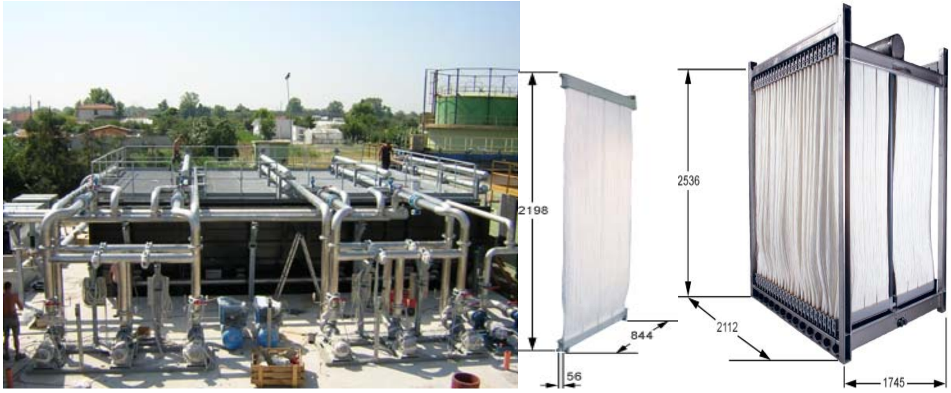


Figure 8.9 a-b-c. Picture of the UF section (a) Zenon membrane module (b) and cassette (c)

Table 8.1. Main features of the UF membranes

Model	ZeeWeed® 500d	Membrane surface per module	31,59 m2
Configuration	Hollow Fibres	Lines	4
Material	Hydrophilic	Cassettes per line	2
Filtration mode	Out-to-in	Membrane surface per line	3032 m2
Nominal pore	0,04 µm	Total membrane surface	12130 m2
		Critical flux	17÷20 LMH

3.3.2 Maintenance cleaning in place, in air and recovery cleaning (mCIP, mCIA, RC)

According to the routinely cleaning protocol, the membranes were cleaned line by line so to avoid the interruption of the filtration. The mCsIP were done usually once a week and consists of a sequence of backwashing with a back flux of 30 LMH and spaced out by prolonged phases of relaxation. The suitable chemical is dosed into the fraction of permeate that is pumped back to the fibres. During the first year of operation, the chemical was a hypochlorite solution at 300 mgCl L^{-1}. This kind of mCIP incurs around 40÷50 minutes. The cleaning in air is not a routinely procedure and includes: (1) the preliminary emptying of the tank; (2) sequence of backwashing, when the hypochlorite solution is left percolating on the fibers. Finally, the recovery cleaning, in the case study done only once after 10 months, includes an overnight soak of hypochlorite solution.

3.3.3 The monitoring protocol

The routinely protocol to monitor the treatment system includes lab analysis, performed according to the *Standard Methods*, and on-line data, processed either in real time or later by the operator. As far as concern the lab analysis, composite samples over 24 hours are taken twice a week from the inflow and outflow in order to determine: pH, Alkalinity, TSS, COD, BOD, TKN, NH_4-N, NO_3-N, NO_2-N, TP, PO_4-P, Chlorides and Sulphides, total pathogens and Escherichia Coli (microbiological analysis only in the outflow). The activated sludge is analyzed to determine MLSS, MLVSS and SVI. Further, the plant is equipped with a number of on-line probes and meters: besides the flowrates over the whole treatment line, the alternate cycles tank adopts on-line probes of DO and ORP, used for the process control automation, and the MLSS are measured both here and into the UF section. Even concerning the UF section, trans-membrane pressure (TMP), flowrates, turbidity, conductivity are measured from each filtration line, while temperature and NOx-N are taken from the whole stream of permeate. Furthermore, also the power requirements are on-line monitored and logged by a gauge of the electrical input located in the main switchboard.

4. One year operation

4.1 The pre-treatments

Operating with MBRs, the trash that is not removed through pre-treatment will build-up in the bioreactor because the membranes represent a complete barrier. From a mass balance point of view, the concentration factor is equal to the ratio of sludge retention time over hydraulic retention time according to the following relation:

$$trash_{ML} = \frac{SRT}{24 \cdot HRT_b} \bullet trash_{in}$$

Where: $trash_{ML}$= trash content in the mixed liquor [mg dry trash/L]
$trash_{in}$ = trash influent to the influent to the bioreactor [mg dry trash/L]
SRT = Solids Retention Time [days]
HRT_b = Hydraulic Retention Time of the bioreactor [hours]

For example, with screenings in MBR feed of 20 dry mg/L, SRT=15 days and HRT = 6hours, the trash content in the mixed liquor would build up to 1200 mg/L. This represents a significant fraction of the mixed liquor that does not contribute to biological treatment, which thereby increases the required reaction volume.

In our case study, after the manifested unfitness of the wedge wire fine sieve (openings 1 mm), this machine was replaced by a punched holes one (hole diameter = 1.5 mm). This new sieve was monitored in details as following described.

The sieving tests were performed with the twofold aim to find out: (a) the removal efficiency of the fine sieve and (b) the trash content into the activated sludge, having also a rough idea on the size of the particles. Hence, two types of tests were carried out: (1) "in-out", on grab samples from the wastewater influent and effluent to the sieve; (2) "trash-test", on samples of activated sludge. The samples of liquor, in the range 180÷200 litres, were passed through sieves having mesh aperture of 2 mm, which were previously dried and weighed. After the sample sieving, the sieves were dried again for 24 hours at 105°C and finally weighed again in order to find out the content of dry trash (see figure 8.10 for the equipment used).

Figure 8.10. Equipment used for the trash tests

Sieving tests were performed according to the method previously described and the results are reported in table 8.2.

Table 8.2. Results of the sieving test: "In-Out" and "Trash Test"

Lab sieve aperture	Test	Dry trash influent	Dry trash effluent	Accumulated into the sludge*	Accumulated into the sludge**
mm	n	dry mg/L	dry mg/L	dry mg_{trash}/L	dry mg_{trash}/L
		Average±st.dev.	Average±st.dev.	Average±st.dev.	Average±st.dev.
2	10	20±15	3±2	75±20	98±65

*Measured by sieving test

**Calculated according to Coté *et al.* (2006) considering SRT 15 days and HRT 11 hours

The retentate by the lab sieve was taken as an index of the trash into the activated sludge. The experimental value (table 8.2, column 5) is in acceptable agreement with the theoretic calculation (table 8.2, column 6) and is considered not significant with respect to the MLSS concentration of 6÷8 g L^{-1} which was operated in the AC tank.

4.2 The biological process

4.2.1 Influent loadings and available reactor volume

Viareggio is a very famous coastal touristy site where the resident population increases drastically in summer times. As a consequence, the influent loadings to the treatment system are subject to relevant seasonal fluctuations. To cope with this peculiarity, the design of the AC-MBR was based on two possible scenarios: with and without tourist, in other words in and out of summer season. However, the unexpected upgrading of the sewers systems, which separated the black from the rainfall runoff wastewaters, caused the increase of the influent pollutant loadings. As a consequence, the treatment plant was overloaded with respect to the design standard (table 8.3).

Table 8.3 Actual influent loadings and plant design data

	Low loading		High loading	
	Real	Planned	Real	Planned
Qin, m^3/d	4080±874	5250	4942±298	6000
LCOD, kgCOD/d	2451±502	2369	3232±512	3254
LNtot, kgN/d	215±24	160	320±33	202
LPtot, kgP/d	22±4	11	30±6	20
LTSS, kgTSS/d	1077±263	548	1204±263	1714
Specific Reaction Volume [1] ($L_{reactor}/PE_{COD}$)	107±0.5	111	82±0.5	81

[1]: Calculated considering unit loading factor of 120 gCOD/PE day

With specific reference to data reported in table 8.3, one can observe the relevant loading fluctuations from spring to summer. In particular, additional loadings of 781 kgCOD/day and 105 kgN/day, corresponding to respective per cent increases of 24 and 33%, were observed in summer times. In terms of validation of process flexibility, these seasonal fluctuations represented a good test for the plant. Furthermore, the before mentioned separation of the sewers systems led the plant to operate with low specific tank volumes (81 $L_{reactor}/PE_{COD}$ during summer) that was considered a good assessment to validate the AC/MBR process.

4.2.2 Operating parameters

The operating strategy in such a municipal MBR is one of the key issues to optimize the removal performances and protect the membrane life, so this topic deserves a detailed discussion. Table 8.4 reports the main operating parameters operated under low and high loadings.

Table 8.4 Main operating parameters for the AC/MBR

Parameter		Low loading	High loading
Liquor Temperature	°C	13,8÷24,3	26,1÷26,5
$MLSS_{ACreactor}$	$g\ L^{-1}$	5.9÷8.3	5.6÷6.0
$MLSS_{UFsection}$	$g\ L^{-1}$	10÷11	7÷8
Solids Retention Time	d	14÷21	13÷15
Hydraulic Retention Time in the AC tank	h	10.6÷13	10.8÷11
Total Recycles of Activated Sludge (Q_{RAS}/Q_{in})		~2	~2

The management of the MBRs is free from problems regarding the sedimentation properties of the activated sludge. That is why these systems owe their success also to the possibility of operating at very high MLSS content (up to 30 g L^{-1}) and SRTs. However, as anticipated before in this chapter, this strategy can have a lot of drawbacks in municipal systems that address towards different operating choices.

High solid content in the mixed liquor was found to be the main parameter that involves the decrease of the oxygen transfer in membrane bioreactors (Krampe and Krauth, 2003). In particular, both the k_La_{20} and the α-factor decreased at higher MLSS, involving worsening of the aeration efficiency and rise of the operating costs (Germain *et al.*, 2007). Moreover, MLSS is often considered at first sight as the main foulant parameter and, although the findings about this argument are sometimes controversial (Le-Clech *et al.*, 2006), high concentrations are often reported to reduce the expectations for membrane life. To sum up, high MLSS seem to increase both operating costs and the expenses for membrane replacements. On the other hand, some studies reported the possible decrease of the excess sludge production thanks to the reduced biomass yields, that could lead to decrease of costs for sludge final disposal (Yoon *et al.*, 2004). However, these results are very controversial and there is a lack of data coming from real applications which can reliably confirm this effect on the biomass metabolism. Furthermore, in municipal plants provided with anaerobic digesters, the waste activated sludge is used to produce biogas and, often, to be co-digested with other organic substrates. Therefore, in these systems the excess sludge is not of major concern for the overall economic balance.

In the light of the before outlined preamble, the operating choices in this case study met the present trend of the full scale MBRs to operate MLSS under 10 g L^{-1} (Van der Roest et al, 2002) and SRT based on the biological process (Daigger *et al.*, 2004). In particular the achievement of complete nitrification of ammonia addressed the operating choices (Battistoni *et al.*, 2006) summarized above (table 8.3). The methodology to decide the operating MLSS was simple but effective. It considered that the internal carbon source was sufficient for the complete nitrates reduction, so the process driver was the ammonia oxidation. Hence, periodic respirometry tests to determine the ammonia utilization rate (AUR) were performed to find the real nitrification rate of the biomass at the process temperature. Then, the nitrification potentialities of the plant were calculated at the different biomass concentrations, taking into account the maximal aerobic time lengths calculated from the simplified mathematical model (described in chapter III). After these tests, the MLSS was operated as low as necessary for the complete ammonia nitrification. This operating strategy makes clear the reason why in high loading periods a lower biomass concentration was held in the bioreactor (see table 8.4).

4.2.3 Validation of the AC-MBR process: removal performances and reliability of the control algorithm

The evaluation of the process is done with the same methodology adopted for the demonstration plant (chapter IV). Therefore both the removal performances and the suitability of the control algorithm are under evaluation. The key objectives are not only the validation of the AC-MBR process as a feasible solution in municipal treatment systems for wastewater reclamation and reuse, but also to validate a suitable operating strategy that can achieve the optimization of wastewater purification and O&M costs.

The most objective information come from the influent and effluent concentrations which are given in table 8.5.

Table 8.5. The influent/effluent characteristics and the gross removal percentages

	High loadings			Low loadings		
	IN Average (±st.dev./aver)	OUT Average (±st.dev./aver)	Removal (%)	IN Average (±st.dev./aver)	OUT Average (±st.dev./aver)	Removal (%)
COD (mg L-1)	657 (±16%)	31,7 (±26%)	95	604(±16%)	37,1 (±47%)	94
NH4-N (mg L-1)	39 (±9%)	1,6 (±50%)	96	34 (±20%)	0,9 (±56%)	97
TN (mg L-1)	64(±11%)	6,1 (±23%)	90	47(±9%)	4,5 (±31%)	90
TP (mg L-1)	7.2(±10%)	2,5 (±32%)	65	5 (±21%)	1,8 (±44%)	64
TSS (mg L-1)	264(±29%)	<1	>99	255(±19%)	<1	>99
COD/TN	12.4 (±23%)	-		13.1(±20%)	-	

Before the analysis of the performances concerning the single parameters, the meeting with the italian standard for water reuse is emphasized. This was true except for the phosphorus that, even being biologically removed for more than 60%, needed further chemical/physical precipitation. However, particular attention must be paid to the nitrogen contents in the permeate which was always under 7 mg L^{-1} notwithstanding the influent abundances in the range 47÷64 mgN L^{-1}.

As far as the single parameters, table 8.5 allow for the following remarks:

TSS. The perfect retention capability of the ultrafiltration membranes allowed always effluent TSS concentrations under the detection limit.

COD. The biodegradability of the influent COD was periodically determined: the ratio readily biodegradable COD (rbCOD) over COD was in the range 0.2 and 0.3, that is a proof of the mainly domestic origin of the discharges. This aspect provided suitable substrates to enhance both the denitrifying heterotrophic and the PAO and/or DPAO growth and activity. Moreover, the MBRs are reported to enhance also the biodegradation of high molecular weight compounds (Cicek et al, 1998) thanks to the perfect retention capability of the UF membrane. As a result the molecules larger than the membrane pores remain in the bioreactor along an SRT, that is much higher than the HRT. As for the total process performances, around 95% of the influent COD was removed both under higher and lower loadings.

P. Regarding the phosphorus behaviour, experimenting the AC applied in full scale plants with secondary settlers, Battistoni *et al* (2003) showed that also the phosphorus biological removal can be performed if the influent is provided with the suitable amount of rbCOD, either internal or external. The same findings were remarked by Fatone *et al.* (2006) for the AC/MBR process, where the aerobic environment of the last membrane tank can even more enhance the biological phosphorus removal. Moreover the low recycles increased both the effective hydraulic retention time (Vtank/(Qpermeate+Qrecycled)) and the MLSS concentration, so to involve more effective biochemical aerated reactions in the ultrafiltration tank. This study showed total phosphorus removals higher than 60% all over the one year operation, respectively, without any chemical/physical precipitation. Moreover, mass balances pointed out that phosphorus concentrations in the activated sludge were 32 gP/kgVSS and 28 gP/kgVSS, respectively. These values allow to reasonably suppose the biological phosphorus uptake.

N. The before mentioned high degrees of biodegradability of the influent COD coupled with the C/N ratio higher than 10 let expect fast and complete nitrates denitrification. On the other side, the influent TKN was more worrying because increased the nitrogen loading rates (NLRs) up to 0,13÷0,15 kgN m^{-3} d^{-1}. However, complete nitrification was expected as consequence of the before mentioned operating strategy. Moreover the climate of the area was never so much cold to involve drastic inhibition of the biological nitrogen removal.

The nitrogen removal efficiencies are evaluated according to the protocols described in chapter III. Even the efficiencies are the same cited before in this thesis: the nitrifying efficiency referred to the total incoming nitrogen (En) and to the amount of the only form of nitrogen that can be nitrified (Enn); the nitrogen removal efficiency referred either to the total incoming nitrogen (Ed) or to the nitrified nitrogen, NOx-N (Edd). In all the used equations the nitrogen discharged with the waste activated sludge stream was experimentally determined and opportunely considered in the mass balances (table 8.6).

Table 8.6 The nitrogen removal efficiencies

	Ed%	En%	Edd%	Enn%
Low loadings	77	84	85	94
High loadings	77	83	87	93

The ammonia nitrification efficiencies (En, Enn) were always high and no significant decrease was observed lowering the SRT from 20.7 to 14.1 days when T increased from 18.7 to 24.3 Celsius degrees. The high denitrification efficiencies (Ed, Edd) allowed very satisfactory TN removals as often are reported to occur. These performances were due to, besides the well balanced influent COD/TN and the high rbCOD/COD ratios, the peculiarity of the AC of not needing any recycle to send back the nitrates in the anoxic tank. This involves the capability of denitrifying all the nitrates.

Once validated the process on the basis of its removal performances, attention is shifted to the reliability of the process control strategy. The first analysis concerned the flexibility of the process with regards to the long term seasonal fluctuations of the inloadings.

About 5000 cycles were analyzed according to the same methodology described in the chapters III and IV. Table 8.7 reports the results of this analysis referred to the high and low loadings periods.

Table 8.7 The cycles performed

	NLR	COD/TN	Cycles/Day	Aerobic Phase		Anoxic Phase	
	kgTN/m^3*day		n	d/d	Minutes	d/d	Minutes
Low loadings	0.10	13.1	14	0,59	61	0,41	42
High loadings	0.13	12.4	12	0,78	97	0,22	28

The cycles time lengths are mainly related to the NLR and the influent C/N ratio, that obviously influenced the aerobic and the anoxic phases, respectively. In this study the high C/N ratios involved always fast and quite complete nitrates denitrification, while the NLRs really drove the process. This effect resulted in longer aerobic phases (from 59 to 78 %) in the summer period and, consequently, in the lower number of cycles per day (from 14 to 12).

As for the detection of the bending points or the intervention of the setpoints branches of the control algorithm, table 8.7 shows the *end-reasons* which caused the switching from aerobic to anoxic phase and vice versa. Here the optimal condition, that is the detection of the bending point, is called α, while ß and γ represents respectively the cases when the time and the DO-ORP absolute setpoints were exceeded.

Table 8.7 End-reason determining the switching between the phases

	Aerobic phase			Anoxic phase		
	α	ß	γ	α	ß	γ
	%	%	%	%	%	%
Low loading	73	19	8	75	7	18
High loading	70	20	10	78	1	21

The nitrogen removal performances are consistent with the high percentages of detected bending points both for the aerobic and anoxic phases. Better performances of the control device were found for the anoxic phases. As a matter of fact, the end of the anoxic phase was optimal for almost all the cycles. In fact when the nitrate knees were not detected, the aeration was switched on for the minimum value of ORP (“γ” cases in table 8.7) that indicates complete and very fast denitrification up to anaerobic conditions. On the other hand, the ammonia breakpoints were identified for around 70%, while over-aeration occurred for around 10% (“γ” cases in table 8.7), usually during night times, and the time setpoints control was used for around 20% (“ß” cases in table 8.7), usually late in the mornings.

4.2.3 The maximal treatment capacity of the AC-MBR system

The analysis of the real aerobic and anoxic phases over one year operation allowed to find out the NLRs that caused the loss of flexibility for the AC process. In particular this limiting conditions are represented by a plateau in the curve of the phases time lengths vs the NLRs (figure 8.11).

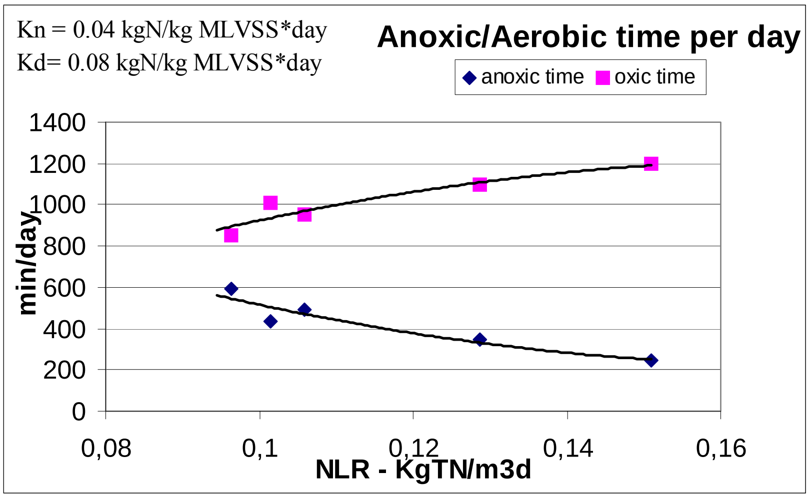


Figure 8.11 Aerobic/anoxic time lengths over one year operation of the AC-MBR plant

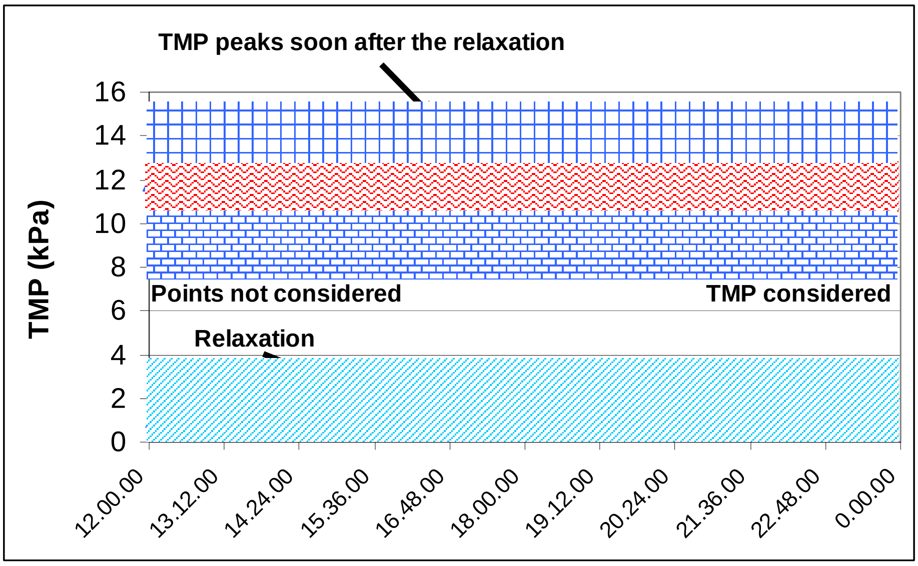
Figure 8.11 shows that, under the nitrification and denitrification rates reported in the top-left corner, the system is reaching a plateau for NLRs in the range 0,15÷0,16 kgN m^{-3} d^{-1}. This changing from dynamic to static process is interpreted as the limit of the process and the before cited NLRs as the maximal treatment capacity. Considering that the existing italian conventional WWTPs are usually operating in the range 0,08÷0,10 kgN m^{-3} d^{-1}, it can be understood how the AC-MBR process can increase the treatment capacity of an activated sludge system.

4.3 The membrane ultrafiltration

4.3.1 Methodology: trans membrane pressure and flux data selection

Before the discussion of the membrane performances, a brief punctuation on the methodology used to process the data is necessary.

Since the filtration cycle was 600 seconds filtration and 60 relaxation, the TMP and the flux data showed low and high random peaks which can affect the calculation of the real membrane permeability. In order to standardize the data processing, a previous data-screening was carried out selecting the periods when the imposed net flux was kept for more than 180 seconds (see figure 8.12 as example of screening for the TMP).



4.3.2 Causes of membrane fouling

Recent literature reviews on membrane fouling in MBRs have been carried out by Chang *et al.*(2002) and, more recently, by Evenblij (2006) and Judd (2006). Dealing with the fouling mechanisms, major role has been widely attributed to Extracellular Polymeric Substances (EPS). More generally, the main factors that influence the filtration performance may be divided into three facets: (1) pre-treatments; (2) nature of feed to the membranes and activated sludge process; (3) membrane separation process itself, in other words the hydrodynamic environment imposed to the filtration modules. Further, each of the aforementioned processes depends on boundary conditions and parameters that can be manipulated.

Nature of the feed

With concern to the membrane fouling, it must be taken into account that the nature of the feed and the organic loading rate can be major factors that influence the amount and/or the bio-production of foulants. In this case study the wastewater was almost domestic, with seasonal fluctuating characteristics according to the summer tourism (table 8.8, columns 1-2). Furthermore, a short period (20÷30 days) discharge of landfill leachate into the municipal sewers was allowed by the local environmental authority (table 8.8, column 3), changing the nature of the feed. Therefore, the MBR had to face severe peaks loadings as demonstrated from the increased standard deviations (table 8.8, column 3).

Table 8.8 Influent concentrations including the singular event

	Municipal WW – High Loading	Municipal WW – Low Loading	Unsteady nature of the feed*
	Average (±st.dev./average)	Average (±st.dev./average)	Average (±st.dev./average)
COD (mg L-1)	657 (±16%)	604(±16%)	417(±31%)
NH4-N (mg L-1)	39 (±9%)	34 (±20%)	41 (±42%)
TN (mg L-1)	64(±11%)	47(±9%)	54(±40%)
TP (mg L-1)	7.2(±10%)	5 (±21%)	4.7(±30%)
TSS (mg L-1)	264(±29%)	255(±19%)	193(±56%)
COD/TN	12.4 (±23%)	13.1(±20%)	8.3(±27%)

*Irregular incomings of landfill leachate which involved random peaks of inloading

Hydrodynamic environment

Basically the hydrodynamic environment imposed to the membranes in a submerged system can be changed manipulating four main parameters: (1) the operating flux; (2) the filtration cycle, (3) the scouring aeration; (4) the flowrate of recycled activated sludge (RAS).

First of all it is important to report the gross permeate fluxes adopted by the membrane manufacturer to calculate the necessary membrane area (table 8.9).

Table 8.9 Gross fluxes used to design the membrane section

	Low loadings		High loadings	
Operating Condition	Average Flux	Peak Flux	Average Flux	Peak Flux
	LMH	LMH	LMH	LMH
4 lines operating (routinery)	17,7	23,1	20,6	26,4
3 lines operating and 1 under cleaning	23,6	30,8	27,5	35,2

The start-up phase lasted about 50 days and began with a net flux of 21.4 LMH, that was increased up to 26.0 LMH by step-increases of 2-1,3-1,3 LMH 3-days long. The operating net flux is close to the critical flux which is reported to be in the range 17÷30 LMH at 20°C (Fan *et al.*, 2006) for the same membrane material, but different modules (ZeeWeed 500c).

As far as the aeration of the system, a couple of two-velocities blowers (reserve excluded) is used for the membrane scouring, while the biological process has two further and automatically controlled blowers. Therefore, the membrane system is engineered with the flexibility to work with 4 possible coarse bubble air flowrates (see table 8.10 for the specific air demand for unit of membrane area -SAD_m- and for unit of permeate -SAD_p-).

Considering the summary of data from pilot MBRs reported by Judd [2], the values of table 8.10 are: (1) lower than the same commercial MBR technology (SAD_m=0,25÷0,54; SAD_p=15÷30); (2) much lower than the flat sheet membranes (SAD_m=0,6÷1,5; SAD_p=24÷90). This involves a decrease of power requirements which is illustrated later. With further concern to hydrodynamic environment and energy savings, attention must be paid also to the RAS flowrate. In fact, while MBRs are usually associated to high number of RAS, both from the membrane tank and between the aerobic/anoxic/anaerobic sections, the AC process is used to operate a low number of recycles (total recycle ratio around 1,5÷2). In this case study the total recycle ratio was about 2 and did not show drawbacks on the membrane permeability and/or its decline.

Table 8.10. Specific air demand per unit of membrane area (SAD_m) and permeate (SAD_p)

Operating modality	Aeration time	SAD_m	SAD_p
	h/h	$Nm^3\ m^{-2}\ h^{-1}$	$Nm^3\ m^{-3}$
A	0,5	0,06	2,3÷2,7
B	0,5	0,12	4,5÷5,5
C	0,5	0,19	5,0÷6,1
D	0,5	0,26	10,1÷12,2

4.3.3 Membrane performances

History of membrane permeability

Once defined the magnitude of the factors that influence the membrane permeability and its possible decline, the variety of events over the first year of operation allows for important considerations on the full scale membrane system. According to the parameters of table 8.11, the whole operation can be divided in four steady state periods and two start-up phases. Furthermore, besides the recovery cleaning (RC) carried out after 8 months operation, also two short term singular events have been observed and are discussed in details later.

Table 8.11 leads to the following comments: (1) giving a cleaning protocol of 1 mCIP per week, the increase of SAD_m is not cost effective, in fact it did not give significant gain of permeability that can balance the increased power requirements; (2) MLSS concentration has a minor effect on membrane permeability, in fact a MLSS decrease from 11 to 8 involved a gain of only 7 LMH/bar; (3) the long period fluctuation of F:M ratio, which has been proposed as fundamental parameter influencing the soluble microbial products (SMP) content and characteristics (Trussell et al., 2006; Kimura et al., 2005; Ng et al., 2005; Barker and Stuckey, 1999; Liu and Fang, 2002), did not show significant effects on membrane permeability within the range studied. Therefore, the membranes did not suffer from the seasonal fluctuations of the influent loadings.

Table 8.11 One year membrane history

	Days	**Net flux**	**Permeability @ 20°C***	**SAD$_m$**	**F:M****	**MLSS$_{UF}$**
		LMH	**LMH/bar**	**m^3/m^2 h**	**gCOD/gVSS d**	**g/L**
1st Start-Up	51	21.4-23.4-24.7-26	170 to 227	0,12		6 to 11
Run1	20	26	227	0,12	**0,27**	11
Run2	50	26	234	0,12	**0,32**	8
Singular event A	**18**	***No chemical cleaning***				
Run3	99	26	243	0,19	**0,25**	8
Maintenance	**45**	***Extraordinary maintenance of the AC tank and RC of the membranes***				
2nd Start-Up	10	26	186 to 190	0,19		4 to 8
Singular event B	**20÷30**	***Irregular peaks inloading***				
Run4	37	26	155	0,19	**0,25**	8

*adjusted according to Mulder (2000) **to the AC tank

Membrane permeability decline and short period events

The effects of the singular events over the first year operation are considered in terms of fouling rates. Given the same operating net flux (26 LMH), the TMPs plotted in figure 4 show the behaviour of the system under (1) routinely operation (table 8.11; run 2), (2) no maintenance cleaning (table 8.11, singular event A) (3) irregular peaks inloading (table 8.11, singular event B). Figure 8.13 shows that coupling a net flux of 26 LMH and 1 mCIP per week can be considered a sustainable O&M practice, because the TMP is almost constant. As for the singular events, the case "A" caused a steady state TMP decline around 0,30 kPa day^{-1}. However, good permeability was re-established (run 3) in about 20 days, using only hypochlorite solution firstly in a membrane cleaning in air (mCIA) and later in the routinely cleaning protocol. More severe fouling was observed when irregular discharge of municipal landfill leachate caused random peaks of inloading. Here, the steady state TMP decline was about 0,74 kPa day^{-1}. Moreover, it should be observed that the severe unsteady operation coupled with the possible incoming of recalcitrant compounds, caused a steady fouling rate over 15-20 days that finally led to an irreversible loss of permeability, not recovered by the routinely cleaning protocol (run 3 vs run 4). This gap may be due to a recalcitrant fouling layer or to the changed characteristics of the activated sludge. To support this last hypothesis, the SVI, which changed within the singular event "B", has been studied and is plotted versus the membrane permeability (Js) in figure 8.14. Considering that Extracellular Polymeric Substances (EPS) are widely indicated as major reason of fouling phenomena, the curve of figure 8.14 seems inconsistent with the fact that sludge settles less well, as measured by the SVI, with increased amount of EPS (Barker and Stuckey, 1999; Liu and Fang, 2002). However, in this case study the SVI was increased by the peaks of inloading and EPS content was not measured. This fact suggests that the SVI cannot be indicated as gross index of the sludge filterability if the reasons of its change are not well known.

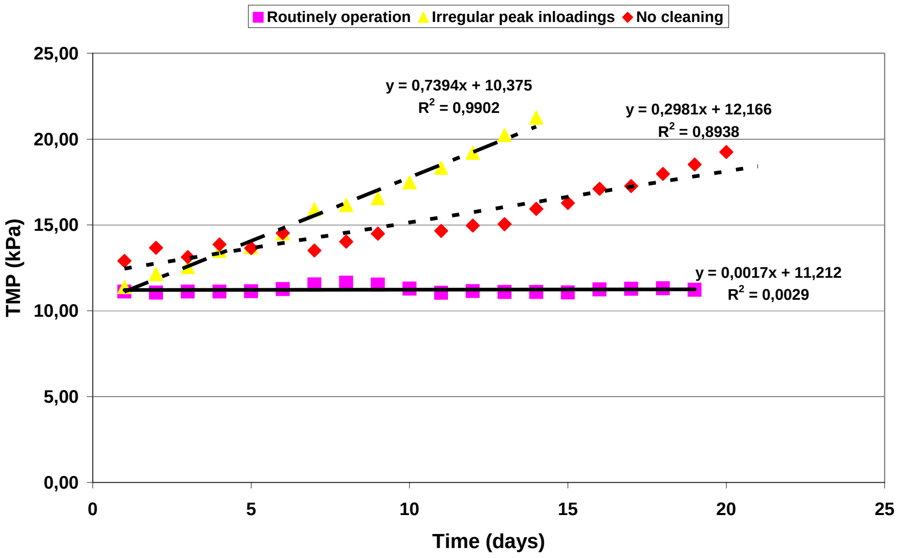


Figure 8.13 TMP decline in: typical routinely operation; irregular peaks inloading; no chemical cleaning

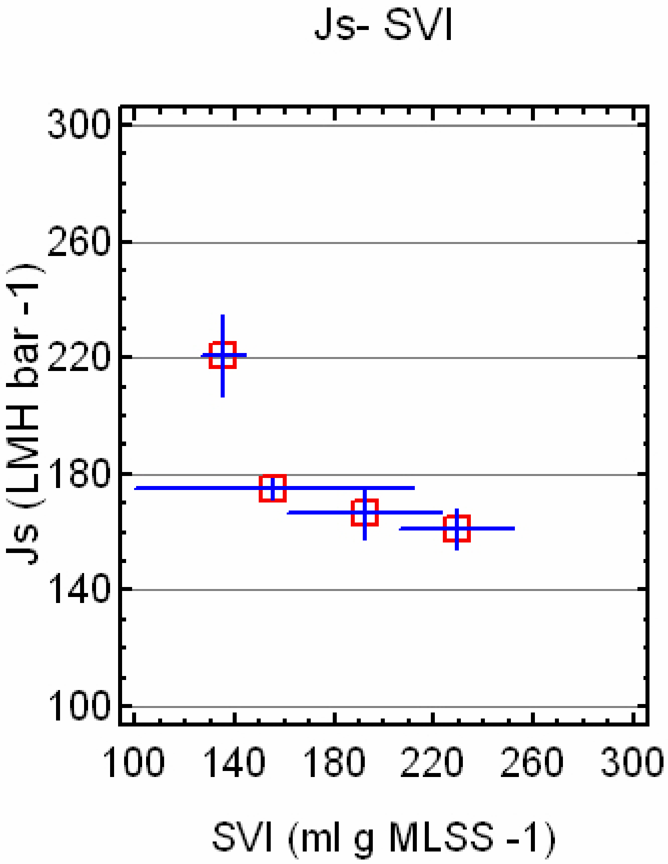


Figure 8.14 Correlation between SVI and membrane permeability (Js) @ 20°C

4.4 Power requirements and O&M costs

4.4.1 Power requirements

Submerged MBRs are favoured as their power requirements are lower than sidestream configuration. Here the continuous cleaning action is carried out by the air scouring and do not require high recycles. However, the total energy required for permeate unit is higher than the conventional activated sludge plants and published papers reported values in the following ranges:

0.6÷1.2 kWh m^{-3} (STOWA, 2005); 0.2÷0.4 kWh m^{-3} (Churchuose, 2002); 0.4÷0.8 kWh m^{-3} (Engelhardt and Linder, 2006).

In this case study three choices regarding both the design and the O&M strategy allowed to obtain successful energy consumptions: (1) the low aeration demand for membrane scouring, already discussed before; (2) the choice of the AC technology, a biological process able to save up to 20÷30 % energy respect to conventional biological processes (Battistoni *et al.*, 2003), (3) the operation according to MLSS as low as required by the biological process, that allows to optimize the oxygen transfer to the biomass (better known as α factor) (Krampe and Krauth, 2003) and save energy in terms of air supply for the biochemical aerobic reactions. Furthermore, the energy saving approach was pursued also from the engineering side installing a frequency regulator for pumps and blowers along the treatment line.

Before the discussion of the real energy consumptions, the power installed over the whole AC-MBR is analysed (figure 8.15).

Figure 6 shows that more than 50% of the total power is installed for the air supply, half for the biological process and half for membrane scouring. Therefore, optimizing the total exploitation of the air supplied was the successful strategy to reduce the power requirements. Moreover, the low number of recycles of activated sludge contributed to have the remarkable consumptions reported below.

As far as concern the energy consumptions of the biological process, the alternate cycles process makes use of energy depending on the durations of the aerobic and anoxic phases, which change according to the influent loading. In particular, in case of COD/N sufficient for the complete nitrates denitrification, the cycles time lengths depend on the Nitrogen Loading Rate (NLR) and, in case of constant incoming flowrate, on the TKN concentration (figure 8.16).

As far as the UF section, a meter of electrical input was installed into the main switchboard including the power required by: blowers for air scouring, pumps for permeate suction the facilities of minor power. The data were on line logged and reported specific energy consumptions of 0.16÷0.25 kWh m^{-3}, according to different operated SAD. As a result, the overall power requirements are in the range 0.44÷0.57 kWh m^{-3}, depending mainly on the TKN influent, for the AC, and the aeration for membrane scouring, for the UF.

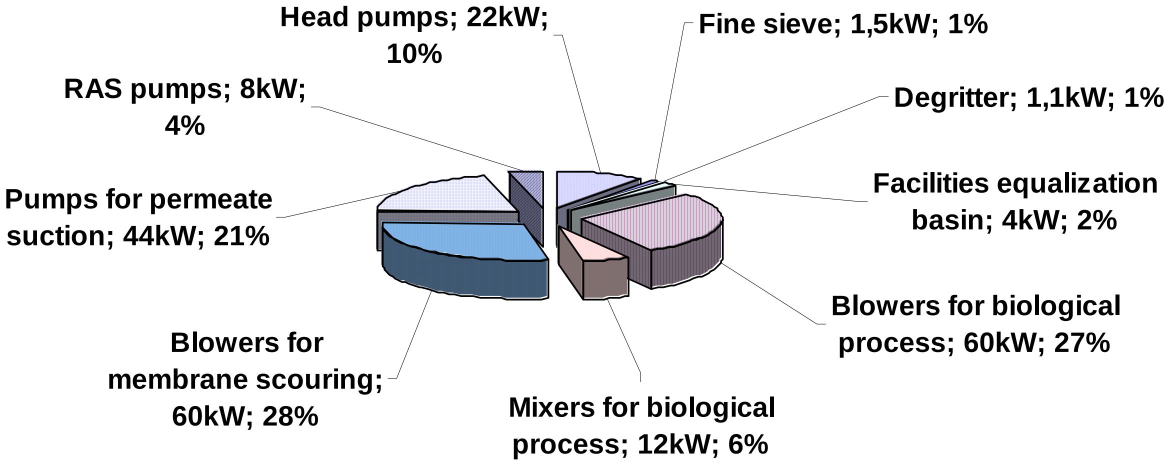


Figure 8.15 Power installed over the whole AC-MBR

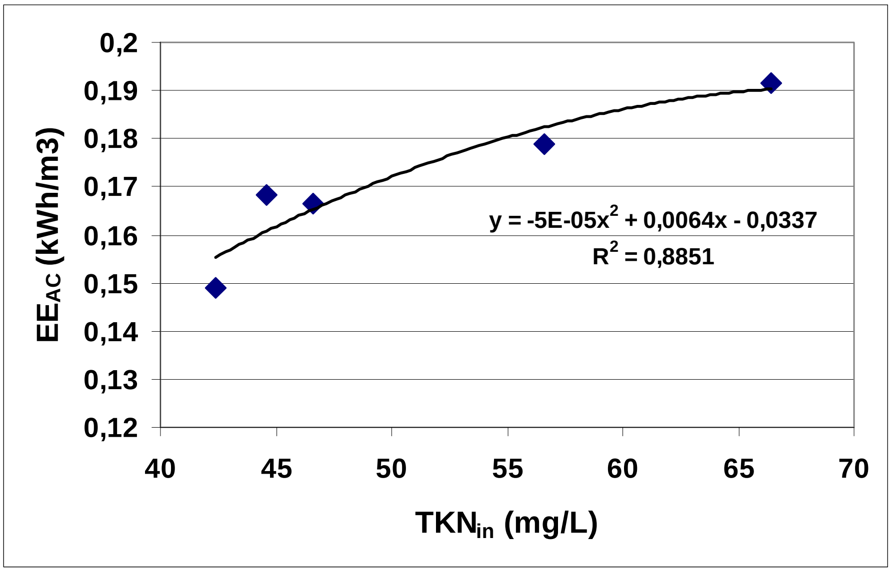


Figure 8.16 Specific electric energy (EE) consumptions of the biological process over one year operation

4.4.2 O&M costs about power consumptions and chemicals purchase

The most recent data about O&M costs of a large full scale MBR reported a specific cost of 0,26 €/unit permeate (Engelhardt and Linder, 2006), inclusive of the personnel and membrane replacement. In this case study, considerations about the membrane life are still too early. Moreover, the complexity of the whole WWTP, composed also by the existing parallel conventional WWTP, at the moment do not allow for the calculation of the personnel cost. However, the real costs relating to the chemicals used to clean the membranes and the power consumptions have been determined. Considering the specific costs of 0.12 € kWh^{-1} for the power and 0.52 € kg^{-1} for the hypochlorite, the specific cost for power and chemicals are given in table 8.12.

Basically the O&M cost seem to be sustainable, also for the Italian scenario where the fee for municipal wastewater treatment is around 0,30÷0,40 € m^{-3}. However, more details about the membrane life are needed to make major conclusions on the convenience of this treatment system.

Table 8.12 O&M costs about chemical purchase and electric energy consumption

Total energy cost/unit permeate	€	0.053÷0.068
Total chemical cost/unit permate	€	0,01
Total cost$_{EE+chemical}$/unit permeate	***€***	***0.063÷0.078***

5. Conclusions

The AC-MBR system has been finally validated on a full scale installation. With particular concern to the PhD activity, it dealt with the carefully supervision of the plant start-up and first-year operation, in order to finally outline the addresses for the optimal management of the plant. The study was complete and took into account the operation and maintenance of both of the biological process and the ultra-filtration section. Facets concerning both design and operation were considered.

As for the design, all the operation units were analyzed in details: the pre-treatments; the equalization basin; the biological reactor; the filtration section. The main conclusions are following itemized:

- head physical pre-treatments composed by (a) a fine sieve (punched hole geometry – holes diameter 1.5 mm) and (b) a degritter adequately oversized with regard to the conventional practice, involved an acceptable trash content into the activated sludge;

- the off-line equalization basin is an energy saving solution. Moreover, it fits the AC-MBR systems because the AC biological process is flexible and can cope well with the fluctuations of influent loadings;
- the configuration of the AC reactor according to two CSTRs in series increase the flexibility of the process allowing the better detection of ammonia break-points and nitrates knees. The AC bioreactor, included in the AC-MBR systems, can rely on lower power requirements respect to the conventional configurations. In fact, the full scale case study demonstrated that the ammonia nitrification was performed also in the aerobic membrane tank. As a matter of fact, the specific use of energy in the AC bioreactor for the ammonia nitrification was 2,8÷3,5 $kWh/kgN_{nitrified}$;
- the long weir all over one side of the membrane tank was a good solution to face critical accumulation of foam and floating materials in the membrane section.

The biological process had to deal with almost domestic wastewater with good C/N ratio (higher than 10) and high nitrogen content (TN influent in the range 42÷67 mg L^{-1}) The operating biomass concentration was decided on the basis of the nitrification potential of the system. In practice, the nitrification potential was periodically determined on the basis of respirometry tests and the biomass was maintained as low as necessary for complete ammonia nitrification. This choice allowed to optimize both the removal performances and the oxygen transfer to the biomass. Therefore, it was an energy-saving strategy because minimized the power requirements for the aeration of activated sludge. Following the strategy just discussed, the plant was operated with MLSS concentration in the range 6÷8 g L^{-1} and sludge age in the range 14÷21 days.

As for the process performances, the removal rates for COD, TN and TP were 94÷96%, 89÷91% and 58÷67%, respectively. These values were always satisfactory notwithstanding the remarkable seasonal loading fluctuation. As for the phosphorus, the mass balance pointed out that the AC-MBR was able to enhance the biological removal by luxury uptake phenomena. As for the nitrogen, the observed maximal treatment capacity, in terms of NLR, confirms the results of the before mentioned demonstration study: loadings up to 0,14÷0,16 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$ were effectively treated achieving the italian standard for non potable reuse.

As far as the management of the filtration process, the main remarks are:

- operating under the hydrodynamic environment characterized by (a) net permeate flux of 26 LMH, (b) Specific Aeration for Membrane Scouring (SAD_m) in the range 0.12÷0.19 $Nm^3 h^{-1} m_{membrane}^{-2}$, (c) Return Activated Sludge ratio in the range 1,5÷2,5, (d) filtration cycle of permeation (600 sec)/relaxation (60 sec); and a cleaning protocol of 1 maintenance cleaning in place (mCIP) per week involved long-term membrane permeability in the range 230÷240 LMH bar^{-1};
- the increase of SAD_m from 0,12 to 0,19 $Nm^3\ h^{-1}\ m^{-2}$ did not involve a permeability gain that could balance the increased power requirements, probably because the major role in fouling amelioration was played by the chemical cleanings. Even with concern to fouling phenomena, the MLSS concentration played a minor role within the range 8÷11 g L^{-1};
- long term fouling phenomena during the routinely operation of the plant were sustainable and the seasonal fluctuations of inloading were well faced by the membrane system. Major fouling rose in case of short term singular events like the failure of the chemical dosage for mCIP or random discharge of landfill leachate into the sewers system, which change the nature of the feed. As a result, the UF system showed to be severely influenced from very unsteady conditions and short term variations of the feed nature.
- the SVI, which changed a lot according to the feed nature, was found out in good correlation with the sludge filterability.

Final considerations may affirm the industrial sustainability of the AC-MBR process. In fact, the specific power requirements for the whole treatment were in the range 0,44÷0,57 kWh/unit

permeate according mainly to: (a) the influent TKN; (b) the SAD_m. The best management of the aeration, achieved both by the choice of the biological process and by the operating strategy, was the main reason of these successful consumptions.
As for the O&M costs, power consumptions and chemical purchase involved costs in the range 0.063÷0.078 €/unit permeate.

In conclusion, the long-term operation of a full scale AC-MBR seems to indicate how this technology is ready for the industrial widespread application. However, although the costs of the membranes are rapidly decreasing, the present situation led to prefer the MBRs only in particular cases supported by strong driving forces. Only further investigations about multi-year operation of the industrial MBRs could allow to evaluate the expectation of membrane life and define the convenience of the membrane systems for municipal wastewater treatment and reuse.

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Chapter IX. Conclusion

1. Introduction

Are the MBRs ready for widespread application? Rapidly growing market and larger and larger treatment capacities of the full scale installations give rise to affirmative answers. Today the membrane bioreactors are presented, in some ways, like the activated sludge at the beginning of the last century. However, in spite of this success of the MBR technology, the most appropriate practice to design and operate these systems in not consolidated. Therefore, besides the pure research aimed to investigate and explain the mechanisms of the processes involved in membrane bioreactors, there is a great necessity of applied research which can encounter the problems typical of real applications. The approach of this three-year research activity has been addressed towards the real applications, examining the potential of the membrane bioreactors for the widespread and sustainable advanced treatment of municipal wastewater.

In particular, the study has been focused on the coupled implementation of membrane bioreactors and process control automation. In fact, the major part of the activity concerned the intermittently aerated and automatically controlled MBRs for municipal wastewater treatment. A control algorithm named “alternate cycles” has been used to control the aeration of the biological process. According to the AC automatic control algorithm, the aeration of the AC reactors is automatically controlled through a bending point based strategy which used the on-line curves of dissolved oxygen (DO) and oxidation reduction potential (ORP). Aeration is switched off (and submerged mixers are switched on) when the ammonia break point is detected, and is switched on (and submerged mixers are switched off) when the nitrate knee is detected. In this way, the lengths of the aerobic and anoxic phases are controlled to be just sufficient for complete nitrification and denitrification, respectively. Furthermore, the complete control algorithm has been provided with secondary branches (secondary levels of process control) which are based on setpoints of the time lengths of the aerobic and anoxic phases and of the absolute values of DO or ORP.
However, different key facets have been dealt with: upgrading design methodology, nutrients and micropollutants removal, membrane fouling and, last but not least, the full scale validation of the process, considered the “happy conclusion” of the work.
The activity has been carried out on three different scale-levels: the big pilot membrane plant, the demonstration and the full scale MBRs. The first pilot plant was used to assess (a) the impact of biomass bulk parameters on the membrane fouling and (b) the role of fouling/cake layer for metals removal. The demonstration MBR allowed to study the nutrients and micropollutants removals from real municipal wastewater. The full scale MBR was finally monitored and supervised over the first year operation to validate the technology previously studied on demonstration scale. All the plants were equipped with the same ultra-filtration submerged membranes, always arranged in commercial modules (ZeeWeed® 500c and 500d). Besides, obviously, the full scale MBR, also the pilot and demonstration plants were always fed with real sewages and, for this reason, where installed in municipal full scale wastewater treatment systems. The overall goal of this manifold and applied approach was to define the industrial feasibility and sustainability of examined technology, in other words, the “know-how” of the system.

The research activity started in 2004 with the demonstration experimentation on a MBR, operating the alternating cycles process, with the following main features: reaction volume of 11 m^3; membrane area of 69,9 m^2; treatable sewage up to 50 m^3/d. Over some 500 days of experimentation, nine steady state experimental runs were carried out feeding always the plant with real municipal wastewater taken from the Treviso full scale WWTP. The aim was to evaluate the maximal treatment capacity in terms of nitrogen removal, dealing with critical low abundances of carbon source (C:N ratios lower than 8÷9). Therefore, the plant was fed with nitrogen loading rates (NLRs) from 0,05 to 0,25 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$ also dosing external N salts to increase the nitrogen content. This strategy was consistent with the approach of taking always into account the real context where the technology should be implemented. In fact, today most of the existing wastewater treatment plants designed for nitrogen biological removal operate under NLRs in the range 0,05÷0,09 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$. Moreover, the existing facilities for wastewater treatment, if adequately upgraded, could be sufficient to effectively treat all the municipal sewages. Therefore, the major aim of the demonstration study was to study the potential of the AC-MBR to upgrade existing plants achieving the reuse purpose with sustainable industrial costs of the treatment. To increase the carbon source, keeping anyway critical low values of C/N ratio, the dosage of external C in form of the liquid phase of the Organic Fraction of the Municipal Solid Waste (OF-MSW_L) was arranged. This substrate was taken from the full scale OF-MSW co-digestion plant of Treviso. The plant was operated under parameters (sludge ages, biomass concentrations, permeate fluxes) actually sustainable in real treatment systems with reasonable operating costs. Therefore, the sludge age was in the range 20÷50 days and the solids content in the range 5÷9 gMLSS L^{-1}. The results of this demonstration part consisted in: (a) the definition of critical values for NLR and C/N ratio, intended in terms of loss of flexibility of the process and achievement of the reuse standard for nitrogen content; (b) the removal of micropollutants from real municipal low loaded wastewater and the direct comparison with the parallel conventional full scale plant; (c) the evaluation of the nitrification and denitrification kinetic rates , coming from both field investigations and respirometry bench scale tests; (d) the suitability and reliability of the control algorithm and device for the treatment of low loaded wastewater in a membrane bioreactor.

The experimentation on the pilot membrane plant lasted about one year. The pilot plant was equipped with a submerged industrial module of hollow fibre membranes (membrane area 21.6 m^2) able to treat up to 16÷18 m^3/d. The experimental facilities were installed in the municipal wastewater treatment plant of Falconara Marittima (central Italy – Adriatic coast) and the experimentations were always carried out using activated sludge and secondary effluent from that full scale plant. Two main goals were pursued in this part of the research: (1) to study the impact of the biomass bulk parameters on the membrane fouling; (2) to know the role of the membrane fouling/cake layer with respect to the metals retention. The study on the filterability of activated sludge was carried out by a large campaign of filtration test at different biomass concentrations; liquor temperatures; permeate fluxes. Each filtration test lasted about four days, in order to exceed the initial conditioning fouling and study the steady fouling rate. The experimental data were treated both directly, to evaluate the impact of the MLSS at different permeate fluxes, both statistically, in order to arrange a mathematical model. The results consisted in the general evaluation of the MLSS concentration which causes the shift from two different behaviours of the fouling phenomena and in the arrangement of a mathematical model, which still needs some experimental clarifications. As far as the metals removal, at the moment the results are almost preliminary but very interesting. They regard the membrane effect, intended both as sieving effect and as role of the fouling/cake layer, with particular attention paid to Cadmium and Nickel.

The experience regarding the full scale MBR concerned the first year of trial operation. The plant was supervised by our research group within this experimental activity. The full scale MBR is located in the Viareggio wastewater treatment system (central Italy – Tirrenic coast), comes from the upgrading of the existing plant and operates the alternate cycles process. Submerged hollow fibres membrane modules are installed with a total area of 12130 m^2. The plant is designed to treat municipal wastewater up to 6000 m^3 d^{-1} for non-potable reuse purposes and has been started up in February 2005. Basically, the main goal of this part was to definitely validate the process for municipal wastewater treatment and reuse. The achievements of this investigation can be resumed in the definition of the best operating conditions which optimize the removal performances and minimize the operation and maintenance costs. Furthermore, the detailed analysis of the case study allowed to confirm the maximal treatment capacity, in terms of NLR, previously found at demonstration scale.

2 Upgrading design methodology

Several studies have attempted to generalize a protocol to design continuously fed activated sludge bioreactors where the aeration is intermittent for the removal of total nitrogen. However, to date the design practice is based on empirical models.

The first task of this study was to develop and validate a methodology to design the upgrading of existing conventional wastewater treatment plants by the alternate cycles system. The experimental activity was carried out at first on bench scale, and then validated on a full scale case study. In particular, the empirical model was based on the results coming from a bench scale pilot plant fed with real wastewater adequately prepared to change, run by run, the organic loading rates. The model was based on the nitrification and denitrification rates, which are expected to be easily measurable for existing plants. According to the experimental data, found in the lab and, then, well validated in a 700 Population Equivalent (PE) plant, the AC technology can be used to retrofit existing municipal plants allowing also for the increase of the treatment capacity in terms of nitrogen loadings. As a matter of fact, in case of carbon source not limiting for the complete nitrates biological denitrification (C/N ratio ≥ 8÷9), the AC process can safely treat up to 0,14÷0,16 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$. This range, compared to the 0,05÷0,09 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$ typically adopted for municipal systems, clearly shows the possibility to treat higher nitrogen loadings with the same treatment facilities. Furthermore, the alternate cycles process has proved to require lower power thanks to the better exploitation of the nitrate-bound oxygen and the low recycles of activated sludge. Actually the full scale AC plants need less power than conventional plants both for small systems (119÷193 Wh PE^{-1} day^{-1} for an over-aerated 700 PE plant) and for larger ones (up to 35÷45 Wh PE^{-1} day^{-1} for a 25000 PE plant).

3. Demonstration membrane bioreactor operating the alternate cycles (AC-MBR): carbon and nutrients removal

The experimental results coming from the demonstration study deal with four main topics: (1) the maximal potential and the behaviour of the AC-MBR system with respect to the nitrogen and phosphorus biological removal; (2) the reliability of the automatic control strategy for wastewater characterized by limiting low C/N ratios; (3) the comparative evaluation of the intermittent system with a parallel MBR operating the multizone predenitrification-nitrification configuration; (4) the capability of the Activated Sludge Model n.2 (ASM2) to simulate the process with the default kinetic rates.

3.1 COD removal

As far as the characteristics of the influent COD, the degree of biodegradability was almost low (rbCOD/COD ~ 0,10÷0,20). However, as expected the removal of COD was generally higher than 90%, and only the non biodegradable soluble COD was found out in the permeate. As a result, the average effluent COD was always lower than 40 mg L^{-1} and lower than 20 mg L^{-1} in seven runs out of nine.

3.2 Nitrogen removal

More interesting results concern the biological removal of total nitrogen. To evaluate the maximal treatment capacity of the AC-MBR system, the loss of flexibility in the alternation of the anoxic/aerobic phases was assumed as a key indicator. The control algorithm was able to adjust optimally the alternation of anoxic and aerobic phases according to the influent characteristics for NLR and C/N up to 0,16÷0,18 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$ and 5÷6, respectively. Within these border lines, the nitrogen forms in the permeate from the AC-MBR system were in agreement with the italian standard for non-potable reuse. Therefore, AC-MBR systems may be adopted both for new wastewater treatment systems as well as to upgrade existing ones, achieving the increase of the treatment capacity and, at the same time, the agreement with the reuse standard.

Considering the use of the carbon source for total nitrogen removal as key performance indicator, the system removed some 0,1 kg of total nitrogen per kg of total influent COD. However, this value was observed under operation often affected by over-aeration phenomena and, for this reason, could be taken as indicator of the minimal performance.

As for the specific biological processes for total nitrogen removal, the ammonia nitrification was often maximal and often limited by the same ammonia concentration, on the other hand the denitrification was limited by the carbon source. The global specific rates, calculated from mass balances, were in the ranges 2÷4 and 1÷2 gN kgVSS h^{-1} for nitrification and denitrification, respectively. The real rates, measured by field analyses carried out once a run, revealed that the system operated denitrification al 1÷1.5 gN kgVSS h^{-1} with endogenous carbon source, while rates in the range 1.6÷2 gN kgVSS h^{-1} were observed with carbon source internal to the influent sewage. The configuration of the MBR, with an initial anoxic selector, followed by two intermittent bioreactors in series, and a final aerobic membrane tank, was effective for the ammonia nitrification. Under low C/N ratios in the influent, in fact, the system can undergo to long anoxic phases and a final continuous aerobic step is useful to smooth possible peaks of ammonia.

3.3 Phosphorus removal

As far as the phosphorus biological removal, the AC-MBR scheme proved to be able to enhance the performances triggering luxury uptake phenomena. The removal reaches values around 60%. However, this phenomenon was observed only when the influent sewage contained external acetate. On the other hand, the other experimental runs showed P biological removal only by assimilation for the biomass growth.

3.4 Suitability of the process control algorithm

As for the behaviour of the alternating system, the denitrification was always the limiting step. Maximal anoxic time lengths were around 1200 minutes/day. These values correspond to the plateau condition, when the dynamic alternating process became rigid with fixed time lengths. The control strategy was validated and the bending point based strategy seemed suitable for the treatment of wastewater poor of carbon source for heterotrophic denitrification. Furthermore, the complete control algorithm was able to face critical boundary conditions thanks to the secondary branches of the algorithm based on absolute setpoints. The statistical analysis of the cycles, which can be performed in real time, allow the remote monitoring of the system and the indirect knowledge of the nitrification and denitrification performances. In fact, a linear correlation was found out between the proportional cases of bending points identification and the real nitrogen removal efficiencies.

3.5 Comparison with multi-zone predenitrification-nitrification configuration

The comparative evaluation of intermittent and multizone schemes pointed out the better performances of the alternating processes for total nitrogen removal operating NLRs in the range 0,05÷0,16 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$. The better performances were attributed to the best enhancement of the biological denitrification, while the almost complete ammonia nitrification was achieved in both the systems. The incoming of nitrogen loadings higher than 0,17÷0,18 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$ caused limitations for the ammonia nitrification in the intermittent MBR. In the light of this scenario, the bending point based control is not preferable because can involve too long anoxic phases and too high ammonia accumulation in the reactor, which may be not completely oxidized in the aerobic phases. In practice, in the case that a real AC-MBR plant would transitorily undergo to NLRs higher than 0,17÷0,18 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$, the AC-MBR system is better to operate according the secondary control level based on easy set points as long as the process operate with the higher rates. This control strategy can guarantee the complete ammonia nitrification and perform nitrates denitrification.

3.6 Activated Sludge Model 2 simulations and comparison with the experimental results

The effluent nitrogen forms as simulated by the activated sludge model, using the default kinetic rates, were found in acceptable agreement with the real effluent from the demonstration AC-MBR in the range 0,05÷0,16 kgN m^{-3} d^{-1}. On the other hand, the behaviour of the phosphorus was not simulated correctly probably due to different kinetic rates for sludge yield. In conclusion, if operating in the range of NLRs before mentioned, the ASM2 can be used as it is to have gross information about the process and also to arrange the first absolute time setpoint on the secondary branches of the control algorithm. These values must, anyway, be adjusted after the initial trial operation of the AC-MBR plant.

4. Metals occurrence and removal

Within the open important debate on the priority pollutants in the urban water cycle, one of the major points which call for much clarity is the real occurrence of the hazardous compounds in the municipal wastewater. Individuating the compounds which are really present in municipal wastewaters, in fact, could avoid the inclusion of useless analyses for the routinely monitoring of the treatment systems. On the other hand, the selection of the *target compounds* would condense the efforts to a limited group of compounds which represent really a risk and should be effectively removed by the treatment facilities. In this study the occurrence and removal of metals in municipal wastewater systems has been investigated in details by a wide sampling/analytical campaign carried out on five selected full scale wastewater treatment plants. These plants were diverse both for treatment capacity and for industries present in the catchments area. Therefore, the raw wastewaters analyzed were ranging from almost domestic to mixed municipal/industrial. The results regard both the definition of the target metals, which should be of major concern when treating municipal sewage, and the destiny of metals in conventional and advanced treatment systems.

As for the occurrence of metals, the main remarks could be resumed as follows:

- As, Hg, Pb, Cd are present in the raw municipal wastewaters in a range of 0,1÷10 μg/L, while Cu, Ni, Cr are in the range 10÷70 μg/L;

- a remarkable part of the influent metal is associated to suspended particulate and is partially removed already in the physical headworks of conventional WWTPs. This demonstrates that the street particles play a role in transporting metals into municipal sewers system;
- the metals in the secondary effluent from conventional treatment systems were found almost dissolved in the liquid phase. The overall concentration were in the following ranges: As (0,1÷5 µg/L); Hg (0,7÷7,7 µg/L); Cu (5÷21 µg/L); Pb (2÷9 µg/L); Cd (0,1÷0,3 µg/L); Ni (2÷12 µg/L); Cr (3÷20 µg/L);
- the metals in the waste activated sludge were found in the following ranges: As (3÷15 mg/kgTS); Hg (2÷5 mg/kgTS); Cu (165÷348 mg/kgTS); Pb (46÷135 mg/kgTS); Cd 1÷3 mg/kgTS); Ni (31÷107 mg/kgTS); Cr (17÷560 mg/kgTS);
- generally, metals were efficiently removed already in conventional plants. Most of the analyzed metals, in fact, were removed for 70÷95% according to the sequence Hg>Ni>Cd>Cu>Cr>Pb. Differently, As was removed in the range 20÷60%;

The whole analytical database regarding the raw wastewaters was also analysed to find possible correlations between the occurrence of different metals. Two methods were attempted: a *statistical approach*, that led to the construction of correlation matrix, and the *solid phase approach*, that trying to take additional information from the metals into the solid phase. While the statistical approach pointed out no significant correlation among the occurrences of the different analyzed metals, the detailed knowledge of the metal contents in the solid suspended particulate demonstrated to be a good tool for the identification of the source (industrial or municipal) of metals in the wastewater.

As for the effect of the membrane systems, the study relied on direct comparisons between conventional plants and MBRs operating in parallel. As it can be expected, this simple evidence gave the most objective results. Basically, the MBRs were more effective than conventional systems also considering the very low influent abundances of metals. The parallel monitoring carried out on a demonstration and a full scale MBR operating in parallel with conventional plants pointed out a better performance of the MBRs in the range 7÷17% in the sequence Cd>Cu>Pb>Cr>Ni>Hg. The As was removed in the range 30÷60%, according very fluctuating performances. Besides the sieving effect of the membrane, also other phenomena seemed to be involved in the metal enhanced removal in membrane systems. In particular, the fouling/cake and/or the concentration-polarization layer seem to play an important role. This effect was investigated both according to the system configuration, tertiary filtration or membrane bioreactor, and according to different operating parameters (MLSS content, permeate fluxes, permeation cycles). Basically, the MBR configuration, intended as direct filtration of the activated sludge, gave higher removal the results achieved are still preliminary, but very interesting. To date, Cd and Ni has been focused and the results showed that the membrane system exerts a stable effect on Cd, while this phenomenon is temporary on the Ni. The affinity of the metals to be biosorbed on the membrane cake/fouling layer probably is the property which could explain these different behaviours. Therefore, present and next researches are addressed towards the understanding of this mechanisms.

5. Organic micropollutants occurrence and removal

Besides the metals, also the occurrence and removal of selected organic xenobiotics has been investigated in real wastewater treatment systems. Owing to the number of plants sampled, only four families of compounds were focused. Notwithstanding this approach, the first screening included more than 80 compounds were analyzed among Polynuclear Aromatic Hydrocarbons (PAHs), Volatile Organic Compounds (VOCs), Halogenated Volatile Organic Compounds (HVOCs) and chlorobenzenes.

As far as the PAHs, abundances lower than 2 μg L^{-1} were observed also in a case when petrochemical industries were present in the catchments area. These pollutants inflow to the wastewater treatment plants mainly associated to suspended particulate matter according to the K_{ow} of the particular hydrocarbon. As for the size of the particles, PAHs are associated also to the grit and , therefore, a first important removal (20÷40%) was observed already in the physical conventional headworks (fine screening and degritting). Then, the biological secondary conventional treatments exert a further removal in the range 20÷50%. As a result, the total PAHs in the treated effluent were in the range 0,1÷0,14 μg L^{-1}. The effect of the membrane systems, evaluated parallely to the conventional plant, was not significant to justify the possible adoption of this technology against the increased capital and operating costs.

The occurrence of VOCs was mainly attributed to organic solvents such as BTEX and trimetylbenzene. The influent abundances were in the range 3÷10 μg L^{-1} for the BTEX, mainly toluene, and 0,1÷1 μg L^{-1} for the trimetylbenzene. The stripping of these compounds was remarkable (40÷60%) already in the initial physical headworks, moreover the biological conventional processes were effective so far to involve further 10÷50% removal. The effect of the membrane system was not valuable because of the very low influent concentrations.

The chlorobenzenes in the raw wastewaters were always under the limits of quantification, while the HVOC where very variable case by case and did not allow any kind of reasonable consideration. However, the maximal HVOC concentrations were some micrograms per litre.

In the view of the investigations carried out, PAHs are already removed from the treated effluents by conventional activated sludge plants. MBRs operating within the experimented parameters (sludge age in the range 10÷40 days) do not give significant enhancement of the already satisfactory removals. Furthermore, the PAHs content in the waste activated sludge was always lower than the limit of quantification (0,5 mg kgTS). This result did not allow reasonable evaluations on the possible capacity of MBRs to enhance the biodegradation or biosorption of these organic xenobiotics.

As far as the VOCs, the organic solvents should be of major concern dealing with municipal wastewater systems. The removals are performed already in the physical headworks by stripping phenomena. Therefore, in case of relevant influent concentrations, these operation units should be put under suction, and the resulting gaseous effluents should be treated adequately. However, the municipal systems may be considered out of these conditions, therefore the capital and operating expenses for the treatment of the gas emissions would be not justified according to the overall environmental and economic balanced.

6. Impact of biomass (bulk) parameters on membrane fouling

Membrane fouling is one of the key issues that limit the widespread application of MBRs. Activated sludge state and concentration are reported to play a key role in these phenomenon. Therefore, in this three-year activity, the influence of biomass bulk parameters has been investigated on pilot scale. In particular, the impact of the biomass concentration on the sludge filterability has been investigated carrying out a long campaign of filtration tests, over one whole year, at 0-2-5-10 gMLSS L^{-1} at 9-18-27-36 LMH. The steady slow fouling rate has been focused performing 4 days long tests and the initial conditioning fouling has been excluded from the data processing.

The main aim was to identify the right mix of operating parameters for the activated sludge filtration, that is the MLSS concentration and permeate flux which can ameliorate membrane fouling and optimize, at the same time, the performances of the biological process.

The results pointed out that a jump of MLSS concentration from 2 to 5 g L^{-1} drastically affects the filterability of the activated sludge, especially operating close or over the critical flux. On the contrary, operating MLSS from 5 to 10 g L^{-1} gave rise to similar fouling rates. In the light of these results, the right compromise between biomass concentration and permeate flux must be pursued to achieve the industrial and economical sustainability of the process. As a result, from one side suspended solid concentration up to 2 gMLSS L^{-1} can increase the membrane permeability, so this strategy can reduce the capital and O&M costs; from the other side, higher biomass concentration can enhance the metals removal. However, in this last case, more severe fouling rates are observed and more frequent chemical cleanings are required for the long-term operation of the membrane system. If the membrane area is not adequately oversized, frequent membrane cleaning could involve too many interruption of the permeation and be in contrast with the continuous feeding of the plant. Moreover, recovering the system permeability through frequent chemical cleanings can decrease the membrane life and increase the costs for membrane replacement.

As general preliminary consideration, the application of higher fluxes seems to be convenient, but further long-term investigations are needed to better evaluate the membrane life and real impact on the retention capability of the membranes. As far as the MLSS concentration, values between 5 and 10 g L^{-1} are not of major concern for the impact on membrane fouling. Therefore, the choice for the MLSS should be driven from the necessity of the biological process and the energy consumptions for the aeration of the activated sludge. This point has been well investigated for the full scale validation of the process and is dealt with in the following paragraph.

After having found the direct remarks about the experimental results, a statistical approach was used to process the data and define a mathematical model which could relate trans membrane pressures, biomass contents, liquor temperatures and permeate fluxes. The statistical approach was supposed the only one appropriated to the scale of the research. However, the comparison of theoretical and experimental results were not fully satisfactory for permeate fluxes in the around of the critical value. Therefore, further tests to thicken the experimental points are needed to validate the model and use it as reliable predictive tool.

7. Full scale validation of the AC-MBR system

The AC-MBR system has been finally validated on a full scale installation. With particular concern to the PhD activity, it dealt with the carefully supervision of the plant start-up and first-year operation, in order to finally outline the addresses for the optimal management of the plant. The study was complete and took into account the operation and maintenance of both of the biological process and the ultra-filtration section. Facets concerning both design and operation were considered.

As for the design, all the operation units were analyzed in details: the pre-treatments; the equalization basin; the biological reactor; the filtration section. The main conclusions are following itemized:

- head physical pre-treatments composed by (a) a fine sieve (punched hole geometry – holes diameter 1.5 mm) and (b) a degritter adequately oversized with regard to the conventional practice, involved an acceptable trash content into the activated sludge;
- the off-line equalization basin is an energy saving solution. Moreover, it fits the AC-MBR systems because the AC biological process is flexible and can cope well with the fluctuations of influent loadings;
- the configuration of the AC reactor according to two CSTRs in series increase the flexibility of the process allowing the better detection of ammonia break-points and nitrates knees. The AC bioreactor, included in the AC-MBR systems, can rely on lower power requirements respect to the conventional configurations. In fact, the full scale case study demonstrated that the ammonia nitrification was performed also in the aerobic membrane tank. As a

matter of fact, the specific use of energy in the AC bioreactor for the ammonia nitrification was 2,8÷3,5 kWh/kg$N_{nitrified}$;
- the long weir all over one side of the membrane tank was a good solution to face critical accumulation of foam and floating materials in the membrane section.

The biological process had to deal with almost domestic wastewater with good C/N ratio (higher than 10) and high nitrogen content (TN influent in the range 42÷67 mg L^{-1}) The operating biomass concentration was decided on the basis of the nitrification potential of the system. In practice, the nitrification potential was periodically determined on the basis of respirometry tests and the biomass was maintained as low as necessary for complete ammonia nitrification. This choice allowed to optimize both the removal performances and the oxygen transfer to the biomass. Therefore, it was an energy-saving strategy because minimized the power requirements for the aeration of activated sludge. Following the strategy just discussed, the plant was operated with MLSS concentration in the range 6÷8 g L^{-1} and sludge age in the range 14÷21 days.

As for the process performances, the removal rates for COD, TN and TP were 94÷96%, 89÷91% and 58÷67%, respectively. These values were always satisfactory notwithstanding the remarkable seasonal loading fluctuation. As for the phosphorus, the mass balance pointed out that the AC-MBR was able to enhance the biological removal by luxury uptake phenomena. As for the nitrogen, the observed maximal treatment capacity, in terms of NLR, confirms the results of the before mentioned demonstration study: loadings up to 0,14÷0,16 $kgN \cdot m_{reaction}^{-3} \cdot d^{-1}$ were effectively treated achieving the italian standard for non potable reuse.

As far as the management of the filtration process, the main remarks are:
- operating under the hydrodynamic environment characterized by (a) net permeate flux of 26 LMH, (b) Specific Aeration for Membrane Scouring (SAD_m) in the range 0.12÷0.19 $Nm^3 h^{-1} m_{membrane}^{-2}$, (c) Return Activated Sludge ratio in the range 1,5÷2,5, (d) filtration cycle of permeation (600 sec)/relaxation (60 sec); and a cleaning protocol of 1 maintenance cleaning in place (mCIP) per week involved long-term membrane permeability in the range 230÷240 LMH bar^{-1};
- the increase of SAD_m from 0,12 to 0,19 Nm^3 h^{-1} m^{-2} did not involve a permeability gain that could balance the increased power requirements, probably because the major role in fouling amelioration was played by the chemical cleanings. Even with concern to fouling phenomena, the MLSS concentration played a minor role within the range 8÷11 g L^{-1};
- long term fouling phenomena during the routinely operation of the plant were sustainable and the seasonal fluctuations of inloading were well faced by the membrane system. Major fouling rose in case of short term singular events like the failure of the chemical dosage for mCIP or random discharge of landfill leachate into the sewers system, which change the nature of the feed. As a result, the UF system showed to be severely influenced from very unsteady conditions and short term variations of the feed nature.
- the SVI, which changed a lot according to the feed nature, was found out in good correlation with the sludge filterability.

Final considerations may affirm the industrial sustainability of the AC-MBR process. In fact, the specific power requirements for the whole treatment were in the range 0,44÷0,57 kWh/unit permeate according mainly to: (a) the influent TKN; (b) the SAD_m. The best management of the aeration, achieved both by the choice of the biological process and by the operating strategy, was the main reason of these successful consumptions.

As for the O&M costs, power consumptions and chemical purchase involved costs in the range 0.063÷0.078 €/unit permeate.

In conclusion, the long-term operation of a full scale AC-MBR seems to indicate how this technology is ready for the industrial widespread application. However, although the costs of the membranes are rapidly decreasing, the present situation led to prefer the MBRs only in particular cases supported by strong driving forces. Only further investigations about multi-year operation of the industrial MBRs could allow to evaluate the expectation of membrane life and define the convenience of the membrane systems for municipal wastewater treatment and reuse.

8. Final remarks and addresses for future research

The long period of dry weather in 2007 has drastically reinvigorated the problems linked to the water scarcity. Therefore, water reuse is more and more indicated as feasible strategy to undertake. In the light of this three-year experience with membrane bioreactors, it is believed that, at the moment, the membrane bioreactors have the same potential for widespread application that the activated sludge had one-hundred years ago.

The intermittent aeration and the process control automation are optimal tools to operate within membrane bioreactor systems to optimize performances and costs, in line also with the recent energy-saving policies. The potential regarding the optimization of total nitrogen removal has been clarified in this thesis. As for the phosphorus removal, the experimentations demonstrated that the intermittently aerated processes can enhance the biological removal performing luxury uptake phenomena. However, further investigations regarding this topic are already in progress and the preliminary results will be achieved in few months.

As for the plant configuration and the process control, the AC-MBR is still managed by two different algorithms: one for the AC biological process and one for the ultra-filtration, generally engineered by the membrane manufacturer. The future perspectives is to merge the two algorithms in one only structure which can optimize the biological and filtration process. At the moment, the first experimentations regarding the best management of the return activated sludge are in progress at demonstration scale.

As for the micropollutants removal, this work contributed to outline the real size of the problem with concern to the municipal wastewater systems. Both a number of target compounds and their abundances have been outlined. In the view of the experimental results achieved also by several further researchers, an important part of the future experimental research is expected to be focused on the levels of micropollutants really present in the urban water cycle. Otherwise, the risk could be to have a lot of excellent results which, anyway, could not be transferred to real problems. As for the membrane effect for metals removal, recent studies are already investigating the positive role of the fouling/cake layer, looking at this problem from a “different perspective”. Indeed, these studies are focused mainly to the treatments for drinking water production, but the same efforts are hoped to be done for municipal wastewater treatment.

As for the actual real scenario for wastewater treatment and reuse, the full scale realization of advanced and sustainable wastewater treatment system is indeed strictly needed. This study demonstrated that the reuse purpose could be achieved also with the economical budget coming only from the present public fee for wastewater treatment. However, there is still a great necessity to consolidate the best design and operation practice and, therefore, much more experiences from full scale case studies are expected to be published and evaluated.