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Effect of sludge age on the performance of a membrane bioreactor: influence on nutrient and metals removal

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Abstract

In this paper the effect of different SRT on the performances of an ultrafiltration pilot MBR operating with real wastewaters was tested to analyse both the ability of the system to remove nutrients and micropollutants and the possible decrease in waste sludge production. Increasing MLSS from 4 to 9 g/l reduced biomass production by 84% and increasing MLSS from 9 g/l to 17 g/l reduced biomass production by 75%. The progressive sludge mineralization was clear since the VSS decreases from 75% TSS to 52% TSS. The industrial fraction of the influent affected the denitrification in all the three periods. The effluent quality increased only when passing from short SRT to long SRT. Ag, Cd and Sn removal was >99% in all the runs. Cu removal was 72–89%. Hg removal was >90% while Pb had varying behavior due to its inconstant presence in the influent (50–65%). B and Se seemed not to be efficiently retained by the biomass in both experimental conditions (0–28% and 0–31%, respectively). Arsenic was a major concern (33–37%). The next step of the research will focus on the possibility of enhancing As removal by looking at alternative technologies to integrate with the UF process.

Keywords: Hollow fiber; MBR; Micropollutants removal; Nutrients removal; SRT; Ultrafiltration

1. Introduction

MBR technology is expected to be more and more utilized in wastewater treatment as a modification of the conventional activated sludge process for the separation of the effluent by membrane filtration instead of sedimentation [1,2]. The MBRs had full-scale applications in a number of areas: industrial and municipal wastewater treatment, leachate treatment, water reuse and reclamation [3]. Since membrane filtration does not rely on the settling of the suspended solids as conventional activated sludge clarifiers, very high solids concentrations and retention

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times (SRT) can be maintained together with the achievement of a high-quality effluent. This latter aspect is of primary importance if we consider very sensitive areas like the case of the lagoon of Venice (northern Italy). The possibility of coupling an efficient biological process to the ultrafiltration (UF) process can lead to the fulfilment of the standards and to the beneficial decrease in waste sludge production if aerobic sludge stabilization can be chosen.

In this paper the effect of different sludge ages on the performances of an UF pilot-scale MBR operating with real wastewaters from Marghera (Venice) area (mixed wastewaters) was tested in order to analyse both the ability of the system to remove nutrients and micropollutants and the possible decrease in waste sludge production.

2. Materials and methods

The MBR system is composed of a stainless-steel reaction tank in which the hollow-fiber membrane unit is immersed [4] and is provided by a centrifuge pump for permeate extraction, air blowers for aeration and membrane cleaning and a mixer. The reactor is discontinuously fed (400 l/cycle; 2.4 m^3/d) and its activity is divided into 1.5 h of anoxic phase (only mixing), 2.5 h of aerobic phase (only aeration) at the end of which filtration takes place. HRT was kept at 14 h. The hollow-fiber membrane was a ZeeWeed-500 (24 m^2 total surface area; 20 nm average pore size). The influent wastewater was taken from the equalization basin of the full-scale WWTP located in Fusina (Venice, Northern Italy) (Table 1).

Table 1
Influent and effluent wastewater quality parameters

Parameter (mg/l)	Feed (mg/l)	Effluent Run 1 (mg/l)	Effluent Run 2 (mg/l)	Effluent Run 3 (mg/l)
TSS	226±79	0±0	0±1	0±1
TCOD	295±116	33±32	40±29	19±11
SCOD	97±51	21±10	39±47	19±8
TKN	42.2± 28.3	1.2±0.4	0.3±0.4	2.0±2.2
NH_4-N	22.8± 11.1	0.3±0.4	0.2±0.1	0.5±0.9
NO_3-N	1.2±2.7	10.2±3.0	5.9±1.7	11.3±2.6
Total P	4.0±1.9	1.0±0.9	0.9±0.4	1.1±0.5

The MBR performance was monitored regularly by the following analyses: COD, SCOD, TKN, pH, NH_4-N, NO_3-N, P and TSS/TVS [5]. Metals concentrations were analyzed in the mixed liquor, in the influent and in the effluent according to the EPA [6].

3. Results and discussion

The MBR system performance was monitored regularly at each SRT condition: 10 d (Run 1), 190 d (Run 2) and >200 d (Run 3). The applied SRT was a direct consequence of the biomass concentration that was already fixed in the experimental period settings according to the limit for oxygen supply suggested by literature [7]. This can be justified by the fact that the experiments were carried out to get a preliminary idea of the optimal operational periods and of the target for future developments of the study.

3.1. Excess biomass production and SRT

If the plot of MLVSS vs. SRT is considered, it is possible to observe the difference in the correlation between the two parameters in different situations (Fig. 1): the trend shown by ASM2 simulation [8] followed the literature and experimental data only for SRT < 20 d (Fig.1a).

For MLSS > 6 g/l, literature data seem inconsistent both with our experimental data and with the model results. In any case, for long SRT the model is not reliable and other types of simulations have to be considered in the further works: in fact, the minimum TVS percentage that the model gives to is 60%. Moving from Run 2 to Run 3 the trend seems to reach a plateau in MLVSS concentration; thus it can be reasonable

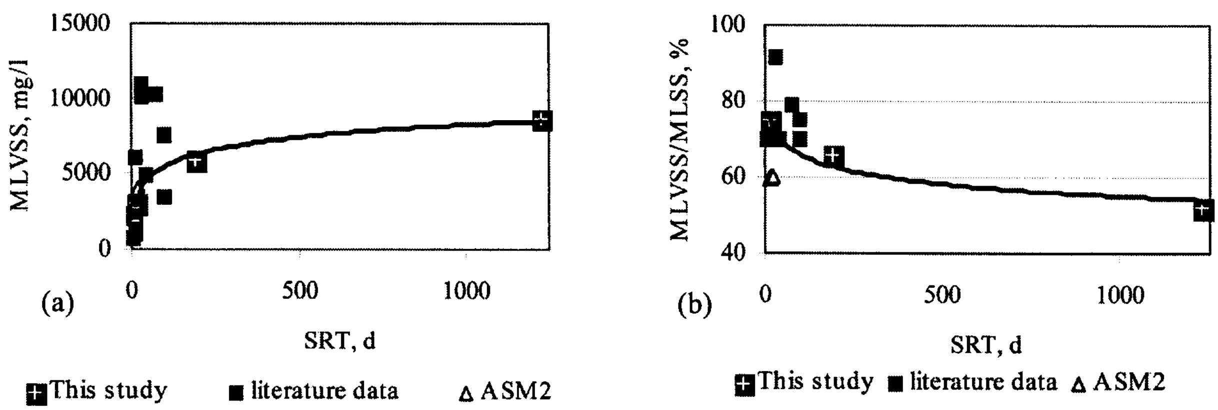

Fig. 1a, b. Plots of MLVSS vs. SRT during the SRT during the three experimental settings, in literature and by ASM2 simulations ([9–14]).

to substitute the real value of SRT with SRT >200 d when working with sludge ages longer than 200 d. The observed biomass production rate is expressed by the observed yield (Y_{obs}) (Table 2).

In substrate-limited wastewater processes the microorganism allocation of the available carbon source is preferentially orientated toward satisfying their maintenance energy requirements [15]. In fact, increasing the reactor biomass concentration from 4 to 9 g/l reduced biomass production by 84% and increasing biomass concentration from 9 g/l to 17 g/l reduce biomass production by 75% (Table 3). The progressive sludge mineralization is clear (Table 4) since the MLVSS fraction decreases operating with very high SRT leads to a stabilized sludge. This has to be taken into account when considering the choice of the anaerobic stabilisation treatment of the wasted sludge for biogas production and energy recovery. The specific biogas production (SGP) of the sole activated sludge is generally about 0.25– 0.35 m^3/kg VS fed [20]. However, this is strictly true only for sludge with a high content of volatile matter (~75–80% MLSS). In fact, some from 75% MLSS to 52% MLSS: this means that works have shown as sludge with a high content of inert matter, or originated from low loaded WWTPs, are characterised by a

Table 2
Average of sludge daily wasted[a] and biomass production rate

	Wasted sludge, gMLVSS/d	Y_{obs}, gMLVSS/gCOD
Run 1 (10 d)	380	0.56
Run 2 (190 d)	37	0.08
Run 3 (>200 d)	10	0.02

lower potentiality in biogas production, generally in the range 0.15–0.20 m^3/kg VS fed [21,22]. This is probably because of the high degree of the sludge stabilisation in the wastewater treatment line (Fig. 2) [20].

Therefore, when considering the typical characteristics of a sludge originated from a MBR process a SGP of 0.10 m^3/kgVSfed could be reasonably expected. This low biogas production could upset the energetic balance of the anaerobic digester; therefore, a good thickening of the sludge fed to the digester has to be obtained in order to maintain heating of the reactor (see Fig. 2b). If this is not possible, the co-digestion of the wasted sludge and other organic wastes should be chosen so to improve the biogas production yields [21]. Therefore, when treating a MBR sludge, one could choose to operate the MBR process with the highest SRT and produce

Table 3
Biomass production rate: comparison between the results of the experimentation and literature data

Reference	Type of treated wastewater	*F/M* (gCOD/gMLVSSd)	Y_{obs} (gMLVSS/ gCOD)	MLVSS (g/l)	SRT (d)
[16]	Synthetic	4.8	0.35	4.2	—
		0.30	3.9	—	
[14]	Theoretical[a]	—	0.38	2.3	5
			0.37	2	5
[11]	Domestic		0.37	0.45–0.7	5
This study	Domestic: 60%; industrial: 40%	0.21	0.56	3	10
[14]	Theoretical[a]	—	0.29	1.8	15
			0.26	6	15
[17]	Municipal	0.03–1[b]	0.35–0.53[b]	25[b]	20–30
[10]	Synthetic	0.13	<0.15	10	30
[14]	Theoretical[a]	—	0.17	10.9	30
			0.16	10.4	30
[18]	Municipal	0.034[c]	0.57	12[b]	38
[11]	Domestic		0.33	4.9	40
[7]			0.25[b]	15[6]	50
[19]	Domestic: 75%; industrial: 25%	—		10[b]	60
This study	Domestic: 60%; industrial: 40%	0.08	0.08	6	190
		0.02	0.02	9	>200

[a]The results were obtained by modeling; [b]MLSS was used instead of MLVSS; [c]kgBOD_5/kgMLSSd.

Table 4
Mixed liquor properties at different sludge ages

Parameter	Run 1 (10 d)	Run 2 (190 d)	Run 3 (>200 d)
MLSS, mg/l	3,663 ± 135	9,006 ± 1,579	16,631 ± 2,337
MLVSS, mg/l	2,980 ± 327	5,917 ± 974	8,658 ± 1,160
MLVSS/MLSS, %	75	63	52

a quite stabilised sludge to be directly disposed after dewatering or, on the other hand, choose to work applying a reasonable SRT so to exploit the benefits deriving from the anaerobic treatment of the wasted sludge. Obviously, the first choice is not economically sensitive as no energy is recovered.

3.2. Nutrients removal

The expected reduction of biomass viability related to %MLVSS reduction did not affect nitrification kinetics when passing from Run 1 to Run 2: AUR increased from a minimum of 0.13 to 2.51 mgNH_3N/gVSSh [4]. A decrease was observed in Run 3 with an average AUR value of 1.15 mgNH_3N/gVSSh but without affecting the final effluent quality (Table 1). Nitrification was at its maximum value in Run 2 confirming that MLSS = 8–10 g/l is the optimal concentration for our system. The influent was essentially muni-

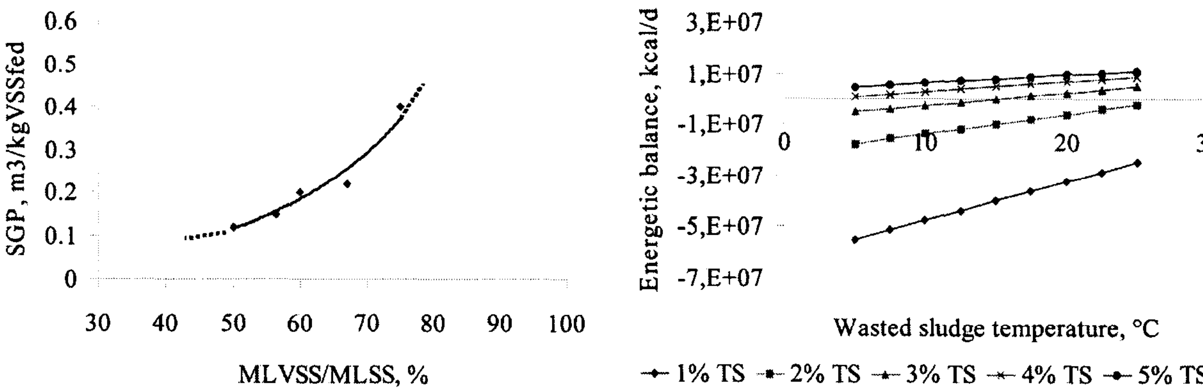

Fig. 2. (a) Influence of the MLVSS content in the activated sludge on the SGP. (b) Energetic balance of an anaerobic digester for different wasted sludge temperature, varying the solids concentration in the feed.

cipal but the influence of the industrial portion affected the denitrification process in all the three periods: in two of the three runs NO_3-N concentration exceeded the standard limits for the discharge in the lagoon of Venice: the possibility of enhancing the organic loading by shortening the operational cycles and/or by the addition of readily biodegradable substrates as could be the products obtained by the anaerobic fermentation of the organic fraction of municipal solid wastes (OFMSW) is a consolidated application [23] and showed good results with an SBR [24]. The best sludge age was confirmed by NUR: 190 d SRT seemed the most efficient operational condition since NUR reached a value of 0.74 mg/gVSSh while in the other two periods only 0.2 mg/ gVSSh was achieved. The effluent quality in terms of total nitrogen and total phosphorus (Table 1) increased only when passing from short SRT to long SRT; on the contrary, a slight quality decrease was observed when moving to very long SRT indicating that 8–10 g/l was probably the optimal biomass concentration.

3.3. Metals removal

The fate of metals in sludge depends significantly on the chemical form and speciation of the metal; a major role in metals removal is also

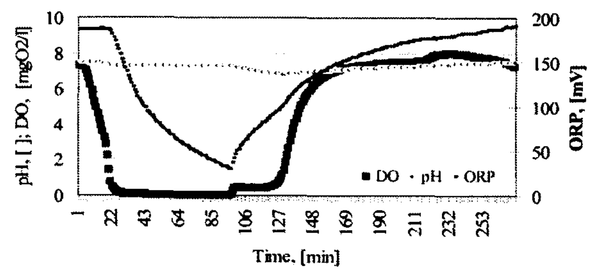

Fig. 3. Typical trend for pH, dissolved oxygen and ORP during one cycle of operation.

played by pH and ORP of the system together with the presence of the suspended organic matter. The alternating of anoxic and aerobic conditions in the studied system makes the understanding of the process more complicated.

In the MBR operational cycle the predominant conditions are aerobic (aerobic/anoxic ratio: 1.7) and the intense aeration which takes place prior to discharging the final effluent gives to range values for pH and ORP of 6.9–7.5 and +30–+190, respectively (Fig. 3). These conditions led to an oxidized environment where metal species can be present in their higher state of oxidation. Metals removal was detected in Runs 2 and 3 (Fig. 4).

The degree of removal was generally increasing for most species with the total biomass in the reactor (Fig. 4). Generally, at pH<8, Cd^{2+} is reported to be the dominant form (>95%) [25],

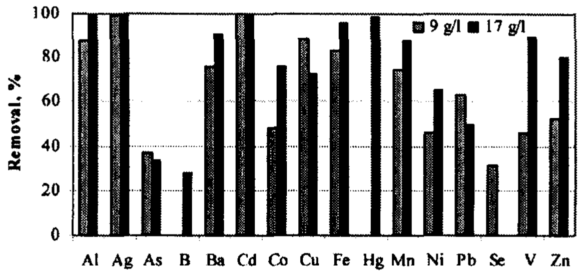

Fig. 4. Percentage of metals removal during Run 2 and 3.

and this could facilitate the adsorption of the metal to sludge particles; in fact, for pH>7 it can precipitate or adsorb to mineral surfaces [26] independently by the presence of organic matter. Copper removal was quite high (72–89%) thanks to the affinity of Cu for organic and humic substances: this can be supported by the fact that the removal decreases with the TVS fraction (Run 2) (Fig. 4). For other species (As, Pb, Se and B) the SRT increase did not enhance their removal rate; this may indicate that adsorption onto biomass is not the main removal process in these conditions of pH and ORP. The removal of Pb had varying behavior due to its inconstant presence in the influent: anyway removal ratios were in the range 50–65%. B and Se seemed not to be efficiently retained by the biomass in both experimental conditions (0–28% and 0–31%, respectively) though they do not represent a serious concern for discharge limits. As was a major concern since its removal ratio was 33–37% and its concentration exceeded the standard limits (e.g., 10 mg/l). In aerobic environments As(V) is dominant usually in the form of arsenate (AsO_4^{3-}) in various protonate states (H_2AsO_{4-}, $HAsO_4^{2-}$ or AsO_4^{3-}) over the pH range typically encountered in water treatment [27]. On the contrary, As(III) is non-reactive below pH 9 because then it is present predominantly in non-ionic form (hydrogen arsenite, H_3AsO_3) [28]. Membrane processes can remove As through filtration and adsorption of As-bearing compounds. Recent research in UF has shown that electric repulsion of UF plays an important role in As rejection beyond that achievable with only pore size-dependent sieving and that uncharged membranes show poor rejection of both As(V) and As(III) [29]. According to this theory, the scarce removal of As could be due to the reduction in electrostatic forces by adsorption of organic matter to the membrane surface that can reduce the surface charge of the membrane and increase the repulsion towards negatively charged As compounds like As(V) protonated forms. The next step of the research will focus on the possibility of enhancing As removal by looking at alternative technologies to integrate with the UF process.

4. Conclusions

The effect of different sludge ages on the performances of an UF-hollow fiber pilot-scale MBR was tested. The following evidence was found:

- increasing the reactor biomass concentration reduced biomass production by up to 84% together with the decrease of MLVSS fraction to 52%TSS;
- the partial stabilization of the activated sludge when applying very high SRT leads to a low content of the volatile matter and a decrease in the biogas production. Therefore, it seems sensible to operate to a biomass concentration <10 g/l so to produce a not stabilized sludge and exploits the benefits originated from the application of the anaerobic digestion process in terms of energy production. However, major efforts to comprehend this problem need to be done in future work;
- the reduction of biomass viability did not affect nitrification kinetics when passing from Run 1 to Run 2: AUR increased from a minimum of 0.13 to 2.51 $mgNH_3N/gVSSh$. A decrease was observed in Run 3 with an average AUR value of 1.15 $mgNH_3N/gVSSh$ but without affecting the final effluent quality;

- on the basis of nitrogen mass balances 190 d SRT seemed the most efficient operational condition since NUR reached a value of 0.74 mg/gVSSh while in the other two periods only 0.2 mg/gVSSh was achieved;
- the effluent quality increased only when passing from short SRT to long SRT; on the contrary, a slight quality decrease was observed when moving to very long SRT;
- metals removal increased with SRT enhancement for Al, Ag, Ba, Cd, Co, Fe, Hg, Mn, Ni, V and Zn; As, B, Cu, Pb and Se removal generally decreased with longer sludge ages; As was a major concern since its removal ratio was 33–37% and its concentration exceeded the standard limits.

In conclusion, it can be stated that the optimal operational conditions to apply for both nutrients and metals removal consist in a MLSS concentration around 9 g/l and a sludge age of 190 d. The next step of the research will focus on the possibility of enhancing, in these operational conditions, As removal by looking at alternative technologies to integrate with the UF process.

5. Symbols

AUR — Ammonia uptake rate, mgNH_3-N $gVSS^{-1}$ h^{-1}
EPS — Extra cellular polymeric substances
GAC — Granular activated carbon
MBR — Membrane bioreactor
MLSS — Mixed liquor suspended solids, mg l^{-1}
MLVSS — Mixed liquor volatile suspended solids, mg l^{-1}; %MLSS
NH_4-N — Ammonia nitrogen, mgN l^{-1}
NO_3-N — Nitric nitrogen, mgN l^{-1}
NUR — Nitrate uptake rate, mg $gVSS^{-1}$ h^{-1}
OFMSW — Organic fraction of municipal solid waste
RBCOD — Readily biodegradable chemical oxygen demand, mgO_2 l^{-1}
SRT — Sludge retention time, d
TKN — Total Kjieldahl nitrogen, mgN l^{-1}
TSS — Total suspended solids, mg l^{-1}
TVS — Total volatile suspended solids, mg l^{-1}; %TSS
WWTP — Wastewater treatment plant
Y_{obs} — Observed yield, mgMLVSS $mgCOD^{-1}$

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