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Impact of decreasing COD/N ratio on nitrogen removal and fouling in a membrane bioreactor for urban wastewater treatment

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ABSTRACT

This research focused on the identification of the minimum COD/N ratio needed for the complete two-step denitrification process. Thus, to quantify the role of low COD/N ratios on nitrification and denitrification rates and on biological suspension filterability, experiments were carried out on a laboratory-scale membrane bioreactor (MBR) with a nitrogen loading rate of 0.16 kg N m^{-3} d^{-1}. The investigation was comprised of two COD/N ratios, 3.5 and 5, and two sludge retention times (SRTs), 40 and 60 d. The best nitrogen removal performances were obtained when working with a COD/N ratio of 5 and a SRT of 60 d; nitrification and denitrification were achieved with total nitrogen removal reaching 82%. Experimental results appeared in good agreement with activated sludge model no. 1 (ASM1) predictions. Nevertheless, the minimum COD/N according to ASM1 was found close to 6.3, underlining that the hydrolysis phenomenon was underestimated when working at high sludge retention. The MBR performances confirm that operation at low organic loading rates is a promising strategy for decreasing energy requirements, without hampering water quality (nitrogen removal). More specifically, it allowed a significant reduction of oxygen requirements for carbon biodegradation and lower suspended solids in the bioreactor even at high SRT, allowing easier control of membrane fouling.

Keywords: Membrane bioreactor; COD/N ratio; Biodegradation; Fouling; Nitrogen removal

1. Introduction

Urban wastewater treatment plants have been developed to remove particulate, colloidal and dissolved organic fractions and, in more sensitive areas, nitrogen and phosphorus compounds. The introduction of a membrane bioreactor (MBR) instead of conventional activated sludge (CAS) has brought numerous advantages such as compactness, a total independence between hydraulic retention time (HRT) and sludge retention time (SRT), high and stable treated water quality, and easier facility control [1–5]. Nevertheless, MBRs still present a significant limitation linked to the greater energy requirements (30%–60%) due to the aeration supply for (i) aerobic reactions in more concentrated biological suspensions and (ii) membrane fouling control [6,7]. For instance, energy consumption of membrane related modules was found to be in the range of 0.5–0.7 kWh m^{-3} [8].

Thus, to maintain the advantages of MBR while reducing the global energy footprint [9], removal of most of the organic compounds during the primary treatment (physical–chemical process) is an option. This concept could also be based on a high-rate efficiency system (optimised flocculation with internal and external solid recirculation) used to extract most of particulate organic matter from wastewater. Thus, the downstream MBR is only used to achieve nitrification/denitrification whilst maintaining a high quality of treated water for potential effluent reuse (Fig. 1).

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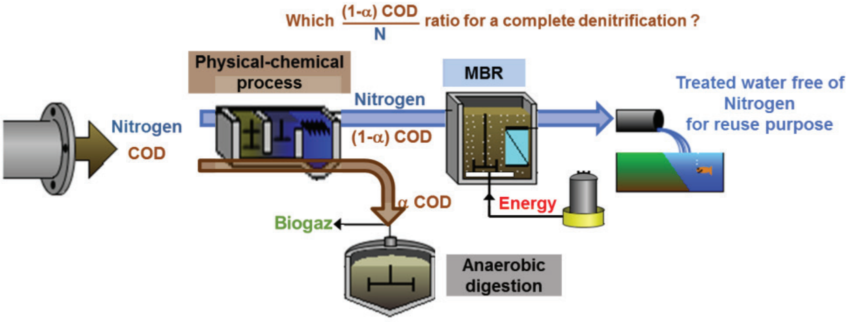


Fig. 1. Concept of intensive urban wastewater treatment.

The main advantages of this concept are, on one hand, to boost biogas production by feeding the anaerobic biogas production process with high-range fresh primary organic sludge [10]. On the other hand, it reduces the MBR energy demand by (i) reducing oxygen needs for COD oxidation (aeration demand for biological reaction) and lastly by (ii) decreasing the air scouring membrane requirement by decreasing biomass concentration (low *F/M* ratio). Subsequently, the biological role of such an MBR is mainly devoted to nitrogen removal by (i) oxidizing ammonium, which is weakly retained in the primary step, into nitrate and (ii) reducing generated nitrate in gaseous nitrogen at the expense of the residual soluble organic matter utilised as an electron donor. As a result, the COD/N ratio of the influent entering the MBR, which directly depends on the COD removal performance of the primary treatment, becomes the key criterion to ensure complete nitrate reduction. This should not be below a certain value; otherwise the denitrification would be incomplete [11–14]. In addition, and as mentioned earlier, the smaller this ratio is, the lower the heterotrophic biomass activity (growth and decay) would be in the MBR, including mixed liquor suspended solids (MLSS) concentration and the production of soluble microbial products (SMP). Hence, the development of an MBR with relatively low suspended solid concentrations becomes possible even with a high SRT under certain COD/N conditions [15–18]. This research thus focused on the quantification of MBR performances, such as nitrogen removal, biomass growth rates and suspension filterability, when working with low COD/N ratios and high SRT. According to Verstraete and Philips [19], a minimum value of 3.5 for the COD/N ratio is required in order to conduct a complete two-step denitrification reaction (denitratation followed by denitritation). This ratio is the stoichiometric ratio required to achieve nitrate reduction in molecular nitrogen. Several authors carried out experimental studies to determine the value of the minimum COD/N ratio. They recommended having COD/N ratios in the range of 3–7 to ensure a complete two-step denitrification reaction. Among those studies, the important differences for the obtained minimum COD/N ratio value are due to the nature of the utilised organic carbon sources, the process design (configuration, continuous or sequenced aeration,…) and the plant scale (laboratory scale or industrial scale). Thus, this study was carried out for two COD/N ratios, 3.5 and 5. These ratio values correspond to the COD removal efficiency by primary treatment of 60% and 45% respectively, considering a daily average value close to 700 mg COD L^{-1}, which is the value generally recorded for raw urban wastewater in France and a daily average COD/N ratio in the range of 10–12 [20]. To be able to monitor the system behaviour easily, several macroscopic indicators (apparent coefficients) were introduced and quantified. In addition, as opposed to most experimental studies investigating the COD/N ratio effect reported in literature, this work was based on a prior modelling analysis using activated sludge model no. 1 (ASM1). The latter helped to identify the values of the COD/N ratio and the SRT which allow the complete two-step denitrification process to take place. A series of simulations was also run to support the obtained experimental results.

2. Materials and methods

2.1. Experimental setup and operational conditions

The lab-scale MBR (Fig. 2) was equipped with two 30 L continuously stirred reaction vessels connected in series, one (N tank) worked in aerobic conditions, and the other (DN Tank) in anoxic conditions. In order to provide nitrates from the aerated tank to the anoxic one, the recirculation pump was set at 552 L d^{-1} providing a recirculation rate (*R*) of 4.6. The flat sheet polyethersulfone membrane module was immersed in the aerobic tank. This ultrafiltration module (Microdyn-Nadir™, Germany) has a filtering surface of 0.34 m^2 and an effective pore diameter of 0.04 μm together with an initial hydraulic resistance of 1.2×10^{12} m^{-1}.

The filtration was carried out at a constant permeate flow rate using a Netzsch volumetric suction pump. The membrane fouling was controlled by the association of (i) the continuous injection of fine air bubbles through air diffusers placed just below the membrane module and (ii) sequences of relaxation and backwashing. Each filtration cycle lasted 10 min, including an 8.75 min filtration period at a flow rate of 16.9 L m^{-2} h^{-1} (LMH), followed by a 0.25 min relaxation (no filtration), then 0.75 min backwashing period with a reverse flow rate of 8.8 LMH and finally 0.25 min relaxation. Thus, the average effective filtration flow rate (J_w) was 14.4 LMH.

Experiments were carried out with synthetic wastewater composed of a mixture of soluble biodegradable organic matter (S_S = sodium acetate and ethanol (1:1)), ammonium salts (S_{NH} = ammonium chloride) and mineral salts (KH_2PO_4) for the phosphorus supply were added to the influent in order to keep the required ratio COD/P equal to 100/1. The bioreactor was inoculated with seeding sludge taken from an activated sludge process treating domestic wastewater under extended aeration (solid retention time of 20 d) in the Montpellier area (France). After 40 d of acclimatization, the pilot was fed according to the process parameter given in Table 1 (J_w, SRT, HRT, OLR, nitrogen loading rate and COD/N ratio).

2.2. Analytical methods

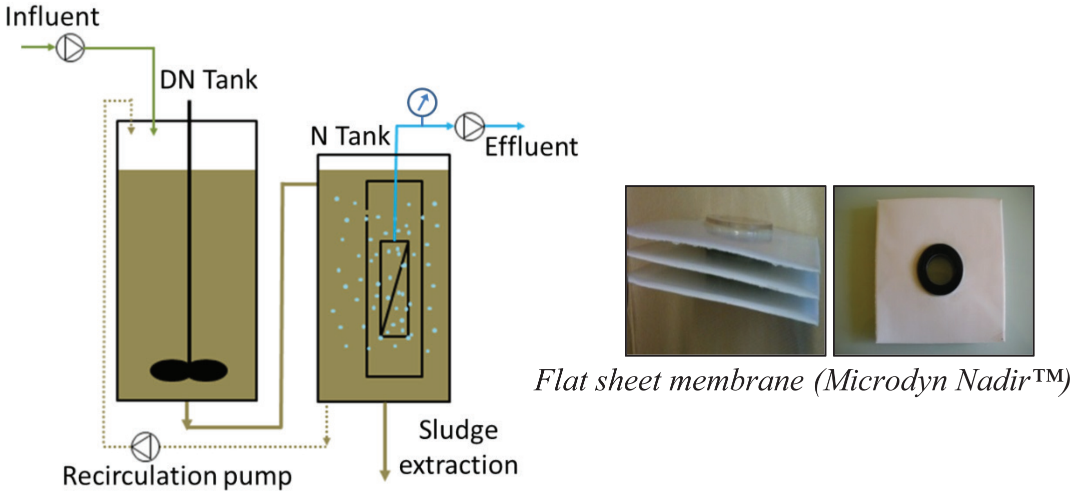
The characterisation of mixed liquor and permeate quality were evaluated through conventional measurements using standard methods (APHA, AWWA, WEF, 2005, Standard Methods for the Examination of Water and Wastewater). Nitrogen compounds (N–NH_4, N–NO_2 and N–NO_3) were analysed by spectrophotometric analyses on a HACH 3900 (method salicylate by Amver 26069-45 Test N'Tube™ and the cadmium reduction method by NitraVer® 5 tests, Hach, Loveland, CO, USA) and/or by a continuous sensor using Varion®Plus 700 IQ probe. COD and nitrogen compound measurements were taken twice a week in the anoxic and aerobic reactors and in the permeate. Mixed liquor samples were filtered on a 1.2 µm glass microfiber (Whatman® GF/C) prior to analysis. The pH value was maintained at 7.2 ± 0.2 by the addition of NaOH (2 mol L^{-1}) in the aerobic tank. To evaluate the biological activity, oxygen uptake rates (OURs) were measured in separate respirometric batch reactors by taking off sludge samples from the bioreactor and measuring oxygen consumption rates under endogenous and exogenous conditions [21].

A specific procedure [22] which consisted of gradually removing the different layers of fouling (rinsing, wiping, chemical cleaning) and measuring their respective hydraulic resistances was used at the end of experiments. Then, the fouling intensity could be linked to reversible deposit (R_c), biofilm (R_{bio}) and non-reversible internal fouling (R_{ads}).

2.3. Respirometry and biokinetic coefficients

The biomass activity was evaluated through the measurement of OURs [21]. OURs were quantified directly inside the reactor chambers and in separate batch reactors by taking off some sludge samples from the bioreactor. Batch OUR measurements were conducted under (i) endogenous conditions (without substrate addition) to compare the specific respirometric needs of autotrophic and heterotrophic populations, and under (ii) exogenous conditions (with an addition of N–NH_4 or COD) to evaluate experimentally stoichiometric criteria such as $gO_{2\text{Consumed}} - gN\text{–}NH_{4\text{Removed}}^{-1}$ and $gCOD_{\text{Removed}} \cdot gN\text{–}NO_{3\text{Consumed}}^{-1}$ ratios.

The "steady state" conditions observed during the four operating phases allowed the calculation of overall biokinetic coefficients. The same coefficients were also computed from simulations run using ASM1. Based on mass balances, the following coefficients describing biomass growth were calculated:



Flat sheet membrane (Microdyn Nadir™)

Fig. 2. MBR experimental setup and flat sheet membrane.

Table 1
Operational conditions

	Days of operation	SRT (d)	HRT (h)	J_W (L h^{-1} m^{-2})	OLR (kg COD m^{-3} d^{-1})	NLR (kgN m^{-3} d^{-1})	COD/N (g COD g N^{-1})
Phase 1	D1–D37	40	12	14.8	0.81	0.16	5
Phase 2	D38–D102	40	12	14.8	0.56	0.16	3.5
Phase 3	D103–D198	60	12	14.8	0.56	0.16	3.5
Phase 4	D199–D254	60	12	14.8	0.81	0.16	5

- Apparent biomass growth rate (r_{app} [g_{VSS} L^{-1} d^{-1}]) (with the absence of biomass in influent and permeate):

$$V * r_{\text{app}} = Q_{\text{extracted}} * \text{MLVSS} \tag{1}$$

with V as the total volume of bioreactor (60 L); $Q_{\text{extracted}}$ as the daily volumetric flux of extracted sludge (L d^{-1}) and MLVSS as mixed liquor volatile suspended solids concentration (g_{VSS} L^{-1}).

- Apparent biomass growth ratio (μ_{app} [d^{-1}]):

$$\mu_{\text{app}} = r_{\text{app}}/\text{MLVSS} \tag{2}$$

- Apparent conversion yield (Y_{obs} [g_{VSS} g_{COD}^{-1}]):

$$Y_{\text{obs}} = r_{\text{app}}/\text{OLR} \tag{3}$$

Assuming that easily biodegradable organic carbon present in the influent was totally consumed by the biomass (the residual COD in the permeate was in fact composed of SMP [22]), the total flux of the removed COD could then be considered as equal to the organic loading rates (OLRs) imposed on the bioreactor as indicated in Eq. (3). The same coefficients were also computed from simulations run using ASM1 by using the default kinetic parameters at 20°C [23].

2.4. Models

ASM1 was adopted to validate the obtained MBR experimental results and default parameters given at 20°C were employed [24]. Simulations were performed with GPSX® software (Hydromantis, Canada). The two tanks were assimilated to be perfectly stirred reactors. Membrane separation was considered as a perfect particle separator with a negligible volume.

ASM1 was also used to model the minimum COD/N needed for a complete two-step denitrification process. Several COD/N ratios could be defined from the influent composition as well as from the activated sludge model (ASM) pathway. Besides, in order to pay attention to the hydraulic configuration, the recirculation rate and the aerobic oxygen concentration, all of these operand parameters must be taken into account for COD/N definition.

Taking only exogenous substrate, which means COD contained in the influent, and assuming perfect anoxic conditions, the minimum COD/N ratio required to ensure complete denitrification ($\text{N–NO}_3^- \rightarrow \text{N}_2$) can be calculated using ASM1 equations. This is estimated using Eq. (4). In the case of partial denitrification ($\text{N–NO}_3^- \rightarrow \text{N–NO}_2^-$) [25], this ratio decreases (Eq. (5)):

$$\frac{\text{COD}}{\text{N}} = \frac{2.86}{1 - \text{Y}_{\text{H}}} \tag{4}$$

$$\frac{\text{COD}}{\text{N}} = \frac{1.14}{1 - \text{Y}_{\text{H}}} \tag{5}$$

where Y_H is the growth yield for heterotrophic bacteria (g_{COD} g_{COD}^{-1}). Using default parameter values [23], the given minimum COD/N ratio is 8.67. However, this value is too high, as many studies reported complete two-step denitrification at much lower ratios. New substrate production due to biomass lysis must be then taken into account for the theoretical ratio determination. Indeed, according to the death–regeneration concept, biomass decay produces particulate substrate (X_S) that needs to be hydrolyzed before consumption. This phenomenon occurs with a COD/N ratio of zero (COD/N = 0). As anoxic processes (substrate hydrolysis and bacterial growth) are slower than the aerobic ones, a correction factor ($\eta = \eta_{\text{H}}\, \eta_{\text{G}}$) is used [23]. Consequently, the total COD available for heterotrophic biomass anoxic growth is given by Eq. (6).

$$Q\ \text{COD} = QS_S + \eta\left(1 - f_p\right) b_H X_{\text{BH}} V_{\text{Anoxic}} \tag{6}$$

where Q is the influent flow rate (L d^{-1}); S_S is the soluble organic substrate (mg L^{-1}); ($1–f_p$) is the fraction of particulate organic matter released during biomass decay; b_H is the decay rate of heterotrophic bacteria (d^{-1}); X_{BH} is the heterotrophic bacteria concentration (mg L^{-1}) and V_{Anoxic} is the volume of anoxic tank (L).

Furthermore, only the recycled part of nitrate $\left(\frac{\text{R}}{1+\text{R}}\right)$ from the aerobic to the anoxic tank is denitrified (used as a final electron acceptor during the oxidation of organic carbon). But, internal recirculation brings back mixed liquor which contains nitrate as well as dissolved oxygen (DO). As a result, perfectly anoxic conditions are not achieved, leading to the loss of a significant amount of COD which is degraded by recycled oxygen as heterotrophic bacteria use oxygen in preference to nitrate as a terminal electron acceptor [26]. Assuming 1 g O_2 is required for the removal of 2 g COD [27,28], with a recycling ratio (R) of 460% and a DO concentration higher than 6 mg O_2 L^{-1}, at least 55 mg COD L^{-1} is consumed only by oxygen recycling. Hence, the minimum COD/N ratio can be evaluated by Eq. (7) combining previous equations (Eqs. (4) and (6)) and taking into account the COD loss:

$$\frac{\text{COD}}{\text{N}} = \frac{\dfrac{2.86}{1-\text{Y}_{\text{H}}}\dfrac{\text{R}}{1+\text{R}} + \dfrac{2\text{R DO}}{\text{N}}}{1 + \eta\left(1 - f_p\right)\text{b}_{\text{H}} \dfrac{\text{Y}_{\text{H}}\text{SRT}^{\text{HRT}_{\text{An}}}/_{\text{HRT}}}{1 + \text{b}_{\text{H}}\text{SRT}\left(1 - \text{Y}_{\text{H}}\left(1 - f_p\right)\right)}} \tag{7}$$

where N is the ammonia concentration in the influent (mgN L^{-1}). The obtained minimum ratio is indeed linked to hydraulic configuration $\left(\frac{\text{R}}{1+\text{R}}\right)$, oxygen content in the underflow loop $\left(\frac{2\text{R DO}}{\text{N}}\right)$ and to SRT as it depends on active biomass concentration. Simulations of theoretical minimum COD/N ratios for different SRT values ranging between 10 and 80 d were carried out with ASM1 parameters set to the default values and under the following operating conditions: HRT = 0.5 d, $\text{HRT}_{\text{Anoxic}}$ = 0.25 d, N = 80 mgN L^{-1}, R = 460% and DO = 6 mgO_2 L^{-1} (Fig. 3).

Simulation results were comparable to the results of Eq. (7) confirming the relevance of this output. Thus, the findings of Eq. (7) show how the choice of operating parameters related to biological reaction (SRT, DO, η: reduction factor due to anoxic condition) and hydraulic configuration (R) can influence the COD/N ratio. For SRT values of 40 and 60 d, the theoretical critical ratio are equal to 6.33 and 6.29, respectively. Unlike the expected results, no significant differences in minimum COD/N ratio values were observed for SRTs of above 42 days. Indeed, when the term described by $b_H SRT\left(1 - Y_H\left(1 - f_p\right)\right)$ becomes very high compared with 1, the minimum COD/N ratio is no longer dependent on SRT (Eq. (7)).

3. Results and discussion

Experimental MBR performances are discussed through the evolution over time of suspended solids, COD and nitrogen concentrations, respirometric activity of the biomass and biokinetic coefficients.

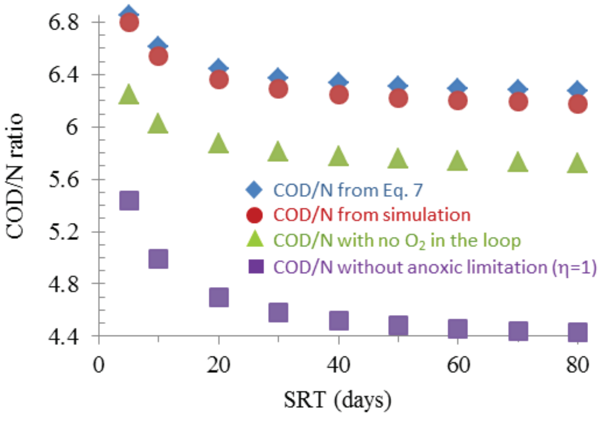


Fig. 3. COD/N evolution with SRT.

3.1. Evolution of suspended solid concentration in the reactor vessels

Fig. 4 shows the evolution of MLSS and mixed liquor volatile suspended solids concentration (MLVSS) in aerobic bioreactors for campaigns 1–4. The concentrations and their evolution were similar in both reactors due to the mixing conditions and the high recycling ratio imposed. In phases 1, 2 and 4, the concentrations of suspended solids were relatively stable. The MLVSS seemed to be clearly an increasing function of SRT and COD/N when comparing phases 1, 2 and 4. This point has already been observed [29] and is in accordance with the ASM3 model:

$$X_I = SRT(f_{XI} b_H X_{BH} + f_{XI} b_A X_{BA}) \tag{8}$$

Moreover, the concentrations of MLSS and MLVSS were roughly similar, meaning that the mineral fraction was very low despite working at high SRT. During phase 3, the addition of buffering mineral salt ($NaHCO_3$) was used to stabilise the pH in the anoxic tank, but such an operation induced salt precipitation, thus modifying the MLSS/MLVSS ratio and increasing the membrane fouling. A remarkable decrease in MLSS was observed. Surprisingly, the biomass concentration appeared lower than when working at a higher SRT with the same COD/N ratio (by comparing phases 2 and 3). This may be explained by an unexpected partial settling of biological flocs weighted by the presence of carbonate in their structure. In phase 4, a relatively low biomass concentration (<6 g L^{-1}) was obtained in the bioreactor in spite of a high SRT of 60 d and a COD/N ratio = 5. These results confirm the potential interest of working at low COD/N ratios, reducing, proportionately, the OLR. A low OLR leads to low biomass concentration, mostly for

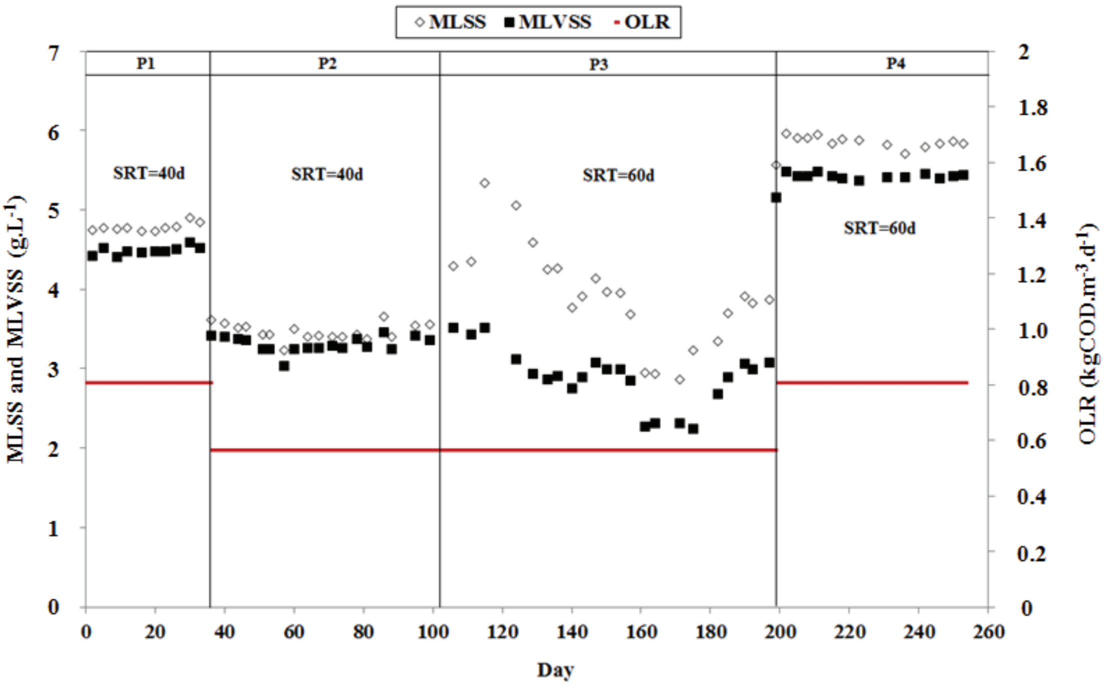


Fig. 4. Aerobic reactor MLSS and MLVSS vs. time for different organic loading rates and different SRTs.

the heterotrophic bacteria. This includes lower production of components released during the active biomass activity, mainly carbohydrates and proteins which means less SMP production. Consequently, lower SMP concentrations imply lower suspension viscosity, which allows sustainable operational conditions. Therefore, it is also possible to have a reduction of energy requirements for aeration, mixing and fouling control on an industrial scale [30–33].

3.2. COD removal

Fig. 5 shows the evolution of soluble COD concentrations in the anoxic and aerobic reactors and in the permeate. The COD concentrations in the supernatant were similar in both reactors. The significant difference between the soluble COD concentration in the permeate and in the supernatant highlights the determining role of the porous membrane barrier on the retention of small particles and large polymeric substances [22]. Regardless of the working conditions, a very low permeate COD concentration (<20 mg COD L^{-1}) was obtained, compared with the influent COD concentration (245–350 mg COD L^{-1}). This is mainly due to the total absence of suspended solids in the permeate, confirming the good separation performances of MBR in comparison to CAS systems. The pore size of the membrane barrier was more crucial during phase 3. The permeate COD concentration was maintained at almost the same level even though the soluble COD concentration in the bioreactor was very high and exceeded 200 mg COD L^{-1} on occasion (phase 3). Such high, fluctuating values indicated high SMP concentrations that were released due to unstable biological conditions caused by salt precipitation.

3.3. Nitrogen removal

Figs. 6 and 7 show the changes in concentration of nitrogen compounds ($N–NH_4^+$, $N–NO_3^-$ and $N–NO_2^-$) in the supernatant of anoxic and aerobic reactors, respectively, during the 252 d of operation. Concentrations of nitrogen compounds in the permeate flux were the same as in the supernatant of the aerobic reactor because these compounds cannot be retained by the membrane barrier. The results revealed that nitrification was complete. Indeed, a total oxidation of ammonium in the aerobic tank was observed whatever the conditions applied: in steady state operation, the average concentration of ammonium in the permeate was always less than 1 mgN L^{-1}, with an average value equal to 0.72 mgN L^{-1} and a standard deviation of 0.18. The ammonium concentration in the anoxic tank effluent corresponded to the value expected (17.5 mgN L^{-1}) according to the influent dilution with the recycling flow (R), proving that no ammonia consumption occurred in anoxic tank.

In the same way, the total concentration of oxidised nitrogen in the effluent (permeate) is close to the expected value (14 mgN L^{-1}) according to a complete oxidation of ammonium in the aerobic tank combined with a total reduction of the recycled oxidised nitrogen form in the anoxic tank. The nitrogen uptake due to the biomass growth was negligible (lower than 5% in accordance with the nitrogen ratio in biomass, 0.12 gN $gMLVSS^{-1}$ and the low biomass production).

Except at the end of phase 3, the reduction of the oxidised forms of nitrogen was achieved in the anoxic tank and the lowest COD/N ratio appeared adapted for a total two-step denitrification process. Nevertheless two periods revealed some limitations to this first conclusion. In fact, complete

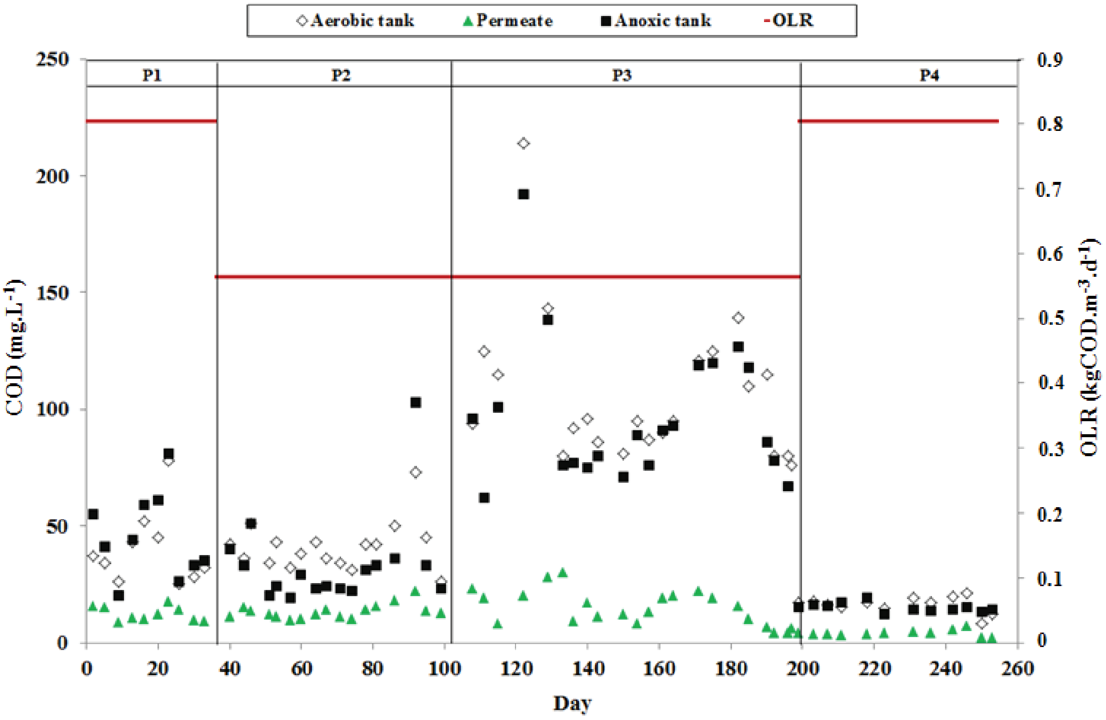


Fig. 5. Soluble COD concentrations vs. time for different organic loading rate.

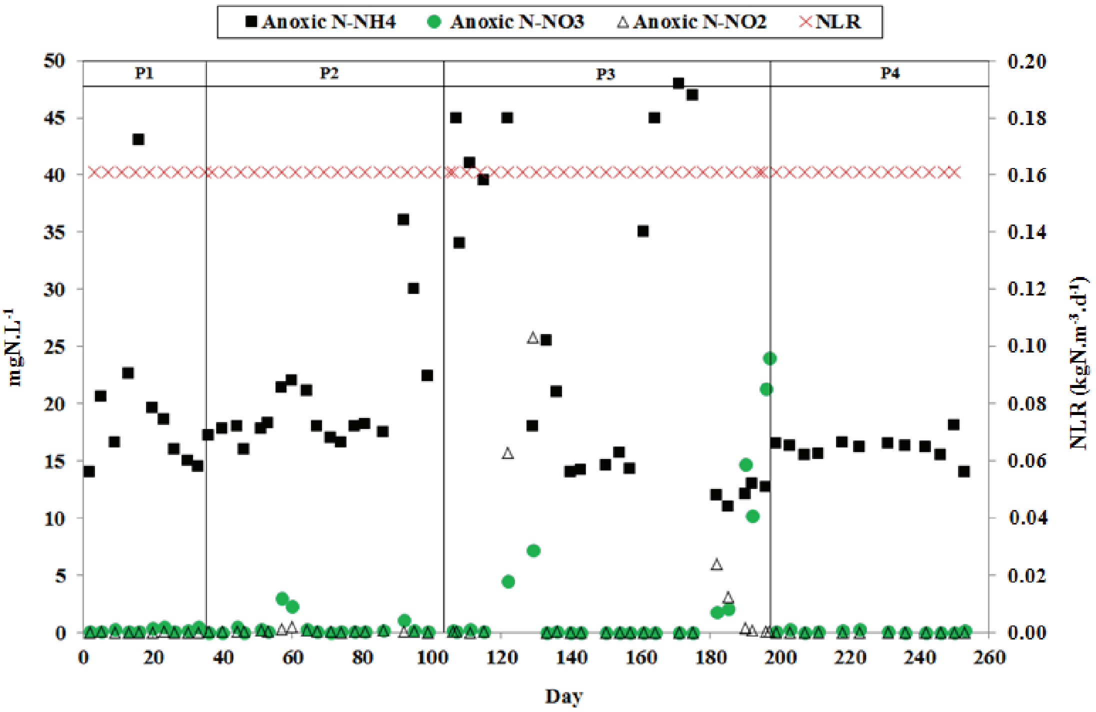


Fig. 6. Nitrogen compound concentrations in anoxic reactor vs. time.

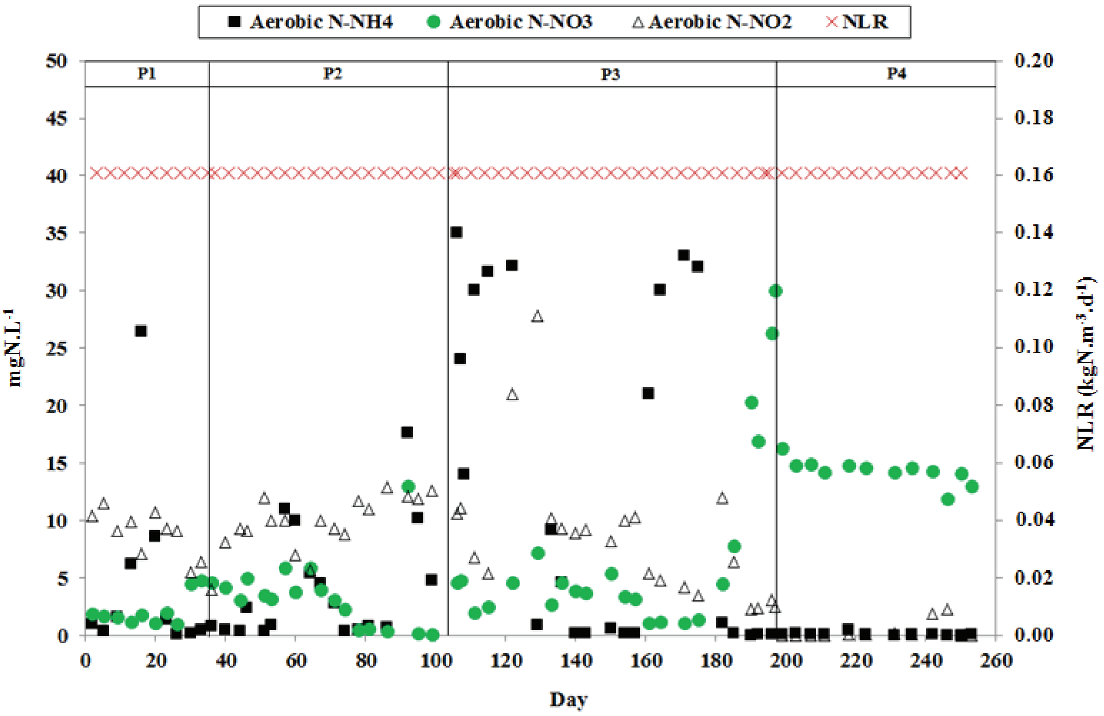


Fig. 7. Nitrogen compound concentrations in aerobic reactor vs. time.

nitrification was not achieved until the end of phase 3 in the aerobic reactor and a significant nitrite accumulation appeared. Thus, the reduction of oxidised forms of nitrogen could result from a shunt of nitrates requiring lower amounts of organic carbon [34,35]. At the end of phase 3, after more than 150 d of operation at a COD/N ratio of 3.5, nitrite oxidising bacteria were sufficiently adapted to these uncommon operating conditions and the nitrate production in the aerated tank recovered. But nitrate reduction was then not achieved in the anoxic tank, confirming the insufficient level of organic carbon when working with the lowest COD/N ratio of 3.5. During phase 4, nitrification was achieved in the aerobic tank and the COD/N ratio of 5 was then sufficient to ensure an efficient two-step denitrification in the anoxic reactor. Moreover, phase 4 showed very stable system performances when working with old sludge age (60 d) and a COD/N ratio of 5 (Figs. 3–6).

3.4. *Activity of autotrophic and heterotrophic microorganisms*

Electron acceptor consumption (O_2 for N–NH_4 or NO_3 for COD) was evaluated experimentally in order to measure stoichiometric criteria such as $gO_{2\text{Consumed}}.gN\text{–}NH_{4\text{Removed}}^{-1}$ and $gCOD_{\text{Removed}}.gN\text{–}NO_{3\text{Consumed}}^{-1}$ (Table 2).

The $O_{2\text{Consumed}}/N\text{–}NH_{4\text{Removed}}$ ratio is in the range of 4.1–4.5 except for phase 2 where nitrite accumulation was effective, justifying a lower value of 3.8. At the end of phase 3, when the nitrification was total, this ratio was then close to 4.3, as expected in order to achieve complete nitrification, whatever the conditions (COD/N or SRT). The $COD_{\text{Removed}}/N\text{–}NO_{3\text{Consumed}}$ ratio varied between 5.9 and 6.7 for phases 1 and 2 (SRT = 40 d) and 4.8 and 5.5 for phases 3 and 4 (SRT = 60 d). Thus, this ratio appeared as dependent on SRT. Such a result could indicate the interest of working at high SRT to favour lower needs of COD to reduce nitrates. These results are not in line with the simulation result (Fig. 3) suggesting that high SRT promotes the hydrolysis phenomenon. For example, Eq. (7) gives a COD/N of 4.52 when η_H is increased from 0.4 to 1 (Table 3).

3.5. *Apparent kinetic coefficients and ASM1 simulations*

Table 4 gives a comparison between experimental data and expected values obtained when simulating bioreactor

Table 2
Ratios between electron donor and acceptor in nitrification/denitrification

	Days of operation	Nitrification $\frac{O_{2\text{Consumned}}}{N-NH_{4\text{Removed}}}$ (kgO_2 $kgN\text{–}NH_4^{-1}$)	Denitrification $\frac{COD_{\text{Removed}}}{N-NO_{3\text{Consumned}}}$ (kg COD $kgN\text{–}NO_3^{-1}$)
Phase 1	D1–D37	4.1	5.9
Phase 2	D38–D102	3.8	6.7
Phase 3	D103–D198	4.3	4.8
Phase 4	D199–D254	4.5	5.5

Table 3
Minimum COD/N ratio (SRT = 40 d)

Minimum COD/N ratio	Eq. (7)	Eq. (7) No hydrolysis limitation (NHL)	Eq. (7) Incomplete denitrification (ID)	Eq. (7) Nitrates shunt
COD/N_m	6.33	4.52	4.01	2.84
This study	5		3.5	

Table 4
Kinetics coefficients: experimental data and ASM1 simulated values

		Phase 1 COD/N = 5, SRT = 40 d	Phase 2 COD/N = 3.5, SRT = 40 d	Phase 3 COD/N = 3.5, SRT = 60 d	Phase 4 COD/N = 5, SRT = 60 d
Aerobic tank MLVSS	Experimental	4.48	3.26	2.99	5.41
(g L^{-1})	modelling	4.62	3.39	4.61	6.29
r_{app} (gMLVSS L^{-1} d^{-1})	Experimental	0.112	0.082	0.050	0.090
	modelling	0.115	0.084	0.077	0.104
μ_{app} (d^{-1})	Experimental	0.025	0.025	0.017	0.017
	modelling	0.025	0.025	0.017	0.017
Y_{obs} (gMLVSS $gCOD^{-1}$)	Experimental	0.138	0.146	0.089	0.111
	modelling	0.142	0.151	0.137	0.129
$N\text{–}NH_{4\text{effluent}}$	Experimental	0.5	0.6	0.3	0.2
(mgN L^{-1})	modelling	0.2	0.2	0.2	0.2
$N\text{–}NO_{X\text{effluent}}$	Experimental	12.8	12.5	12.9	13.1
(mgN L^{-1})	modelling	12.6	25.4	25.0	12.7

performances using ASM1 (taking into account the functioning conditions indicated in Table 1).

The kinetic coefficients linked to the biomass growth rates were calculated. r_{app} appeared as an increasing function of the COD/N ratio, proving that heterotrophic species remained the dominant populations in the MBR, despite the low OLR. Except for phase 3, negligible differences (<15%) were observed between experimental and simulated values. μ_{app} and Y_{obs} decreased when the SRT increased. No significant gap was reported between simulation and experimental data for μ_{app}, and the differences remained low (<15%) for Y_{obs}, except for phase 3. By simulation, MLVSS appeared as a growing function of COD/N and SRT, as expected. Experimental results confirmed such a prediction (except for phase 3).

Concerning nitrogen removal, ASM1 simulations confirmed a low value of ammonium (<1 mg L^{-1}) in the effluent regardless of the operating conditions. In particular, there was a good concordance (<5%) between experimental data and simulations for the oxidised nitrogen concentration in effluent when working at a COD/N equal to 5, whatever the SRT.

Conversely, when working with the lowest COD/N ratio (3.5), significant differences were observed for oxidised forms of nitrogen compounds. Indeed, the ASM1 model assumes a complete nitrification (ammonium is totally oxidised to nitrate) and it predicts that only a partial denitrification can be obtained because of the lack of COD during phase 2 and 3 (COD/N = 3.5). The differences between model simulations and experimental results can then be explained by the phenomenon of nitrate shunt observed experimentally when working with an insufficient organic matter supply (COD/N = 3.5), thus making the reduction of nitrites possible with lower COD requirements.

3.6. Membrane fouling dynamics

The dynamics of membrane fouling was quantified through the evolution with time of the trans-membrane pressure (TMP), as shown in Fig. 8.

The real and apparent fouling rates and daily variation of the hydraulic resistance are summarised in Table 5. The real rate was calculated based on the instantaneous evolution of the TMP, whereas the apparent rate corresponded to the mean TMP rise measured during a number of consecutive filtration cycles. Fig. 9 shows the instantaneous values of TMP and how the fouling rates were calculated. The difference between both rates is basically due to the backwash effect on hydraulically reversible fouling.

According to Fig. 8, the TMP varied from 4 to 13 kPa and seemed controlled by the continuous supply of air to the membrane and backwashing except during occasional dysfunctional periods, notably during phase 3, when carbonate salt was added to the biological suspension for pH control. Nevertheless Fig. 9 clearly demonstrates the role of backwash by comparing the changes in TMP during the filtration time with an average TMP evolution after successive cycles of filtration, relaxation and backwash. Backwash is recognised as an effective tool for minimizing pore blocking but it probably plays an important role in the deconstruction of the biofilm and cake deposit. As found in our previous work [9], the low MBR MLVSS and the low TMP value observed highlighted backwash efficiency to provide sustainable filtration conditions.

Only five membrane cleaning procedures were operated during the whole experimental period (254 d), at the beginning of phases 2 and 4 and at the end of phases 2 and 4. The third cleaning was due to a one-time addition of a buffering

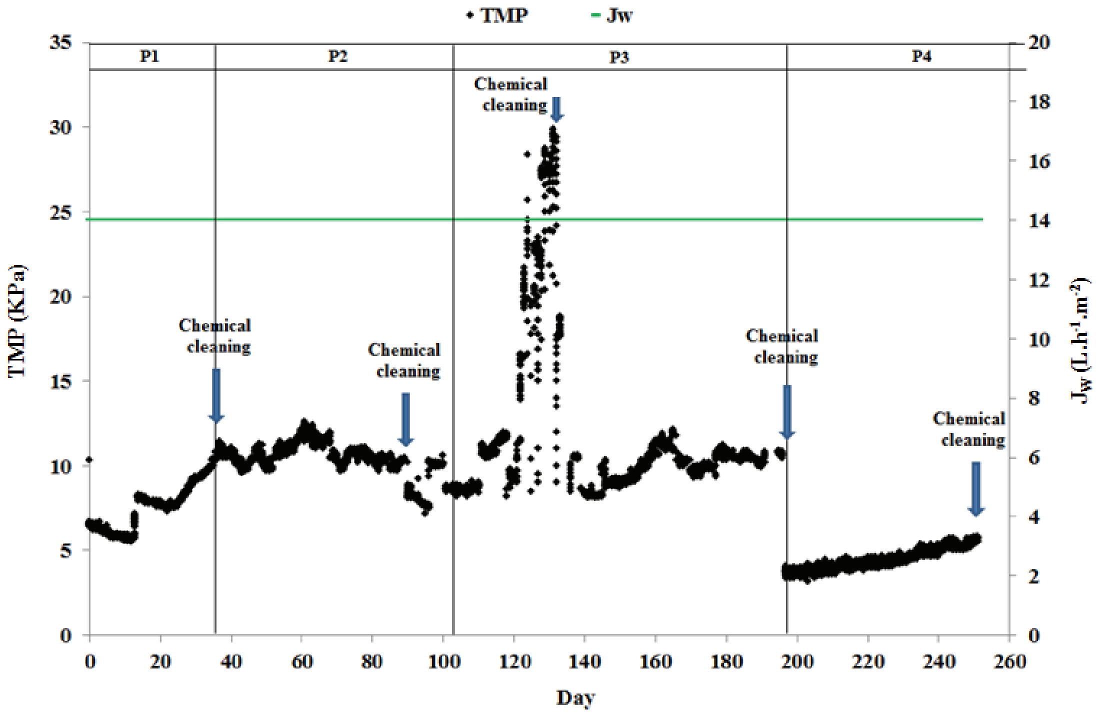


Fig. 8. Evolution of the trans-membrane pressure (TMP) with time during the different operating phases.

Table 5
Real and apparent fouling rates and average variation of the hydraulic resistance with time

	Real fouling rate (kPa d^{-1})	Apparent fouling rate (kPa d^{-1})	dR/dt (1012 m d^{-1})	dR/dt (references) (1012 m d^{-1})	Organic loading rate (kg COD m^{-3} d^{-1})
Phase 1	21.1	0.15	0.032	0.31 [37]	3
Phase 2	72.2	0.1	0.022	0.14 [38]	2
Phase 3	126.4	0.16	0.033	0.168 [39]	0.7
Phase 4	2.9	0.03	0.007		

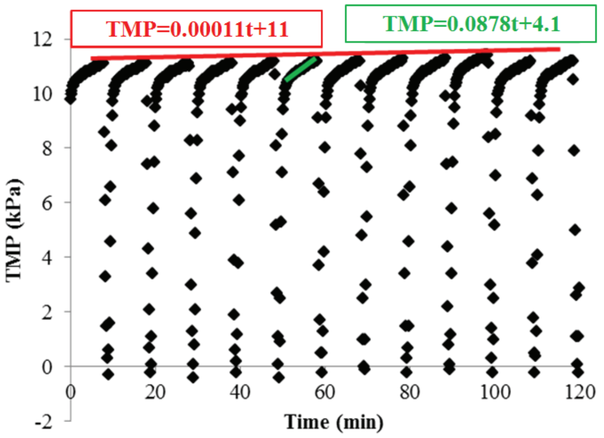


Fig. 9. Role of backwash on fouling rates: changes in TMP vs. time during the 120 min of operation for phase 3.

mineral salt (sodium bicarbonate) used to stabilise the pH. As this addition (i) did not prove to be useful and (ii) had negative effects on fouling, it was rapidly stopped. The cleaning procedure [22] enabled the origin of the fouling to be identified. This procedure was performed at day 254 of operation showing the relative impact of fouling on total hydraulic resistance. The initial membrane resistance remained the main cause of the total hydraulic resistance (71%). The fouling was mainly due to biofilm (irreversible fraction of deposit attached on the membrane surface) 22%, then the reversible deposit accounted for 6% of the total resistance. The internal fouling (adsorption of molecules with membrane material), which was only reversible by chemical cleaning, was negligible (1%).

These results are consistent with previous studies from our group and with those in the literature [9,16,36] and indicate that working at low COD/N ratio remarkably reduced the membrane fouling rate due to a slower rise in TMP compared with MBR operated at a higher COD/N ratio.

4. Conclusion

When treating domestic wastewater, the combination of a high rate primary treatment with a downstream MBR modifies the COD/N ratio in MBR influent. Then, the MBR role is mainly devoted to nitrogen removal. Such functioning conditions should minimise the energy requirements. Experimental results indicated a critical COD/N value of 5, allowing a perfect control of nitrification and denitrification operations. Moreover, high removal efficiency with no decline of the membrane performance was observed. Thus, the following points can be underlined when working with such COD/N ratio:

- The high rate primary treatment allows a significant reduction of oxygen requirements for biological activities by reducing the heterotrophic biomass development.
- Low biomass concentrations, lower than 6 gMLVSS L^{-1}, were reached in the bioreactor even with a high SRT (60 d) and no accumulation of mineral solids was observed despite the very high SRT value.
- As the heterotrophic activity was reduced, the soluble COD effluent was due to bacterial by-products and was always kept under 20 mg COD L^{-1}.
- The filtration management was easier to maintain thanks to low fouling rates (<0.16 kPa d^{-1}) leading to lower aeration rates needed for fouling control.
    - The ASM1 pathway was linearised making it possible to identify the influence of operating parameters on minimal COD/N ratio needed for a complete two-step denitrification. Nevertheless, experimental performances were better than simulation results, confirming the positive impact of old sludge age to overcome the anoxic limitations.

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Symbols

MBR	—	Membrane bioreactor (functioning under low COD/N ratio)
ASM	—	Activated sludge model
ASP	—	Advanced separation process
b_H	—	Decay rate of heterotrophic bacteria [0.62], d^{-1}
CAS	—	Conventional activated sludge
COD	—	Chemical oxygen demand (6), mg COD L^{-1}
DO	—	Dissolved oxygen, mgO_2 L^{-1}
dR/dt	—	Average variation of the hydraulic resistance with time, m d^{-1}
EPS	—	Extracellular polymeric substances
f_p	—	Fraction of particulate organic matter released during biomass decay (0.08)
J_w	—	Filtration flux, L m^{-2} h^{-1}
HRT	—	Hydraulic retention time (0.5), d^{-1}
HRT_{Anoxic}	—	Hydraulic retention time in anoxic tank (0.25), d

LMH — Industrial unit to quantify specific permeate flux, L m^{-2} h^{-1}
MLSS — Mixed liquor suspended solids concentration, g L^{-1}
MLVSS — Mixed liquor volatile suspended solids concentration, g L^{-1}
N — Nitrogen concentration (70), mgN L^{-1}
NLR — Nitrogen loading rate, kgN m^{-3} d^{-1}
N–NO$_x$ — Oxidised forms of soluble nitrogen compounds; sum of nitrate and nitrite concentrations, mgN L^{-1}
N–NO$_2^-$ — Nitrite concentration, mgN L^{-1}
N–NO$_3^-$ — Nitrate concentration, mgN L^{-1}
N–NH$_4^+$ — Ammonium concentration, mgN L^{-1}
OLR — Organic loading rate, kg COD m^{-3} d^{-1}
OUR — Oxygen uptake rate, mgO$_2$ L^{-1} h^{-1}
Q — Influent flow rate (120), L d^{-1}
$Q_{\text{extracted}}$ — Daily volumetric flux of extracted sludge, L d^{-1}
R — Recycling ratio between anoxic and aerobic tank (460), %
R_{ads} — Hydraulic resistance due to non reversible internal fouling, m^{-1}
R_{bio} — Hydraulic resistance due to biofilm formation on the membrane, m^{-1}
R_c — Hydraulic resistance due to reversible deposit on the membrane surface, m^{-1}
R_m — Hydraulic resistance of the clean membrane, m^{-1}
r_{app} — Apparent biomass growth rate, g$_{\text{VSS}}$ L^{-1} d^{-1}
SMP — Soluble microbial products, mg COD L^{-1}
SRT — Solid retention time, d
S_S — Concentration of soluble biodegradable organic matter, mg L^{-1}
TMP — Trans-membrane pressure, Pa
V — Volume of reactor (120), L
V_{Anoxic} — Volume of anoxic tank (30), L
X_{BH} – Heterotrophic bacteria concentration, mg L^{-1}
Y_{obs} — Apparent conversion yield, g$_{\text{VSS}}$ g$_{\text{COD}}^{-1}$
Y_H — Growth yield for heterotrophic bacteria (0.67), g$_{\text{VSS}}$ g$_{\text{COD}}^{-1}$
α — Ratio of COD removed by the ASP
μ_{app} — Apparent biomass growth ratio, d^{-1}
η — Anoxic correction factor ($\eta = \eta_G\ \eta_H$)
η_G — Anoxic growth factor (0.8)
η_H — Anoxic hydrolysis factor (0.4)

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