

Optimization of Membrane Bioreactors for the Treatment of Petrochemical Wastewater under Transient Conditions

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The main objective was to study the appropriateness of membrane bioreactor (MBR) technology in treating petrochemical wastewater under the variable conditions of the petrochemical industry. Five experimental periods were carried out; in the first period the operating conditions of the full scale MBR were examined, and then changes were introduced, such as the addition of more external carbon source, the decrease of the anoxic compartment volume, alternations in configuration and an increase of the influent load. Laboratory batch experiments were conducted in order to assess the impact of spent caustic soda on nitrification. Finally, the impact of fouling and clogging layers on the removal of trace metals/metalloids was studied during the long-term operation of the MBR. The results showed that the composition of petrochemical wastewater affected the biological processes. Specifically, in the pre-denitrification configuration ammonification was not effective, while ammonium oxidation was high. The addition of higher concentration of acetic acid compared to the one added to the full scale plant increased the denitrification rate and the organic carbon oxidation. The decrease in the volume of the anoxic compartment and the abolition of internal recycling reduced the rate of denitrification. Doubling the influent wastewater flow did not significantly affect the quality of the treated effluent. The unwanted biofilm layer was more effective than activated sludge in the uptake of certain metals/metalloids.

1. Introduction

Petrochemical refinery industries result in the production of significant quantities of wastewater from several processes including desalting, vacuum distillation, hydrocracking, catalytic cracking, catalytic reforming, alkylation etc (Al Zarooni et al., 2006; Tobiszewski et al., 2012). These effluents contain various contaminants including hydrocarbons, spent caustic soda, cyanides etc (Botalova et al., 2009; Fatone et al., 2009). Typical petrochemical effluents have significant concentrations of suspended solids, organic matter, oil and grease, sulphide, ammonia, phenols, hydrocarbons, benzene, toluene, xylene, polycyclic aromatic hydrocarbons (PAHs) (Al Zarooni et al., 2006; Diyaudddeen et al., 2011; Tobiszewski et al., 2012). The conventional processes that are applied for the treatment of petrochemical wastewater can only partially remove the contaminants. Often, the existing regulations governing the reuse and/or discharge of petrochemical effluents require the adoption of advanced treatment techniques including membrane processes (Ravanchi et al., 2009). Several researchers have applied membrane processes to treat petrochemical and refinery wastewater. Shariati et al. (2011) employed a membrane sequencing batch bioreactor (MSBR) to treat synthetic petroleum refinery wastewater and achieved high (>97%) removal of aliphatic and aromatic hydrocarbons. A cross-flow membrane bioreactor (MBR) was used to treat refinery wastewater accomplishing total organic carbon (TOC) and ammonia concentrations in the permeate of 10.4-31.3 mg L⁻¹ and 0.21-21.3 mgL⁻¹ respectively (Rahman and Al-Malack, 2006). Viero et al. (2008) found that an MBR treating oil refinery wastewater could effectively remove phenols (average removal >98%). It is expected that a shift from conventional biological treatment systems to MBRs will take place in

the petrochemical industry in the near future, which may transform the petroleum industry from a net consumer of freshwater to a net producer. Over the last years, there is a shift in large petrochemical sites from the traditional areas of United States, Europe and Japan to other parts of the world, such as Asia (Van Camp, 2005). Therefore, several former large petrochemical areas are experiencing gradual divestment, reconversions to different industrial productions and/or irregular operations. High flexibility is a major skill required to the MBR technology, which must cope to drastic variations of the pollutant loads and types (Di Fabio et al., 2011). In this work, a pilot scale MBR was operated at different conditions aiming to optimize its performance and provide feedback from the world's largest MBR plant treating petrochemical wastewater, located in Porto Marghera, Venice. A challenge to this was the transient nature of petrochemical effluents. The study focused on chemical oxygen demand (COD) and nitrogen removal, the inhibitory effects of caustic soda and to the removal of heavy metals from undesirable biofilm developing due to fouling and clogging problems.

2. Materials and Methods

2.1 Full scale and pilot MBRs in Porto-Marghera

The full scale MBR plant of Porto-Marghera receives wastewater from different chemical and petrochemical industries active in the area. It was upgraded to an MBR in order to meet the strict legislation governing the effluents discharged into the Lagoon of Venice (Cattaneo et al., 2008). The lagoon receives municipal and industrial effluents and strict limits have been set for specific substances that are contained in the discharged effluents. All effluent streams were equalized in tanks and the wastewater was then fed for clariflocculation where FeCl_3 and anionic polyelectrolyte were dosed, while spent caustic soda from the nearby cracking plant was used to control the pH. After the physicochemical treatment the effluents were fed to the pilot and full scale MBRs. The pilot scale MBR was operated for 2 years and received the same industrial effluents as the full scale MBR. The pilot-scale MBR had a working volume of 4.24 m^3 (aerobic compartment: 2.20 m^3 , anoxic compartment: 1.46 m^3 , membrane module compartment: 0.58 m^3). Table 1 summarizes the operating characteristics of the 5 experimental periods that were conducted. The membrane module consisted of hollow fibres (ZeeWeed 230, GE Water & Process Technologies). The membranes were made of polyvinylidene fluoride, had a nominal pore size of $0.04 \mu\text{m}$ and a surface area of 21.7 m^2 . The permeate flux ranged between $10\text{-}18 \text{ L m}^{-2}\text{h}^{-1}$.

Table 1: MBR operating characteristics in the five experimental periods

Parameter	1 st period	2 nd period	3 rd period	4 th period	5 th period
Time of operation (d)	142	91	62	50	50
HRT (h)	18.3	15.8	15.3	21.5	10.7
SRT (d)	90	90	90	70	50
$Q_{\text{influent}} (\text{m}^3 \text{d}^{-1})$	5.5	6.4	6.6	4.7	9.4
r_{sludge}	2.6	2.0	2.2	2.2	1.7
r_{internal}	0.8	0.74	0.73	-	-
$\text{MLSS}_{\text{aerobic}} (\text{g L}^{-1})$	3.7	3.0	3.6	3.9	4.8
$(\text{MLVSS}/\text{MLSS})_{\text{aerobic}} (\%)$	72	78	72	78	75
F/M [$\text{kg COD} / (\text{kgVSS}\cdot\text{d})$]	0.048	0.042	0.109	0.086	0.11

HRT: hydraulic retention time, SRT: solids retention time, r_{sludge} : recycled sludge, r_{internal} : internally recycled sludge, MLSS: mixed liquor suspended solids, MLVSS: mixed liquor volatile suspended solids, F/M: food to microorganisms ratio, VSS: volatile suspended solids.

2.2 MBR configurations

Initially, the pilot scale reactor was inoculated with activated sludge from the full-scale MBR. Subsequently, 5 experimental periods were conducted to optimize the pilot MBR performance under different operating conditions. This way valuable feedback for the full scale plant can be provided. In the 1st period (Figure 1a) the operating conditions of the full scale MBR were simulated, since the influent wastewater was fed into the anoxic reactor (i.e. pre-denitrification). In the 2nd period (Figure 1b) the wastewater was fed to the aerobic reactor and the configuration was altered to nitrification, post-denitrification. In this period, the usual practice of adding an external carbon source to the denitrification zone was not followed in order to reduce the operating expenses. In the 3rd period (Figure 1c) acetic acid was added to the aerobic reactor as an external carbon source to promote the heterotrophic biomass growth, while influent wastewater was introduced to the anoxic tank, as in the 1st period. Both the anoxic and the aerobic reactors received readily biodegradable organic matter to increase biomass activity. In the 4th and 5th periods (Figure 1d) one of the two anoxic tanks and the internal recirculation were abolished to test the system with lower anoxic reactor volumes and lower energy requirements. The configuration of the 4th period was maintained in the

5th period, with the difference that the influent flow rate and thus the organic and nitrogen load were doubled. The goal was to simulate the conditions of the full scale MBR when only one of the two existing lines was used. In all 5 periods acetic acid was dosed together with the petrochemical wastewater to both the pilot and the full scale MBR. In the 3rd period higher concentration of acetic acid than the one dosed to the full scale MBR was practiced. The operating characteristics of all 5 periods are summarized in Table 1.

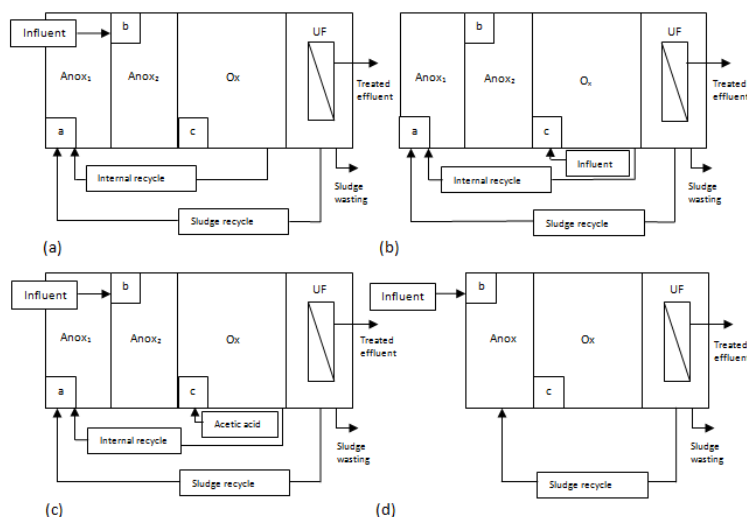


Figure 1. Different configurations of the pilot scale MBR

2.3 Biomass activity and inhibition of nitrification by caustic soda

Heterotrophic and autotrophic biomass activity was assessed through the determination of the specific oxygen (sOUR) and specific ammonium (sAUR) uptake rates in batch experiments, following the procedure developed by Kristensen et al. (1992). Denitrification potential was assessed by measuring the specific nitrate uptake rate (sNUR). In the case of sOUR an automatic respirometer was used. To examine the impact of spent caustic soda on nitrification, batch sAUR tests were conducted. Certain volume of caustic soda was added to the biomass, based on the lowest observed dilution factor (1/150) in the actual system. A control test was carried out without the addition of spent caustic soda.

2.4 Sampling and characterization of suspended and clogging sludge

Samples from the suspended activated sludge (SAS) and the clogging sludge (CS) were taken for a period of 6 months following one year of continuous operation of the pilot MBR. The membrane module was periodically lifted from the ultrafiltration tank and the clogging sludge was collected from 3 different zones over the length of the membrane. A homogeneous and composite was then collected for the determination of metals/metalloids using inductively coupled plasma-mass spectrometry (ICP-MS).

3. Results and discussion

3.1 Petrochemical wastewater characteristics

Table 2 shows the characteristics of the wastewater that was fed to the MBR for the 5 periods.

Table 2: Physicochemical characteristics of petrochemical wastewater fed to MBR

Parameter	Periods				
	1 st	2 nd	3 rd	4 th	5 th
pH	9.4 ± 0.4	8.7 ± 0.4	8.5 ± 0.4	9.3 ± 0.5	9.0 ± 0.4
TSS (mg L ⁻¹)	36.4 ± 29.7	31.5 ± 29.6	29.9 ± 22.8	31.3 ± 18.9	39.8 ± 25.1
COD (mg L ⁻¹)	108.0 ± 19.7	74.1 ± 31.5	195.8a ± 22.1	101.7 ± 28.1	222.7 ± 27.1
NH ₄ -N (mg L ⁻¹)	4.7 ± 2.6	3.7 ± 1.3	4.4 ± 1.5	5.6 ± 2.0	5.0 ± 2.2
NO ₂ -N (mg L ⁻¹)	0.02 ± 0.05	0.50 ± 0.41	0.32 ± 0.25	0.68 ± 0.39	0.39 ± 0.30
NO ₃ -N (mg L ⁻¹)	0.08 ± 0.02	0.13 ± 0.25	0.03 ± 0.07	1.62 ± 1.34	2.11 ± 1.64
TKN (mg L ⁻¹)	9.8 ± 3.3	11.8 ± 3.8	16.9 ± 7.6	10.0 ± 1.6	17.4 ± 2.9
PO ₄ -P (mg L ⁻¹)	0.1 ± 0.2	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.2	0.4 ± 0.1
Cl ⁻ (mg L ⁻¹)	967 ± 343	1601 ± 330	1278 ± 250	821 ± 126	913 ± 119
SO ₄ ²⁻ (mg L ⁻¹)	452 ± 166	235 ± 31	250 ± 40	123 ± 4	169 ± 45

Where:

TSS: total suspended solids, NH₄-N: ammonium nitrogen, NO₂-N: nitrite nitrogen, NO₃-N: nitrate nitrogen, TKN: Total Kjeldahl nitrogen, PO₄-P: phosphate, Cl⁻: chloride, SO₄²⁻: sulfate

Recently, several industries in the petrochemical area of Porto-Marghera were shut down or subjected to temporary and irregular cessation runs, introducing drastic variability in influent loads and resulting in a reduction of the organic strength of petrochemical effluents. This industrial effluent has low COD, low nitrogen and phosphorus concentrations; its characteristics do not favour biological treatment. Acetic acid was always added to increase the organic loading to the minimum possible F/M.

3.2 Permeate quality and performance of biological processes

Table 3 shows the characteristics of MBR permeate compared to the existing limits concerning the discharge of effluents into the lagoon of Venice. The treated effluent met the limits for all the parameters except sulphates which were sometimes above the limit. During the 2nd period, high NO₃-N concentrations in permeate were observed. In the 3rd and 5th periods higher permeate TKN concentrations were obtained. The ammonium concentration of the permeate was very low (usually <0.5 mg L⁻¹), showing that the oxidation of ammonium to nitrate was effective. Since the ammonium concentration in the influent was low, the ammonification of soluble organic nitrogen is considered important in order to provide sufficient ammonium for nitrification. During the 1st, 3rd, 4th and 5th experimental periods ammonification was not effective, with the average organic nitrogen removal ranging from 29 - 60%. It seems that the nature of the wastewater inhibited to some level the ammonification process. Consequently, in the aforementioned periods the nitrification rate was influenced by the low availability of NH₄-N. In the 2nd period, where the nitrification / post-denitrification scheme was applied denitrification was not effective due to the low organic carbon to total nitrogen ratio (6 gCOD/gTN) of influent wastewater and the fact that external carbon source was not added to the anoxic reactor. These conditions were applied to examine whether autotrophic denitrification via-sulphide occurs. The latter process is often observed in petrochemical effluents, since it is favoured when the biodegradable organic carbon is low and in the presence of significant sulphide concentrations (Vaiopoulou et al., 2005). However, autotrophic denitrification did not seem to occur probably due to sulphide oxidation in the aerobic reactor. Therefore, the alternation to the nitrification, post-denitrification configuration without any external carbon source addition to the anoxic reactor resulted in very low nitrogen removal. Despite this, the average nitrogen concentration of the permeate was close to the limit of 10 mg L⁻¹, showing that this configuration can be a viable solution.

Table 3 Physicochemical characteristics for MBR permeate for the 5 examined periods

Parameter	Periods (mean value ± standard deviation)					Limits
	1 st	2 nd	3 rd	4 th	5 th	
TSS (mg L ⁻¹)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	35
COD (mg L ⁻¹)	23.1 ± 5.2	23.0 ± 7.1	26.9 ± 8.1	14.9 ± 8.1	29.3 ± 6.0	120
TKN (mg L ⁻¹)	2.4 ± 2.5	1.7 ± 1.8	5.0 ± 4.7	2.9 ± 2.0	4.6 ± 2.6	-
NH ₄ -N (mg L ⁻¹)	0.16 ± 0.37	0.09 ± 0.15	0.10 ± 0.01	0.31 ± 0.17	0.10 ± 0.08	2
NO ₂ -N (mg L ⁻¹)	0.11 ± 0.01	0.04 ± 0.08	0.08 ± 0.19	0.02 ± 0.01	<0.01	0.3
NO ₃ -N (mg L ⁻¹)	0.94 ± 0.56	8.99 ± 2.81	0.95 ± 0.81	1.71 ± 1.30	2.12 ± 1.18	-
TN (mg L ⁻¹)	3.30 ± 1.17	10.97 ± 3.27	5.91 ± 4.90	4.86 ± 2.52	6.37 ± 2.86	10
PO ₄ -P (mg L ⁻¹)	0.13 ± 0.07	0.03 ± 0.10	0.01 ± 0.06	0.20 ± 0.10	0.10 ± 0.20	0.5
Cl ⁻ (mg L ⁻¹)	960 ± 344	1616 ± 299	1287 ± 207	734 ± 84	927 ± 146	-
SO ₄ ²⁻ (mg L ⁻¹)	436 ± 182	246 ± 20.1	261 ± 32	129 ± 24	223 ± 31	500

TN: total nitrogen

In the 3rd period, the average nitrogen removal was similar (slightly lower) compared to that of the 1st period, but the fluctuation was higher with occasionally low nitrogen removal (<30%). This could be attributed to inhibitory compounds contained in petrochemical wastewater. Nitrate reduction was adversely affected by the high dissolved oxygen (DO) concentration of the mixed liquor that was recycled from the membrane tank (DO>6 mg L⁻¹) and from the aerobic reactor (DO~4 mg L⁻¹). Consequently, during the first 3 periods the anoxic reactor was partly used to deoxygenate the recycled sludge. During the 4th and 5th periods the internal recirculation was abolished in an effort to reduce this problem. In the 5th period, the HRT was decreased by 50% by doubling the influent flow rate (compared to the 4th period), while the influent nitrogen concentration was higher than that of 1st and 4th periods. In the 4th and 5th periods, despite the decrease of the volume of the anoxic reactor by 20% and the abolition of internal recirculation, the nitrogen removal was only slightly less compared to the control period (i.e. 1st). The COD removal was moderate (69-86%) owing to the low influent COD concentration. The carbon source addition did not increase the permeate COD. The lower permeate COD measured in the 4th period (i.e. Table 3) is most likely related to the inflow characteristics, with the soluble non biodegradable COD from industrial

discharges being lower. The permeate quality was not significantly affected by sudden variations of the treatment scheme. Consequently, the MBR ensured high treated effluent quality with respect to COD at all times.

3.3 Biomass activity and inhibition

Figure 2 shows the specific organic carbon oxidation activity and the nitrification and denitrification rates obtained through sOUR, sAUR and sNUR measurements. The denitrification rates were not in accordance with the nitrogen removal obtained. For example, despite the low nitrogen removal obtained during the 2nd period the measured sNUR was significant and similar to that of the 1st period. This finding corroborates the statement that the composition of the influent wastewater affects the biological processes. In batch sNUR tests, excess of nitrates and easily biodegradable organic matter were added, thus enhancing denitrification. The addition of organic carbon to the anoxic reactor (i.e. influent wastewater) and to the aerobic reactor (i.e. acetic acid) in the 3rd period resulted in high sOUR and sNUR. In the 4th period, slightly lower sNUR and sOUR were measured compared to the control period, while in the 5th period the denitrifiers activity was very similar to the control one. Despite the reduction in the anoxic reactor's volume and the abolition of internal recirculation heterotrophic biomass activity was maintained at the same levels. Doubling the influent load was beneficial providing more substrate for biomass growth.

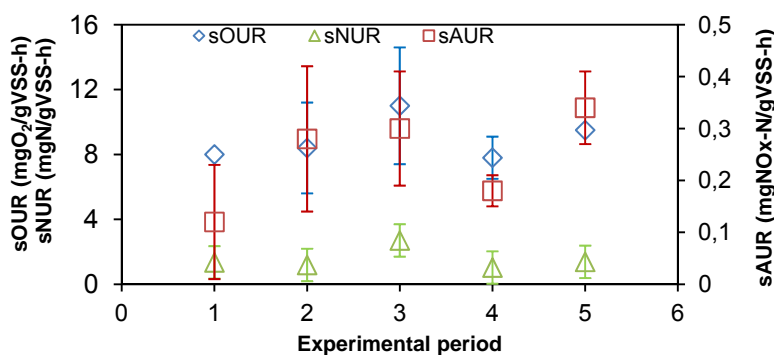


Figure 2. sOUR (mgO₂/gVSS-h), sAUR (mgNO_x-N/gVSS-h) and sNUR (NO_x-N/gVSS-h) obtained for the 5 periods (all values corrected to the reference temperature of 20°C)

The inhibitory effect of spent caustic soda on sAUR autotrophic biomass activity was also examined. Caustic soda is used in petrochemical industries to remove hydrogen sulphide and phenols from the intermediate and final product streams. Usually, the discharges of spent caustic soda receive physicochemical prior the biological treatment. In this case, spent caustic soda was fed directly into the biological reactors, as this was the practice followed in the full scale plant. This effluent was characterized by high sulphide, pH, salinity, hydrocarbon and phenol concentrations. Since its flow rate was very low compared to the total wastewater flow rate, significant dilution took place. It was found that the addition of spent caustic soda under the worst conditions of the lowest dilution (1/150) resulted in a decrease of the nitrification rate from 0.25 to 0.11 mg N/gVSS-h (56% decrease). However, during the pilot MBR operation the worst scenario was never reached. In addition, spent caustic caused only temporary inhibition of the ammonia oxidation. This may suggest that the toxicants had major effects on the catabolism of the autotrophic nitrifying biomass, while the anabolism was not irreversibly affected.

3.4 Metals in suspended and clogging sludge

The metals concentrations entering the biological reactor were found to be in the range of 0.1-100 µg L⁻¹ (except for Fe), as high as the levels that are commonly encountered in municipal wastewater.

Metals/metalloids in the CS were found in the following descending order: Fe>Al>Zn>Cr>Cu>Ni>Pb>As>Cd. The CS was more effective than SAS in the removal of specific metals/metalloids in the following order: As>Zn>Ni>Cd>Fe (Table 4). This was probably attributed to the synergistic effect of extracellular polymeric compounds and metal-resistant bacteria. The CS also had a higher accumulation of organic matter, phosphorus and nitrogen compared to SAS.

Table 4: Metal concentration in wastewater entering the MBR, in the SAS and in the CS

Metal / Metalloid	Influent wastewater ($\mu\text{g L}^{-1}$)	CS anaerobic lay-zone (mg kgSS^{-1})	CS aerobic lay-zone (mg kgSS^{-1})	SAS (mg kgSS^{-1})	Metals accumulation in CS - anaerobic lay-zone (%)	Metals accumulation in CS- aerobic lay-zone (%)
Fe	889.4 \pm 61.6	38258	54932	17990	113	205
Al	74.9 \pm 77.3	1391	933	2543	-45	-63
Zn	33.5 \pm 77.1	715.2	627.5	121.0	491	419
Cr	11.8 \pm 71.3	265.3	271.5	281.0	-6	-3
Mn	22.5 \pm 55.8	184.1	421.2	350.5	-48	20
Cu	4.3 \pm 87.8	83.4	72.7	69.0	21	5
Ni	4.4 \pm 72.1	58.8	71.7	18.0	227	298
Pb	2.3 \pm 110	24.6	21.8	21.0	17	4
Mo	8.7 \pm 34.8	10.2	19	2.9	252	555
As	2.4 \pm 36.2	7.9	9.4	1.0	690	840
Co	0.3 \pm 51.6	3.5	4.1	2.5	40	64
Cd	<0.5	2.2	1.5	<0.01	>219	>149

4. Conclusions

This work showed that the MBR was able to cope with the variable petrochemical effluents, producing permeate that satisfied the strict limits of discharge into the Lagoon of Venice. Acetic acid addition was effective, as it increased the denitrification rate. The decrease of the anoxic reactor volume resulted in a reduction of the denitrification rate, but it did not severely compromise the treated effluent quality. The spent caustic soda inhibited the autotrophic bacteria up to 56%. In the pre-denitrification configurations ammonification was low, resulting in an average organic nitrogen removal of 29–60%. Nitrification was very satisfactory with the ammonium concentration in the permeate usually being below 0.5 mg NH₄-NL⁻¹. The low denitrification during the nitrification, post-denitrification configuration was attributed to the low organic carbon to total nitrogen ratio and the lack of carbon source addition.

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