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Treatment of petrochemical wastewater by employing membrane bioreactors: a case study of effluents discharged to a sensitive water recipient

S. Malamis[a,*], E. Katsou[a], S. Di Fabio[a], N. Frison[b], F. Cecchi[a], F. Fatone[a]

[a]*Department of Biotechnology, University of Verona, Strada Le Grazie 15, Verona 37134, Italy; email:* *malamis.simos@gmail.com* *(S. Malamis)*
[b]*Department of Environmental Sciences, Informatics and Statistics, University Ca'Foscari of Venice, Dorsoduro 2137, Venice 30121, Italy*

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ABSTRACT

This work was conducted at the largest petrochemical membrane bioreactor (MBR) plant in the world. The effectiveness of MBR technology to treat petrochemical effluents was studied. The treated effluent is discharged in a very sensitive water body and needs to satisfy strict limits. To optimize MBR operation a pilot-scale MBR was set-up that received the same petrochemical effluents as the full scale. In the pre-denitrification configurations, ammonification was not effective. Variable removal of heavy metals/metalloids was obtained by the MBR with As, B, Ba, Mo, Al, Ni, Se, Sb, V and Zn removal being less than 40%, Pb, Hg, Cu, Ag, Cr, Mn and Co removal of 40–70% and only Fe removal being higher than 70%. Sludge clogging was observed in the membrane module; the accumulation of COD, N, P, As, Zn, Mo, Ni, Cd, Sb, Fe, Se and Co in the clogged sludge was higher than that in the activated sludge. The adoption of MBR coupled with suitable physicochemical pre-treatment was able to safeguard the treated effluent quality.

Keywords: Petrochemical effluents; Membrane bioreactor; Nitrification/denitrification; Heavy metals; Clogged sludge

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 [1,2]. Petrochemical wastewater is usually characterized by significant concentrations of suspended solids, chemical oxygen demand (COD), oil and grease, sulphide, ammonium, phenols, hydrocarbons, benzene, toluene, ethylbenzene, xylene and polycyclic aromatic hydrocarbons (PAHs) [3,4]. The conventional processes that are applied for the treatment of petrochemical wastewater can only partially remove the contaminants. Often, existing regulations governing the reuse and/or discharge of petrochemical effluents require the adoption of advanced treatment techniques including membrane processes [5]. The application of membrane bioreactors (MBRs) is widely recognized as an effective option for enhanced wastewater treatment in the

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*Corresponding author.

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industrial and urban sectors [6]. Among the best available techniques for wastewater treatment and reuse, MBRs are important because of their rapidly improving cost/benefit ratio [7,8]. This is attributed to the decrease in membrane module cost, the longer warranty provided by manufacturers, the improved energy efficiency and the improvements in design and operation practices [9].

A membrane sequencing batch bioreactor was employed by Shariati et al. [10] to treat synthetic petroleum refinery wastewater resulting in high (>97%) removal of aliphatic and aromatic hydrocarbons. In the study of Rahman and Al-Malack [11] a cross-flow MBR was used to treat refinery wastewater accomplishing total organic carbon and ammonium concentrations in the permeate of 10.4–31.3 mg L^{-1} and 0.21–21.3 mg L^{-1}, respectively. Viero et al. [12] found that the average removal of phenols by an MBR treating oil refinery effluents was 98%. However, the presence of high phenol concentrations adversely impacted on the removal of organic matter. Qin et al. [13] operated a submerged MBR for the treatment of petrochemical wastewater; the resulting MBR permeate satisfied the discharge standards.

MBR processes retain particulate and colloidal matter, including macromolecular substances larger than the absolute pore size of the membranes. Thus, metals that are bound-adsorbed to activated sludge are effectively removed by the MBR process. Some research studies identify a "small" superiority of MBR over conventional activated sludge (CAS) processes for removing heavy metals from domestic effluents. Santos and Judd [14] summarized the findings of various studies comparing the performance of MBR and CAS for the removal of heavy metals from municipal wastewater and concluded that MBR marginally achieve higher metal removal than CAS (64–92% instead of 51–87%). Similarly, Bolzonella et al. [15] found that MBR improve heavy metal removal by 10–15% due to the more efficient retention of suspended solids and due to the cake layer effect that increases the selectivity of the membrane.

The removal of volatile organic compounds (VOCs) from wastewater with the use of MBR has also received some attention. Min and Ergas [16] examined the volatilization and biodegradation rates for acetaldehyde, butyraldehyde and vinyl acetate in an MBR for varying organic loading rates and found that the overall removal of the three VOCs was higher than 99.7% for the examined loading rates. Fatone et al. [17] studied the occurrence, removal and fate of 16 PAHs and 23 VOCs in Italian municipal wastewater treatment systems consisting both of CAS and MBR. MBR enhanced the biodegradation of PAHs, since their concentration decreased in the mixed liquor with increasing sludge age.

In this work, a pilot-scale MBR was operated at different conditions aiming to provide feedback for the world's largest MBR plant treating petrochemical wastewater. The study focused on selected VOCs, PAHs, metals and metalloids removal, as well as on nitrogen and COD removal.

2. Materials and methods

2.1. Location of activities

The full-scale MBR plant receives wastewater from different chemical and petrochemical industries, which are active in the area. It was upgraded to an MBR in order to meet the strict legislation governing the effluents discharged to a sensitive water body [18]. This water recipient receives municipal and industrial effluents and limits have been set for specific substances that are contained in the discharged effluents. The petrochemical streams were equalized in tanks and then the wastewater was fed to the clariflocculation tanks where ferrous sulphate was dosed. After the physicochemical treatment the effluents were fed to the pilot and full-scale MBR. The pilot-scale MBR was operated for two 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 and membrane module compartment: 0.58 m^3). The membrane module was supplied by GE Water and Process Technologies (ZeeWeed 230) and consisted of hollow fibres. The membranes had a nominal pore size of 0.04 μm and were made of polyvinylidene fluoride. The membrane surface area was 21.7 m^2. The permeate flux ranged between 10 and 18 $L\,m^{-2}\,h^{-1}$.

2.2. MBR configurations

Five experimental periods were performed to test the pilot-scale MBR under different operating conditions and to optimize its performance. This way, valuable feedback for the full-scale plant can be provided. In the beginning, the reactor was inoculated with activated sludge from the full-scale MBR. The operating characteristics of all five periods are presented in Table 1. Influent wastewater had received physicochemical treatment for the removal of suspended and colloidal material, which was enhanced by the addition of ferrous sulphate. In the 1st period (Fig. 1(a)) the operating conditions of the full-scale MBR were simulated, since the influent wastewater was fed into

Table 1
Operating characteristics of the pilot MBR during the five experimental periods

Parameter	1st period	2nd period	3rd period	4th period	5th period
HRT (h)	18.3	15.8	15.3	21.5	10.7
SRT (d)	90	90	90	70	50
Q_{influent} ($m^3 d^{-1}$)	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	–	–
$MLSS_{\text{aerobic}}$ ($g L^{-1}$)	3.7 ± 0.4	3.0 ± 0.5	3.6 ± 0.6	3.9 ± 0.6	4.8 ± 0.8
$MLVSS_{\text{aerobic}}$ ($g L^{-1}$)	2.7 ± 0.3	2.3 ± 0.3	2.6 ± 0.5	3.0 ± 0.4	3.6 ± 0.6
F/M (kg COD/(kgVSS d))	0.048	0.042	0.109	0.086	0.11

Note: r_{sludge}: recycled sludge, r_{internal}: internal recirculation of nitrate, MLSS: mixed liquor suspended solids, MLVSS: mixed liquor volatile suspended solids, F/M: food to micro-organisms ratio, VSS: volatile suspended solids.

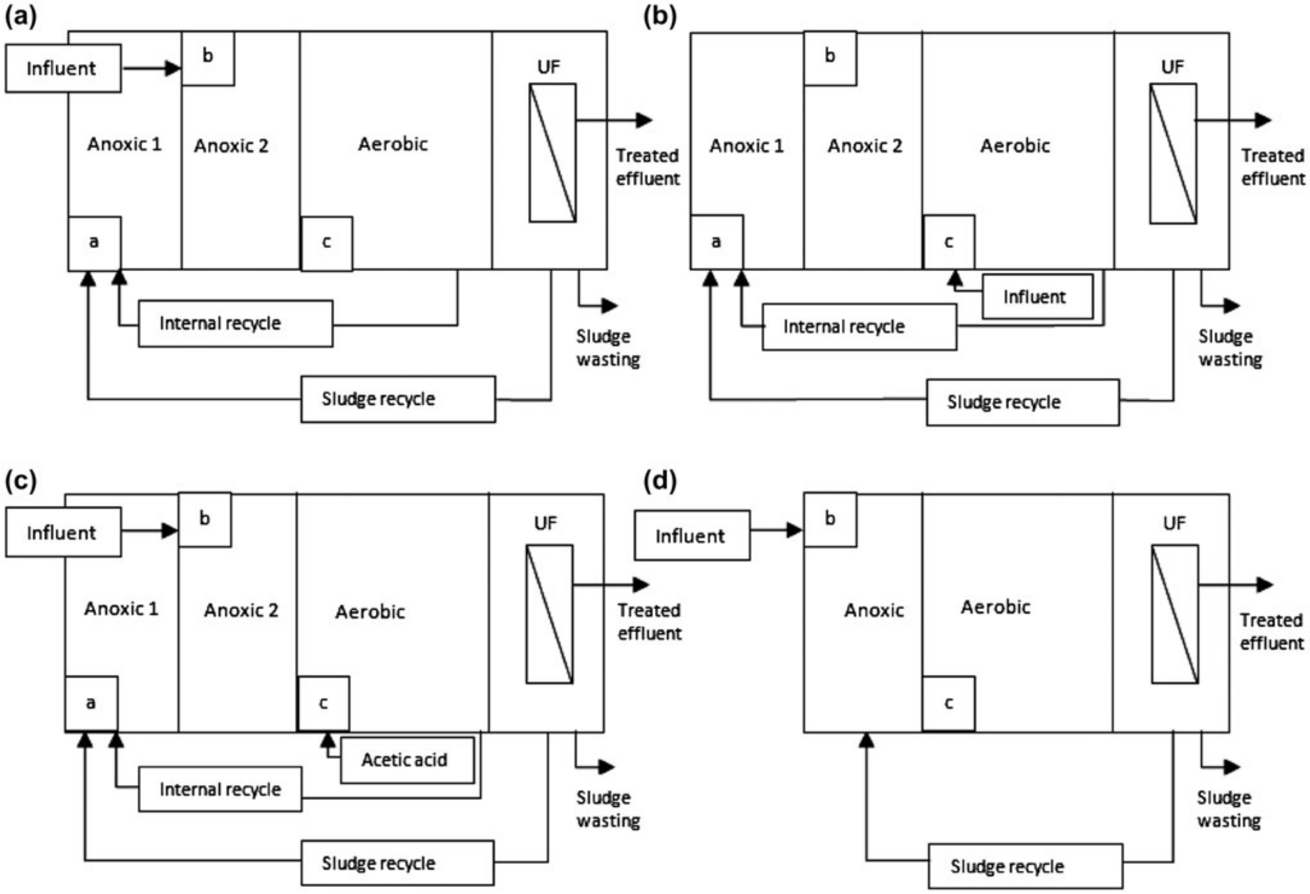

Fig. 1. Configurations applied in the pilot-scale MBR.

the anoxic reactor and pre-denitrification took place. Another anoxic reactor received the external recirculation of the mixed liquor from the membrane tank and the internal recirculation flow from the aerobic reactor. In the 2nd period (Fig. 1(b)) the wastewater was fed to the aerobic reactor and the configuration was altered to nitrification, post-denitrification. Internal recycling was carried out from the aerobic to the anoxic zone in order to introduce nitrate to the anoxic zone. The main purpose was to decrease the endogenous decay of heterotrophic biomass in the aerobic reactor and increase the fraction of active biomass within the activated sludge. 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 (Fig. 1(c)) 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 heterotrophic biomass growth in the aerobic reactor compared to the 1st period and to achieve a higher denitrification rate than that of the 2nd period. In the 3rd period higher concentration of acetic acid than the one dosed to the full-scale MBR was practiced. The 3rd period aimed to address the main operational deficiencies observed in the previous two periods.

During the 4th and 5th period (Fig. 1(d)) 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. This way we simulated the conditions of the full scale with the petrochemical wastewater to both the pilot- and the full-scale MBR.

2.3. Ammonium oxidation and nitrogen removal

The ammonium oxidation efficiency was determined by considering the influent and effluent ammonium loads. The nitrogen removal efficiency was determined by considering the nitrogen loads in influent, effluent and the excess sludge.

2.4. Sampling and analytical methods

The samples were collected in the two year operation of the pilot-scale MBR. The mixed liquor samples were collected from the aerobic and anoxic reactors. Samples of influent wastewater and permeate were collected by two peristaltic pumps automatically timed to sample a liquid aliquot at 3 min h^{-1} and obtain a daily composite sample. All samples were stored in plastic bottles and were kept at 4˚C prior to analysis. The samples from the suspended activated sludge (SAS) and the clogged sludge (CS) were taken within a six-month time period following the operation of the MBR for one year. The membrane module was periodically lifted from the membrane tank and the CS was collected from three different zones over the length of the membrane. A homogeneous and composite sample was then collected for the determination of metals/metalloids.

The analysis was conducted at a maximum of one d following the collection time. The parameters of pH, alkalinity, total suspended solids (TSS), volatile suspended solids (VSS), COD, ammonium (NH_4-N), and total Kjeldahl nitrogen (TKN) were measured according to standard methods [19]. Moreover, nitrate (NO_3-N), nitrite (NO_2-N), orthophosphate-P (PO_4-P), fluoride (F^-) and sulphate (SO_4^{2-}) were determined using ionic chromatography (ICS-900 Thermo Scientific). MLSS and MLVSS were determined in sludge according to standard methods [19]. B, Al, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Ba, Pb, As, Hg, Se and Sb were determined using the US EPA method EPA200.8/94; Fe was determined according to APAT IRSA-CNR 29/2003 3020 [18]. The metals/metalloids were determined using inductively coupled plasma-mass spectrometry. PAHs, benzene and toluene were measured by gas chromatography mass spectrometry using an HP 6890 Plus gas chromatograph (Hewlett-Packard, Palo Alto, CA) coupled with a Micromass Autospec Ultima mass spectrometer (Waters, Framingham, Mass) following the US EPA methods (EPA 8270C/96 and EPA 8260B/96).

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 five experimental periods. The wastewater stream was characterized by low total and ammonium nitrogen, very low phosphorus concentrations and low COD; these characteristics did not favour the biological processes [3,20,21]. Ammonification was an important process for nitrogen removal, since the concentrations of organic nitrogen are much higher than those of ammonium nitrogen.

The petrochemical wastewater characteristics were variable and so was the biodegradable fraction of total COD. Acetic acid was added to increase the organic loading. TKN was higher in the 3rd and 5th period compared to the other periods. Over the last years, several industries in the petrochemical area were shut down or subjected to temporary and irregular cessation runs, introducing significant variability in influent loads and resulting in a reduction of the organic strength of petrochemical effluents. As a result, the full-scale MBR received much lower and fluctuating concentrations of organic matter and nutrients compared to previous years as well as to the design treatment potential.

Table 2
Physicochemical characteristics of petrochemical wastewater fed to MBR

	Periods				
Parameter (mg L^{-1})	1st	2nd	3rd	4th	5th
TSS	36.4 ± 29.7	31.5 ± 29.6	29.9 ± 22.8	31.3 ± 18.9	39.8 ± 25.1
COD	108.0 ± 19.7	74.1 ± 31.5	195.8 ± 22.1	101.7 ± 28.1	222.7 ± 27.1
TKN	9.8 ± 3.3	11.8 ± 3.8	16.9 ± 7.6	10.0 ± 1.6	17.4 ± 2.9
NH_4-N	4.7 ± 2.6	3.7 ± 1.3	4.4 ± 1.5	5.6 ± 2.0	5.0 ± 2.2
NO_2-N	0.02 ± 0.05	0.50 ± 0.41	0.32 ± 0.25	0.68 ± 0.39	0.39 ± 0.30
NO_3-N	0.08 ± 0.02	0.13 ± 0.25	0.03 ± 0.07	1.62 ± 1.34	2.11 ± 1.64
PO_4-P	0.1 ± 0.2	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.2	0.4 ± 0.1
SO_4^{2-}	452 ± 166	235 ± 31	250 ± 40	123 ± 4	169 ± 45

3.2. Performance of biological processes

The MBR permeate characteristics are given in Table 3, while a comparison is made with the existing limits concerning the discharge of effluents into the local very sensitive water body.

The COD concentration of influent wastewater was low, particularly in the 1st, 2nd and 4th period. The latter can explain the moderate COD removal efficiency (on average 69–86% for all periods). The addition of extra acetic acid did not result in any significant change in the permeate COD. In the 4th period, the lower permeate COD is probably related to the inflow characteristics, with the soluble non biodegradable COD from industrial discharges being lower. In the 5th period, the higher permeate COD concentration was due to the higher influent loads introduced to the system. The MBR performance was evaluated under transient conditions (i.e. shift between the different multi-zone schemes). 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.

Fig. 2 summarizes the ammonium and nitrogen removal efficiencies for the examined periods. Ammonium removal efficiency was based on the influent ammonium load that was readily available for the nitrification process, since a significant part of nitrogen remained in organic form. The lowest ammonium removal efficiency was obtained in the 4th period and is probably attributed to the toxic action of petrochemical wastewater substances and/or to some peak loading of nitrogen. The nitrogen removal was very low during the 2nd period, since external carbon source was not dosed to the anoxic reactor for the denitrification process.

The ammonium concentration in the permeate was very low in all periods (usually <0.5 mg L^{-1}), showing that the oxidation of ammonium to nitrate was effective. The higher NH_4-N content of the treated effluent in the beginning of the 4th period is most likely attributed to some peaks of nitrogen loading and/or to temporary and irregular inhibitory effects caused by influent wastewater. On the other hand, the ammonification was not effective in all periods (except the 2nd), since the average organic nitrogen removal was lower than 65%. The nature of the petrochemical wastewater seems to inhibit, to some level, the biological conversion of organic nitrogen to ammonium. In the 2nd period, ammonification was much higher than in

Table 3
Physicochemical characteristics of the treated MBR effluent

	Period (mean value ± standard deviation)					
Parameter (mg L^{-1})	1st	2nd	3rd	4th	5th	Limits
COD	23.1 ± 5.2	23.0 ± 7.1	26.9 ± 8.1	14.9 ± 8.1	29.3 ± 6.0	120
TN	3.30 ± 1.17	10.97 ± 3.27	5.91 ± 4.90	4.86 ± 2.52	6.37 ± 2.86	10
NH_4-N	0.16 ± 0.37	0.09 ± 0.15	0.10 ± 0.01	0.31 ± 0.17	0.10 ± 0.08	2
NO_2-N	0.11 ± 0.01	0.04 ± 0.08	0.08 ± 0.19	0.02 ± 0.01	<0.01	0.3
NO_3-N	0.94 ± 0.56	8.99 ± 2.81	0.95 ± 0.81	1.71 ± 1.30	2.12 ± 1.18	–
PO_4-P	0.13 ± 0.07	0.03 ± 0.10	0.01 ± 0.06	0.20 ± 0.10	0.10 ± 0.20	0.5
SO_4^{2-}	436 ±182	246 ± 20.1	261 ± 32	129 ± 24	223 ± 31	500

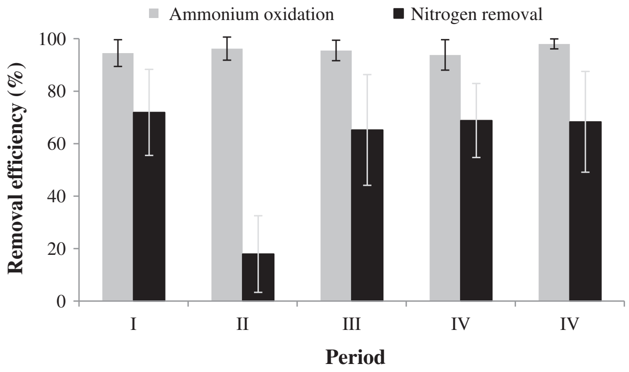

Fig. 2. Ammonium oxidation and nitrogen removal efficiency.

the other periods, probably due to the longer shutdown of the production of acrylic fibres. In this period, the nitrification post-denitrification configuration was not coupled with external carbon source in the anoxic reactor. These conditions were applied in order to examine if autotrophic denitrification via-sulphide took place. This process is favoured under limiting organic carbon and in the presence of significant sulphide concentrations, which are commonly met in petrochemical effluents [22]. Although these conditions were observed in the 2nd period, autotrophic denitrification did not seem to occur probably because sulphides were oxidized in the aerobic reactor. As a result the nitrate removal was negligible. In the 3rd period the average nitrogen removal was slightly lower than the one obtained during period 1. However, the fluctuation was much larger with occasionally very low nitrogen removal. This can be attributed to inhibitory effect of compounds contained in petrochemical wastewater.

The internal and sludge recirculation of the mixed liquor from the aerobic reactor (DO ~ 4 mg L^{-1}) and from the membrane tank (DO > 6 mg L^{-1}) to the anoxic reactor was not beneficial for denitrification. As a result, in the first three periods, the first anoxic compartment was partly operated as an aerobic reactor to deoxygenate the recycled sludge. In the last two periods the internal recirculation was abolished in an effort to mitigate this problem. In periods 4 and 5, despite the reduction of the anoxic compartment volume by 20% and the abolition of internal recirculation, the nitrogen removal was only slightly lower compared to period 1. Moreover, 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. To conclude, the MBR permeate usually met the strict limits for the examined parameters shown in Table 3.

3.3. Organic and inorganic micropollutants removal

The removal of heavy metals/metalloids, PAHs, benzene and toluene from the clariflocculation unit

Table 4
Metal/metalloid occurrence and removal of metals/metalloids in the MBR pilot plant

Metal/Metalloid	Frequency of occurrence (%)	Influent concentration to MBR (aver. ± var. coef.) (μg L^{-1} ± %)	Removal by MBR (aver. ± var. coef.) (% ± %)
Al	100	74.90 ± 77.3	27.0 ± 32.6
Ag	5	0.27 ± 27.0	54.5 ± 6.5
As	91	2.38 ± 36.2	18.8 ± 25.6
Ba	100	20.12 ± 55.5	20.2 ± 26.7
B	100	302.07 ± 68.9	17.2 ± 26.7
Cd	0	<0.50 ± 0.0	–
Co	21	0.33 ± 51.6	40.1 ± 32.3
Cr	98	11.81 ± 71.3	62.3 ± 32.4
Cu	94	4.25 ± 87.8	41.4 ± 31.8
Fe	100	889.44 ± 61.6	85.0 ± 14.3
Hg	79	0.23 ± 58.2	52.1 ± 29.1
Mn	100	22.50 ± 55.8	66.3 ± 26.0
Mo	100	8.70 ± 34.8	13.6 ± 22.8
Ni	97	4.37 ± 72.1	25.0 ± 30.2
Pb	97	2.25 ± 110	45.4 ± 37.1
Sb	21	0.62 ± 38.9	38.1 ± 32.9
Se	56	4.28 ± 51.1	9.2 ± 23.1
Sn	72	1.54 ± 75.1	42.3 ± 31.2
V	98	4.08 ± 82.5	31.3 ± 28.8
Zn	99	33.53 ± 77.1	28.2 ± 32.6

and the MBR were investigated. Table 4 shows the metals/metalloids concentrations after the clariflocculation unit and the removal achieved by the pilot MBR. The metals/metalloids after flocculation-clarification were in the range of $0.1–100\ \mu\text{g L}^{-1}$, which is similar to the levels that usually occur in municipal wastewater treatment plants. The petrochemical effluent fed to the MBR was characterized by significant Fe and B concentrations, while Cr, Pb, Ni, Cu and As were present at levels below those of typical municipal wastewater, on average lower than $12\ \mu\text{g L}^{-1}$ over the year. Co, Ag and Sb had frequencies of occurrence below 50%; Cd was always below the limit of quantification. The average removals of metals/metalloids by MBR were as follows: lower than 40% for As, B, Ba, Al, Ni, Se, Sb, V and Zn, in the range of 40–70% for Pb, Hg, Cu, Ag, Mn, Cr and Co and higher 70% for Fe.

Fig. 3 shows the arsenic, lead, mercury, cadmium, PAHs, benzene and toluene concentrations of the influent petrochemical wastewater that was fed to the clariflocculation unit, the effluent from the clariflocculation unit fed to the MBR unit and of the MBR permeate. The clariflocculation unit resulted in significant removal of arsenic, while the MBR could not effectively remove arsenic. The low removal of As by the MBR is mainly related to its chemical species, arsenate (As^{5+}) and arsenite (As^{3+}). Arsenate can be present as $H_2AsO_4^-$ and $HAsO_4^{2-}$, which are both soluble and negatively charged, so they do not react with binding sites in the activated sludge. Arsenite is present in as a neutral molecule (H_3AsO_3) exhibiting low chemical reactivity [15]. The lead decreased to very low concentrations by the clariflocculation process ($<4\ \mu\text{g L}^{-1}$) and the MBR further reduced the lead concentration. The cadmium concentration was always below the limit of quantification

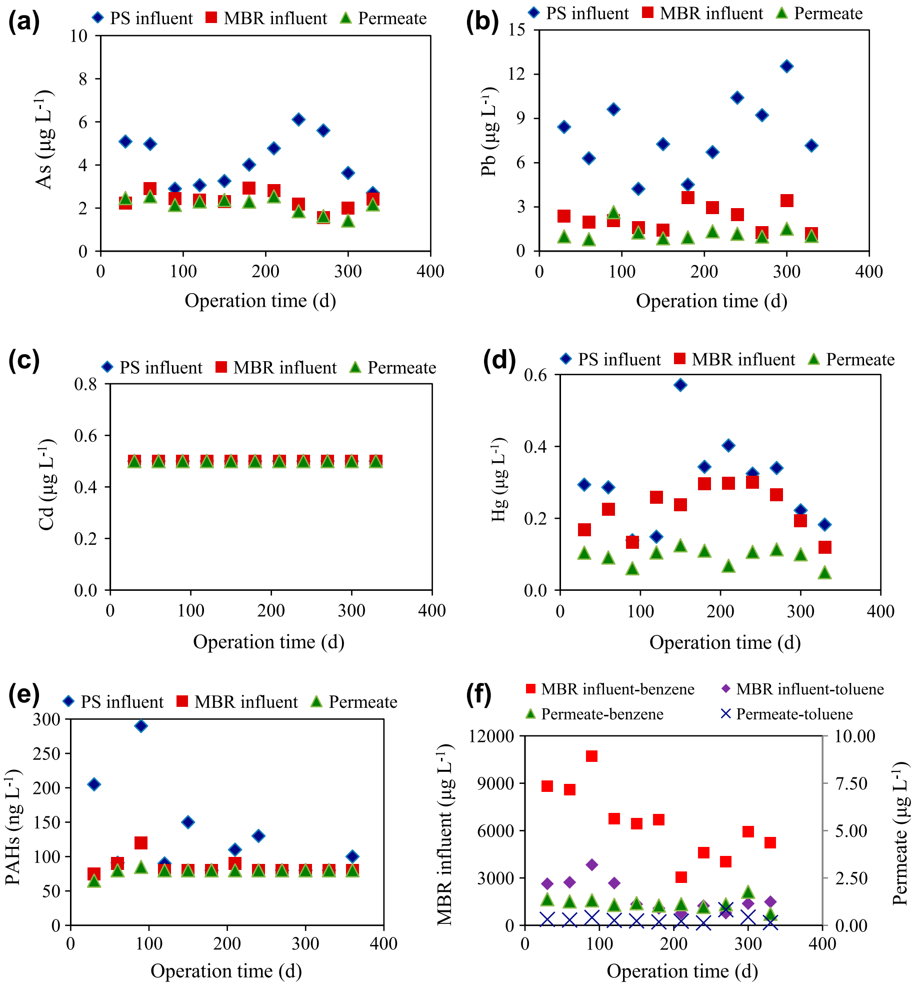

Fig. 3. (a) Arsenic, (b) lead, (c) cadmium, (d) mercury, (e) PAHs and (f) benzene and toluene concentrations in influent wastewater (PS influent), and the effluent from the clariflocculation unit fed to the MBR (MBR influent) and the MBR permeate.

of 0.5 μg L^{-1}. The mercury concentration of petrochemical effluents was low (0.23 μg L^{-1}) and the MBR process reduced it to even lower levels of the order of 0.1 μg L^{-1}. The MBR permeate had Pb, Cd and Hg and PAHs concentrations that were consistently below the strict limits of 10, 1, 0.5 and 1 μg L^{-1}, respectively, set for the discharge of the treated effluent. Only the arsenic concentration exceeded the limit of 1 μg L^{-1} as the permeate concentration was usually around 1.5–3 μg L^{-1}.

PAHs were effectively removed in the physico-chemical stage as they are associated to particulate and colloidal matter. The sum of the PAHs entering the MBR was almost always lower than 100 ng L^{-1}. The benzene and toluene were effectively removed by the MBR mainly through the process of volatilization, with the permeate having a benzene and toluene concentration lower than 2 μg L^{-1}. The coarse bubble aeration in the membrane tank enhanced the volatilization of such compounds.

3.4. Metals/metalloids accumulation

The accumulation of metals/metalloids in the SAS and in the CS was also examined. Despite the fact that coarse bubble aeration was employed to minimize membrane fouling, CS was observed to accumulate between the membrane fibres (Fig. 4). Two types of CS were identified: (i) CS in the outside part of the membrane module that was mainly exposed to aerobic conditions and (ii) CS in the interior of the membrane module that was mainly exposed to the anaerobic conditions. The appearance of CS in the aerobic lay-zone was essentially different from the CS in the anaerobic lay-zone as different redox conditions were experienced. The concentration of COD, TKN and P were higher in the CS than in SAS (Fig. 4). The COD was 525 mg (g TS)$^{-1}$ in the SAS, 723 mg (g TS)$^{-1}$ in the aerobic CS, and 719 mg (g TS)$^{-1}$ in the anaerobic CS. This shows the important role of CS in the removal of wastewater compounds. The higher concentrations of organic carbon and nutrients in the CS demonstrate that this layer was able to sorb, to a greater extent, colloidal and soluble compounds than SAS. Chang et al. [23] observed that COD removal during the ultrafiltration of activated sludge was mainly attributed to sieving/adsorption on the cake that was deposited on the membrane surface and to a lower extent to the adsorption in the membrane pores and on the membrane surface. Regarding the effect of anaerobic and aerobic conditions on CS, major influences on the COD, TKN or P contents were not observed.

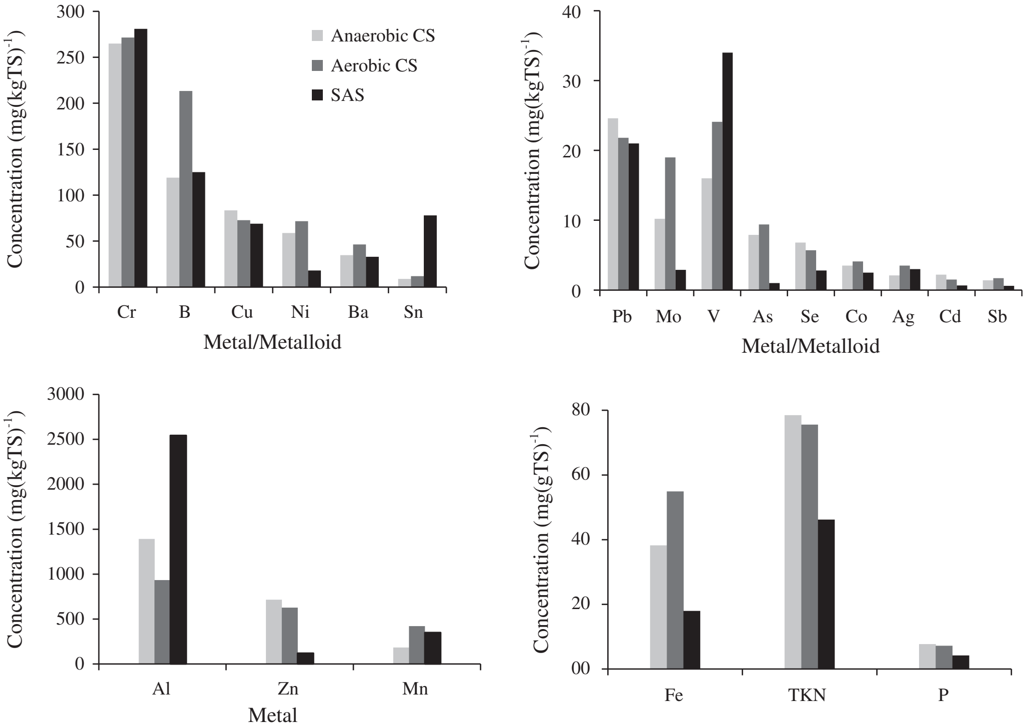

Fig. 4. Concentration of metals, metalloids, TKN and P in SAS at the interior (anaerobic) and exterior (aerobic) of clogged sludge.

Heavy metals and metalloids in the CS were found in the following descending order: Fe > Al > Zn > Cr > B > Cu > Ni > Ba > Pb, V > Mo > Sn > As > Se > Co > Ag, Cd, Sb. As seen in Fig. 4 specific metals/metalloids were found to accumulate much more in CS than in SAS, following the order As > Zn > Mo > Ni > Cd > Sb > Fe > Se > Co. This was probably attributed to the synergistic effect of extracellular polymeric compounds and metal resistant bacteria. Several researchers have linked the increased content of EPS to the enhanced metal binding potential of the biofilm [24,25]. Chang et al. [23] found that the activated sludge—biofilm sludge was more effective in the removal of cadmium compared to SAS. Additionally, oxidative (aerobic) conditions had a minor positive influence on metal bio-precipitation.

4. Conclusions

The MBR coupled to the physicochemical pre-treatment step demonstrated to safeguard the effluent quality for petrochemical effluents. The performance of the MBR with respect to metals/metalloids removal was variable since As, B, Ba, Mo, Al, Ni, Se, Sb, V and Zn were poorly removed (<40%), Pb, Hg, Cu, Ag, Cr, Mn and Co were removed at 40–70% and Fe at > 70%. The PAHs were effectively removed by the clariflocculation unit, while benzene and toluene were removed by the MBR to the level of 1–2 $\mu g\ L^{-1}$. Specific metals/metalloids were found to accumulate much more in the CS than in the SAS, following the order As > Zn > Mo > Ni > Cd > Sb > Fe > Se > Co.

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