MEMBRANE BIOLOGICAL REACTOR (MBR) FOR TREATMENT OF WASTEWATER CONTAMINATED BY PETROLEUM ORGANIC COMPOUNDS

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Abstract Nowadays, increasingly stringent environmental legislation relating to freshwater conservation and pollution abatement requires the application and development of reliable technologies for wastewater treatment. Submerged membrane bioreactor (MBR) is a technology which is able to fulfill those specific purposes. In the present studies lab scale MBR performance was monitored during five months in order to investigate a long-term operational stability in removal of organics and ammonia from synthetic wastewater contaminated by petrochemical compounds. The MBR treatment was very effective, and the reduction by more than 90% of chemical oxygen demand (COD) and total organic carbon (TOC) were obtained. Moreover, so high as 500 µl/L of petroleum contamination did not influenced the performance of the nitification process, and total oxidation of ammonia was always ensured. The MBR influent and MBR effluent wastewaters were characterised using a solid phase extraction (SPE) followed by HPLC- UV-DAD analyses. Nearly complete removal of petroleum originated non-polar micropollutants was observed.

Keywords Membrane Bio-reactor; nitrification; petroleum organics, HPLC analysis

INTRODUCTION

The membrane bioreactor (MBR) is a system which combines traditional activated sludge treatment process with microfiltration (MF) or ultrafiltration (UF) membrane for solid- liquor separation. Two basic MBR configurations exist: the external (side stream) and the internal (submerged). However, due to the high cost of pumping of activated sludge from separate unit process back to bioreactor makes side stream configuration unpractical for full-scale municipal wastewater treatment plants (Gander et al. 2000). In contrast, submerged system, where the membranes are immersed in biological reactor, is a more economic solution and is increasingly becoming an important innovation technology in wastewater treatment since its introduction in 1990's. Ever since unit costs for application of commercially available submerged MBR systems reduced by up to 30-fold and the further reductions are expected (DiGiano *et al.*, 2004). Such significant reduction in the costs of both membranes and processes over the past 10–15 year was possible due to improvements in process design, improved operation and maintains schedules and greater membrane life (Kennedy and Churchouse, 2005).

MBRs offer several advantages in comparison to conventional activated sludge process , e.g., smaller footprint (more compact installation), unlike secondary clarifiers, the quality of solid separation is not dependent on mixed liquor suspended solids (MLSS) concentration and characteristic (e.g. settleability), high sludge age (up to 300 days), less sludge production (Churchouse, 1997**;** Takht Ravanchia 2009). MBR is a highly effective treatment process and especially is recommended for wastewater treatment in areas requiring a high quality effluent (such as discharge to bathing waters or water reuse) or specialization in the microbial community (e.g. high strength liquors, effective nitrification) (Gander et al. 2000). One of the main drawback of MBR technology is related to managing membrane fouling (Le-Clech,et al. 2006).

The most significant barrier to the more widespread installation of MBRs still remains cost, there are a number of drivers which mitigate this factor (Judd, 2006). However, the MBR process has now become an attractive choice for the treatment and reuse of industrial wastewaters such as paper mill; food production; fuel port facilities (Galil and Levinsky 2007, Qin et al. 2007, Takht Ravanchia et al. 2009) and municipal wastewaters (Gander et al. 2000, Judd, 2006, Yang et al. 2006). It is evidenced by constantly rising numbers of facilities and their capacities worldwide (Yang et al. 2006).

Some chemicals present in influents of wastewater treatment plant may inhibit irreversibly sensitive biological processes, such as nitrification (Dokianakis et al. 2006) and consequently cause failure of the treatment. On the other hand inappropriate treatment of some industrial wastewaters i.e. from petrochemical or oil refinery sector, often have an impact on the fauna and has a toxic effect close to the outfall (Wake, 2005). Among mutagenic chemicals that have been identified in such effluents there are polycyclic aromatic hydrocarbons (PAHs).

The aim of the studies was to investigate operational stability of removal of organics and ammonia nitrogen in MBRs from synthetic wastewater contaminated by petrochemical compounds. The performance of biological treatment was evaluated by physicochemical analysis such as nitrogen forms, COD, TOC etc. additionally, monitoring of micropollutants (PAHs) in wastewaters was performed using HPLC-UV-DAD after pre-treatment in solid phase extraction (SPE) system.

Materials and methods

Figure 1 shows schematic diagrams of lab scale microfiltration membrane bioreactor (MBR). MBR was equipped with submerged A4 Kubota membrane (cartridge type 203), which was made of chlorinated polyethylene and had the nominal pore size of 0.4 μm and an effective surface of 0.3 m^2. The experiments were carried out in the reactor operated under aerobic conditions (oxygen concentration in the tank: 1–4 mg/L). The continuous aeration provided for both MBRs limited membrane fouling. The MBR was operated at room temperature of 22 ±1.5^{o}C and at the working volume of 10.5 L.

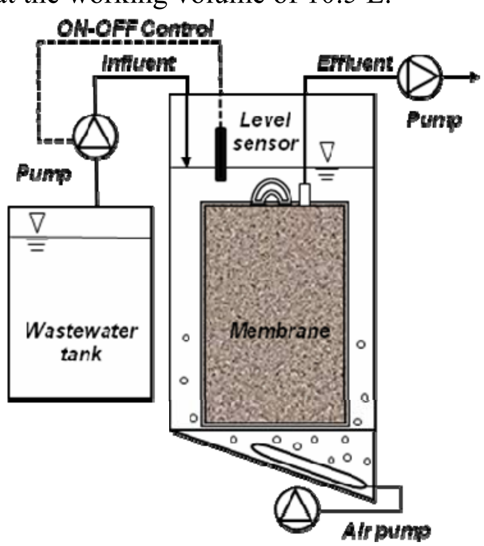

Figure 1: Schematic diagram of the MBR

For the start-up, MBR was filled with activated sludge from the local municipal wastewater treatment plant (WWTP) and fed with synthetic wastewater. The synthetic wastewater composition used to feed the MBRs is shown in Table 1. The feed was pumped into MBR (inlet) and pumped out of MBR (permeate) using peristaltic pumps (Zalimp, Poland). Then, the feed of MBR was supplemented with different doses of petroleum organics (P-30 fraction). P-30 fraction was a vacuum distillate of crude oil furnished by PKN Orlen oil refinery (Poland). The following doses of this petroleum substance were used in the experiment: 50, 200, 500 and 1000 μl/L in Period I, Period II, Period III and Period IV respectively. Emulsified wastewater was prepared by mixing P-30 fraction with water solution of a surfactant (Tween 80) in a blender.

Table 1. Composition of synthetic wastewater in tap water

Component	MBR A and B
Dry meat extract (mg/L)	80
CH_3COONa (mg/L)	700-1300
Yeast extract (mg/L)	10
NH_4Cl (mg/L)	200-250
K_2HPO_4 (mg/L)	27
KH_2PO_4 (mg/L)	10
$MgSO_4.7H_2O$ (mg/L)	15
Tween 80 (μL/L)	5-15
P-30 fraction (μL/L)*	0-1000

The analyses included COD (Chemical Oxygen Demand- dichromate method, Merck), BOD_5 (5- day Biochemical Oxygen Demand - Oxi Top WTW system) and petroleum ether extractable organics (PEEO), (gravimetric method- PN-86C-04573/01)

Ammonium nitrogen, nitrite and nitrate nitrogen were determined according to standard Merck methods using Spectroquant®test. The pH values and the oxygen concentration were analyzed using pH-meter (WTW 340i) and oxymeter (WTW 340i) respectively. Volatile suspended solid (VSS), mineral suspended solid (MSS) and mixed liquor suspended solid (MLSS) were measured by heating (gravimetric method- PN - 72/C - 04559/03). Alkalinity was measured by titration method.

The quality of the feed and reactor permeate wastewater obtained during the studies is shown in Table 2.

Table 2. Characteristics of the MBRs influent and effluents

Parameters	MBR influent	MBR effluent
COD (mg/L)	655-3290	50-202
BOD_5 (mg/L)	460-1150	0-14
NH_4^+-N (mg/L)	40-75	0-4 (50)*
NO_2^--N (mg/L)	0	0.1-2.2
NO_3^--N (mg/L)	0	39-71(0.0)*
PO_4^{3-}-N (mg/L)	7.11	n.a.
pH	7.1-7.5	7.6-8.2

*experimental period IV (dose 1000 μl/L)

The detection of polycyclic aromatic hydrocarbons (PAHs) in the raw and biologically treated wastewater was performed using high performance liquid chromatography (HPLC - UVD 340u, Gynkotek). The acetonitrile, water , methanol (grand, POCH – Gliwice, Poland) was applied as a mobile phase in a gradient mode elution. The chromatographic separation of the sixteen PAHs was performed using SUPELCOSIL ™ LC-PAH HPLC Column protected by SUPELCOSIL™ LC-18 Supelguard (Supelco). For solid-phase extraction Supelclean Envi-18 sorbent was applied and performed according to protocols suggested by Busetti and co-workers (2006).

RESULTS AND DISCUSSION

In the initial stage (acclimation), the biomass of activated sludge from a WWTP was acclimated to the synthetic wastewater medium (without any petrochemical contaminants) (Table 1) and to hydrodynamic conditions of the MBR system. The synthetic wastewater was readily degradable (BOD_5/COD=0.7), consequently acclimation proceeded very rapidly and already after one week of the process above 93% of COD (Fig. 2a) and 99.7 % of BOD_5 were removed.

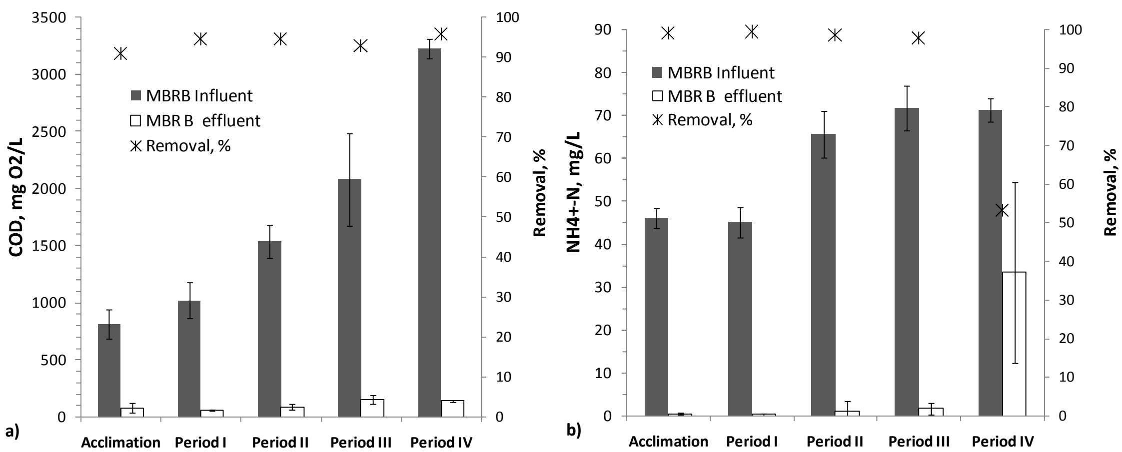

Figure 2. COD (a) and NH_4^+-N (b) concentrations in raw and treated wastewater vs. Time (period)

After 1.5 month of operation, the surfactant addition of oil/water emulsion into the feed of MBR system was initiated. The lowest dose (P-30 amounted to 50 µl/L) of petrochemical contaminants (period I) did not influence organics removal (Fig. 2a) nor oxidation of ammonia nitrogen (Fig. 3b) in MBR. The ammonia oxidation to nitrate with efficiency 99% was achieved in the system.

Next, the MBR was fed with synthetic wastewater in which concentrations of pollutants (surfactant oil/water emulsion) rapidly increased to 200, 500 and 1000 µl/L of P-30 fraction for period II, III and IV respectively. It can be noticed by an increase of COD concentration in the MBR versus period (Fig 2b). For instance COD was 3.2-folds higher in the period IV than in the period I, which corresponded to an increase of petrochemical organics from 4 to 70% in synthetic medium. On the other hand, an increase in COD content in the feed were balanced by the increase of MLSS concentrations in the bioreactor (Table 3). Thus, organic loading rates (OLR) (gCOD/gMLSS d) did not dramatically fluctuate among all periods (Table 3).

Even though BOD_5/COD ratio in the influent of MBRB were decreasing from 0.7 in the acclimation and period I to 0.5, 0.4 and 0.3 for period II, period III and period IV, the organics removal was at very high level. Irrespectively of the P-30 content in the influent of MBR B the removal of organics above 93% of COD and 99.2% of BOD_5 was ensured. For instance at highest dose of contaminants in the period IV (average COD=3250 mg/L) the COD concentrations were below 140 mgO_2/L in effluent on average.

Such a great elimination of organics in MBR system (even though the biodegradability-BOD_5/COD ratio decrease) can be attributed to the retention of emulsified wastewater by MF membrane in bioreactor. It is conceivable that petroleum oily pollutants were partly accumulated in MBR increasing the concentration of MLSS, which was related to the 90% increase of MLSS organic fraction (VSS) in the period IV.

Table 3. Operation parameters of MBR

Parameters (units)	Acclimation	Period I	Period II	Period III	Period IV
OLR (gCOD / gMLSS d)	0.298	0.345	0.278	0.393	0.479
ALR (gNH_4^+-N / gMLSS d)	0.021	0.012	0.013	0.016	0.012
MLSS (g/L)	3.5	4.3	4.7	6.5	8.3
Duration period, d	45	28	45	24	16
HRT (h)	28	25	26	23	22
SRT (d)	89	79	77	83	51

Similarly reduction of COD, exceeding 94% was obtained by Scholz and Fuchs 2000 for treatment of oil contaminated synthetic wastewater (COD ranging from 5262 to 7877 mg/L) in MBR with external tubular cross flow ultrafltration unit. More recently, high removal efficiency of both COD and hydrocarbons in hollow-fibre MBR (MF unit) for wastewater coming from the washing of mineral oil storage tanks was proved by Alberti and co-workers (2006). In that case, the reactor performance of reduction of COD ranged from 93% to 96% , for concentration ranging from 1300 to 7964 mg/L and HRT from 7.9 to 31.8 d.
Apparently, oily pollution up to the concentration of 500 µl/L (P-30) did not influence ammonia oxidation in MBR system. It can be observed that ammonia loading rate (ALR, g NH_4^+-N/ gMLSS d) in the period IV decreased by 25% in comparison to the ALR in the period III (Table 3). This was due to increase MLSS in the reactor, but not necessarily indicated that nitrifies concentration in the period was higher as well. Actually, it should be noted that volumetric ammonia loading rate in the period III and IV was the same, and amounted 88.5 g NH_4^+-N/ m^3 d.
The conditions for accommodation of slowly-growing nitrifying bacteria became less favorable in the period IV, when the concentration of oily contamination was 1000 µl/L. A few days after the exposition of activated sludge in the MBR to the highest dose P-30 fraction, the ammonia nitrogen concentration increased significantly to 50 mg/L in the effluent of reactor. It proved the inhibition of nitrification process (Fig.2a, Table 2).

The removal of hydrocarbons was also determined by petroleum ether extractable organics (PEEO) and HPLC analysis. PEEO parameter which represent oil and grease contaminated was eliminated by more than 90% (Fig. 3a) in MBR system.
Figure 3b depicts sample extract from synthetic wastewater from influent and effluent of MBRB (period II – 200 µl/L of P-30 fraction). The chromatograms obtained for the MBR influent and effluent wastewaters show complete removal of the majority of compounds. Similar profiles of chromatograms were obtained on different days for from the period III, IV (P-30 ranged from 500 to 1000 µl/L).
Identification of analytes in the chromatograms was based on retention times, combined with structure confirmation , which was performed by matching the UV-DAD analyte spectra.
Finally the following for PAHs: naphthalene, fluorene, phenanthrene, anthracene were identified and quantified. The analyses proved that hydrocarbons (including PAHs) originated from petroleum contamination were almost completely removed during the biodegradation/membrane filtration. Similarly Fatone and co-workers (2005) confirmed high removal capability of micropollutants (i.e. metals and PAH) in MBR process. This effect can

meaningfully be ascribed to a permeate quality, complete elimination of suspended solids, in which pollutants are adsorbed.

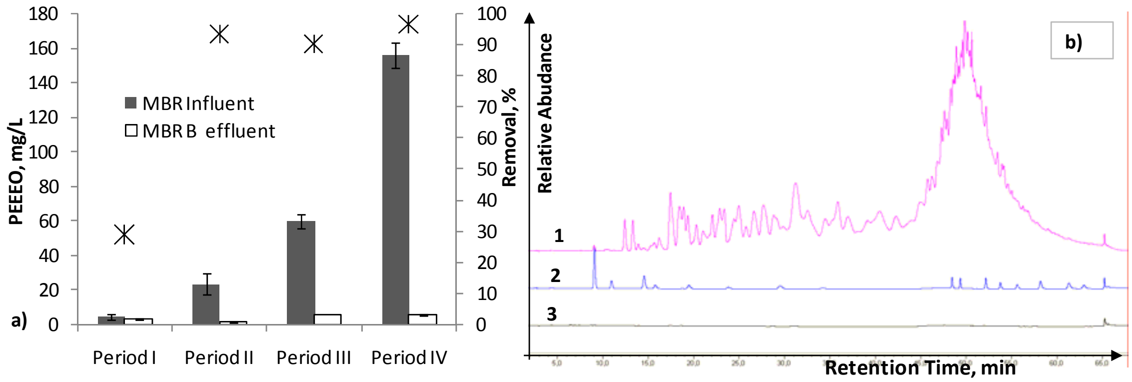

Figure 3 PEEO in MBRB vs. time (periods) (a) and chromatograms obtained in the HPLC analyses with UV-DAD detector set at 220nm , normalized scale: 1- Influent (period 2), concentration factor =250, 2- analytical standard of 16 PAHs (about 2ppm of each PAH) , 3-Effluent (period 2), concentration factor=500

CONCLUSIONS

The performance of a laboratory-scale MBR treating synthetic wastewater contaminated by petroleum organics was investigated. The research proves that the process of eliminating pollutants from synthetic wastewater proceeds effectively and removal in 93%, and 99% for COD and BOD_5 were obtained respectively. The organics removal efficiency was not affected by the maximal tested dose of petroleum contamination (1000 μl/L). In contrast to organics, ammonia removal in MBR was influence by petroleum chemical and inhibition of nitrification was noted for contaminates amounted to 1000 μl/L. The chromatographic analyses showed almost complete reduction of oily hydrocarbons contained in the synthetic wastewater.

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