



Novel low-fouling membrane bioreactor (MBR) for industrial wastewater treatment

Shamim Ahmed Deowan^a, Francesco Galiano^b, Jan Hoinkis^{a,*}, Daniel Johnson^c,
Sacide Alsoy Altinkaya^d, Bartolo Gabriele^e, Nidal Hilal^c, Enrico Drioli^f, Alberto Figoli^{b,*}

^a Institute of Applied Research (IAF), Karlsruhe University of Applied Sciences, Moltkestr. 30, 76133 Karlsruhe, Germany

^b Institute on Membrane Technology, ITM-CNR, Via P. Bucci, Cubo 17/C, I-87030 Rende, Italy

^c Center of Water Advanced Technologies and Environmental Research (CWATER), College of Engineering, Swansea University, Swansea SA28PP, United Kingdom

^d Department of Chemical Engineering, Izmir Institute of Technology, 35430 Urla Izmir, Turkey

^e Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 12/C, I-87030 Rende, CS, Italy

^f Department of Chemical Engineering, University of Calabria, I-87030 Rende, CS, Italy

ARTICLE INFO

Article history:

Received 23 December 2015

Received in revised form

28 February 2016

Accepted 1 March 2016

Available online 17 March 2016

Keywords:

Wastewater treatment

Textile industry

Membrane bioreactor (MBR)

Low fouling membrane

Polymerisable bicontinuous microemulsion (PBM)

ABSTRACT

A novel antifouling coating of ultrafiltration (UF) commercial membranes, based on a polymerisable bicontinuous microemulsion (PBM) technique, was developed and tested for the first time in a membrane bioreactor (MBR) using an artificial model textile dye wastewater and compared with a commercial uncoated UF membrane. The results showed that the commercial MBR module faced severe fouling problems whereas the novel coated PBM MBR module reduced the fouling significantly. The analysis of fouling rate using a resistance model confirms that PBM coated membrane has a higher antifouling effect. The antimicrobial properties of the PBM membrane contributed by polymerisable cationic surfactant acryloyloxyundecyltriethylammonium bromide (AUTEAB) guaranteed an anti-bio-fouling effect preventing the growth of microorganisms on the membrane surface. In addition, the PBM MBR module showed $10 \pm 1\%$ higher blue dye removal efficiency and a similar rate of COD removal efficiency of about $95 \pm 1\%$ compared to commercial module. However, water permeability was slightly lower due to extra resistance of the PBM coating. Root mean squared (RMS) roughness measurement and analysis of AFM images confirmed that the stable novel membrane coating still existed and showed antimicrobial effect even after 105 days of operation. The results obtained demonstrated the potential of the low fouling PBM membrane.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Membrane Bioreactor (MBR) technology is recognised as a promising technology to provide water with reliable quality for reuse and is very attractive for industrial e.g. textile wastewater treatment. The implementation of membrane (micro-/ultra-filtration) for solids retention into biological treatment system leads to several substantial improvements compared to conventional biological processes [1]. However, application of state-of-the art MBR technology for textile wastewater treatment as a single-step process is rather limited and typically requires downstream post-treatment such as nanofiltration or reverse osmosis systems [2], combined anaerobic-aerobic MBR processes [3,4] or modified MBR membranes.

* Corresponding authors.

E-mail addresses: jan.hoinkis@hs-karlsruhe.de (J. Hoinkis), a.figoli@itm.cnr.it (A. Figoli).

On the other hand, severe fouling is a limiting factor for application of MBR technology especially in high-strength industrial wastewater like textile wastewater and need to be mitigated for real field application [5]. Membrane fouling is the main limitation for faster development of this process, particularly when it leads to flux losses that cleaning cannot restore [6]. Once the membrane is affected by fouling and extensive chemical cleaning is not able to regain the flux, the membrane needs to be replaced which may account up to 30–50% of the operation cost. To overcome the membrane fouling problems, many researchers have modified and tested membranes for MBRs applying different techniques. Yu et al. modified a hollow fibre membrane surface of MBR by NH_3 and CO_2 plasma treatment and showed that the fouling indices of the modified membrane was lower than the unmodified membrane [7–9]. Although the plasma treatment process has many advantages, such as a very shallow modification depth compared to other surface modification techniques, it still has drawbacks. For example, the chemical reactions of the plasma treatment are

rather complex, so the surface chemistry of the modified surface is difficult to understand in detail and thus, currently it is not possible to extend plasma treatment to large-scale operation. To overcome the disadvantages of plasma treatment, Yu et al. applied the surface graft polymerisation method to improve the membrane permeation in MBRs [10]. The performance of the modified membrane was better than the unmodified but resulted in an increase in membrane production cost. Asatekin et. al. obtained a novel NF membrane by coating a commercial PVDF UF membrane with the amphiphilic graft copolymer PVDF-g-POEM [11]. This material exhibited high fouling resistance for a variety of model biofoulant solutions and a high effluent quality. However, the pure water permeability was much lower than that of UF membranes, currently employed in MBRs [12]. Bae and Tak prepared TiO₂ embedded polymeric membranes by a self-assembly process and applied them to the filtration of MBR sludge [13,14]. TiO₂ embedded membrane shows less fouling propensity due to higher hydrophilicity compared to virgin membranes and it can be applied in membrane modification for fouling control in MBRs. Zhao et al. prepared a composite microfiltration membrane by blending polyvinylidene fluoride (PVDF) and hydrophilic graphene oxide (GO) nanosheets and applied them in submerged MBR [15]. Among the obtained results, higher critical flux, sustained permeability, lower pore plugging resistance and less EPS accumulation were noticed due to changed surface properties of GO modified PVDF membrane. However, the modified membrane size (0.0162 m²) needs to be scaled up considering the cost factors to test the applicability of pre-commercialisation of the concept [15].

In general, the research strategy for reducing fouling should address development of low fouling membranes with much narrower pore size distributions, stronger hydrophilicity and larger porosity than the currently used membranes. But none of the above mentioned modified membranes have been scaled up so far due to some significant drawbacks, such as a complicated manufacturing process, increased production costs, complex surface chemistry of modified membranes [7–10], process limitations [13–14] and very low permeability [11].

Another promising approach to mitigate the fouling is the membrane surface modification by developing novel low-fouling membrane materials based on the polymerizable bicontinuous microemulsion (PBM) technology [16,17]. The purpose of membrane surface modification is to reduce the fouling and/or biofouling by addressing parameters such as membrane roughness, hydrophilicity and membrane charge, which are strongly related to fouling [18,19]. Some researchers have prepared PBM membranes by identifying the pore size and optimizing the polymerization conditions (i.e. temperature and microemulsion conditions) but they have not been applied in surface modifications [20–23]. On the other hand, Shao et al. [24] and Cheng et al. [25] prepared some surface modified membranes with antifouling properties following different preparation techniques and found improved performances in lab tests, but they have not been applied yet for MBR applications.

In this study a nano-structured low-fouling UF membrane coating was prepared using PBM technique in the direction of overcoming fouling problems in textile wastewater treatment by MBR processes. This can be considered an innovative approach to prepare surface modified MBR membranes with antifouling properties. The prepared novel coated membranes were formulated into a MBR module and it was assessed for its feasibility as an antifouling MBR module compared to traditional membranes. The study was performed in a lab-scale MBR set up. The water permeability, COD removal efficiency, textile dye removal efficiency, evaluation of critical flux (CF) and existence of coating after the MBR experiment, antifouling properties, antimicrobial properties were studied. Finally, the performance of the novel

coated MBR module was compared to a commercial MBR module. As reported in our recently published paper [17], improved hydrophilicity, smoother surface, channel-like structure and antimicrobial activity are main benefits exhibited by PBM membranes making them ideal candidates to be applied in wastewater treatment processes. PBM technique offers low cost membrane production due to use of majority of the commercially available chemicals used for membrane preparation and has great potentiality for MBR processes with the specific aim of fouling mitigation regarding industrial wastewater treatment.

2. Materials and methods

2.1. Novel low fouling membrane

The novel low fouling membrane, used for the MBR treatment, was prepared by PBM process following the optimized process given in a recently published paper [17]. In addition a study of the fouling rejection of humic acid by several formulations of these membranes were reported by Johnson et al. [26]. The chemicals used for preparing PBM membrane were: methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), acryloyloxundecyltriethyl ammonium bromide (AUTEAB), ethylene glycol dimethacrylate (EGDMA), ammonium persulfate (APS), N,N,N',N'-tetramethylethylenediamine (TMEDA). AUTEAB is a lab synthesised surfactant and the other chemicals were purchased from Sigma Aldrich (Germany). The microemulsion was prepared in a double-necked round bottom volumetric flask following the steps described by Galiano et al. [17]. Firstly, the monomer methyl methacrylate (MMA) and co-surfactant 2-hydroxyethyl methacrylate (HEMA) were mixed. Next, water was added to the system followed by AUTEAB. The solution was then mechanically stirred for 5 min and when a clear and transparent solution was obtained, the cross-linker EGDMA was added. Once a clear microemulsion was obtained, the redox initiator APS was added to a concentration of 0.3% v/v and TMEDA was added according to the concentrations reported in literature. The microemulsion was then purged with nitrogen gas at 20 ± 2 °C and left to react. The microemulsion was subsequently cast on a commercial PES ultrafiltration (UF) membrane (NADIR® PM UP 150, Microdyn-Nadir [27]) (see Table 1) in an inert N₂ gas saturated casting chamber.

The casting knife air-gap used was 250 µm. A N₂ saturated environment was needed to exclude any contact with air or oxygen since they interfere with the polymerisation process. The temperature of the casting chamber was also kept constant at 20 ± 2 °C during the polymerisation and over 24 h. The thickness and pore size of the PBM coating was studied by Galiano et al. by SEM [17]. The thickness ranged from a minimum of 0.2 to a maximum of 3 µm and the study showed a pore size ranging between 0.03–0.05 µm. The membrane sheets with dimensions of 30 cm × 30 cm were made and then laminated in collaboration with Microdyn-Nadir (Germany) for the production of the envelopes to be used as MBR modules. The membrane module including three envelopes produced in this way covered an active membrane surface of 0.33 m². The novel coated PBM MBR and PES UF MBRs are named as PBM MBR and Com1 and Com2 MBR modules (Fig. 1), respectively.

2.2. Experimental set-up

A small lab-scale submerged membrane bioreactor treating model textile dye wastewater (MTDW) was used for carrying out the experiments. The MBR was equipped with adequate sensors (pressure, flow, pH, conductivity sensors etc.) as well as the LabVIEW (National Instruments, USA) data acquisition system in order

Table 1
Technical data of PES UF membrane [27].

Membrane properties	Technical data
Active layer	PES
Support layer	PET
MWCO	150 KDa
Pore size	0.04 μm
Water permeability (WP)	> 250 L/m ² h bar (measured at 20 °C)

to monitor all sensors (Fig. 2). The hydraulic volume of the employed MBR reactor was 57 L. The membrane reactor was seeded with biological sludge from a local laundry wastewater treatment plant. The experiments were carried out following the operating conditions as mentioned in Section 2.6. The active membrane surface area of commercial MBR module Com1 as well as the novel PBM MBR module (Section 2.1) was 0.33 m².

The experiments with commercial PES UF MBR membrane module (named Com1) have been carried out for 105 days and subsequently under similar operating conditions (Section 2.6) experiments were carried out replacing Com1 by the novel coated MBR membrane module denoted as PBM for the same period. After the experiments with PBM membrane, similar experiments were performed for 45 days using another commercial PES UF MBR membrane module (denoted as Com2) to verify the operating process conditions. For benchmarking, submerged commercial and novel MBR modules were tested in the same MBR tank sequentially to compare the performances of both modules. To keep the operating process conditions constant, MTDW has been employed as reported in Table 2, due to the fact the composition of real textile dye wastewater changes over the time and season of the year. The operating conditions for both modules were similar. In addition to the MBR set up, a manually operated cross-flow testing unit with active membrane area of 80 cm² from OSMO Membrane System GmbH (Germany) for model textile dye test to determine membrane resistance was applied.

2.3. Model textile dye wastewater (MTDW) compositions

MTDW is mainly based on a red reactive azo dye (Acid Red 4, MW: 380.4 Da, maximum absorption wavelength: 505 nm) denoted as Red and a blue anthraquinone dye (Remazol Brilliant Blue R, MW: 626.5 Da, maximum absorption wavelength: 595 nm) denoted as Blue in this paper (Fig. 3). They represent typical industrial dyes being widely applied in the textile industry.

Glucose was added as a C-source as well as typical salts such as NaCl, NaHCO₃. A common industrial detergent (Albatex DBC) was also added. Moreover, NH₄Cl was added to increase the Total-N value to achieve the recommended COD/N ratio, as reported in literature [15]. The final COD/N ratio of the MTDW was 27:1. The composition of MTDW is shown in Table 2.

2.4. Characterisation of model textile dye wastewater (MTDW)

The characteristics of MTDW process parameters like Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD₅), pH, and electrical conductivity etc. were analysed and reported in Table 3 (adapted from [29]).

2.5. Operating conditions

The MBR experiments were carried out at a temperature of 20 ± 2 °C, transmembrane pressure (TMP) in the range of 30–50 mbar, feed pH 7 ± 0.5 , permeate flux of 2–4 L/(m² h), hydraulic retention time (HRT) of 25–150 h, air supply rate 1.0 ± 0.1 m³/h, and mixed liquor suspended solids (MLSS) 8–12 g/L. The F/M ratio was maintained at 0.05–0.1 Kg COD/(kg MLSS d) and organic loading rate (OLR) 0.5–1.5 kg COD/(m³ d). The dissolved oxygen (DO) of the system was kept at 4–8 mg/L. The operation mode of the system was: suction 8.5 min-relaxation 0.5 min-backflush 0.5 min-relaxation 0.5 min-suction 8.5 min.

Some of the operating parameters have a wide range, e.g. HRT, which occurred due to process fluctuations. Sludge retention time (SRT) is not mentioned here since no sludge was removed from the reactor for the whole experimental period (except small samples for analytical purpose).

2.6. Analytical methods

The COD was analysed with COD cell tests (Method: 1.14541) from Merck KGaA (Germany). The concentrations of red and blue dyes were determined by use of a spectrophotometer (Model: UV-1800) from Shimadzu (Japan) using Beer's law at wavelengths of 505 nm and 595 nm respectively. Oxygen sensors (Model: Oxi340i meter and CelloX[®] 325 O₂ electrode) from WTW GmbH (Germany) were used to determine oxygen. All values of pH and temperature were measured with two pH meters (Model: pH 323 m and Sentix[®] 41-3 electrode) integrated with a temperature sensor from WTW GmbH (Germany). Conductivity measurements were performed with a conductivity meter (Model: Cond 315i meter) from WTW GmbH (Germany). All AFM measurements were performed with a Multimode AFM with Nanoscope IIIa controller (Veeco, USA) using manufacturer supplied software. Tapping mode measurements in air were performed using TESP (nominal spring constant 20–80 N/m) cantilevers (Bruker AXS). *E.coli* (ATCC 25922) bacteria was chosen as test microorganism and antimicrobial activity was investigated using agar medium prepared from Mueller-Hinton-Agar (Merck Cat. No: 1.05437.0500).

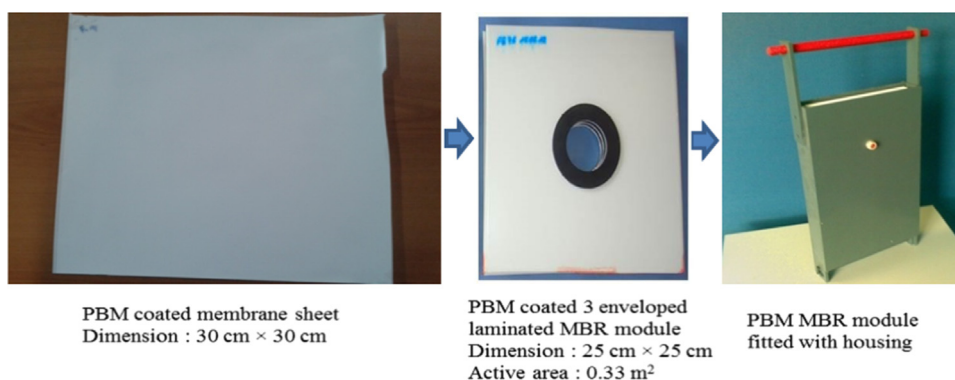


Fig. 1. Preparation of PBM MBR module.

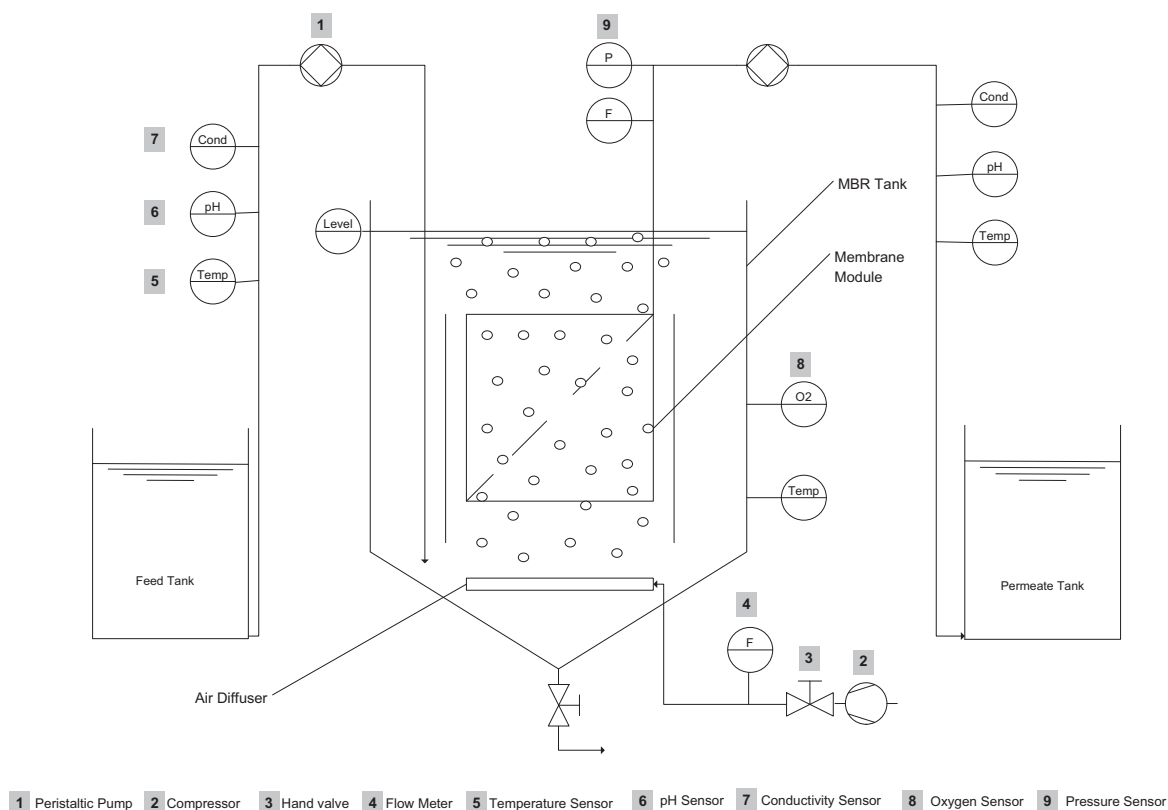


Fig. 2. Schematic of lab-scale membrane bioreactor.

Table 2
Compositions of Model Textile Dye Wastewater (MTDW).

No.	Dyestuffs and chemicals	Concentration (mg/L)
1	Remazol Brilliant Blue R	50
2	Acid Red 4	50
3	NaCl	2500
4	NaHCO ₃	1000
5	Glucose	2000
6	Albatex DBC (Detergent)	50
7	NH ₄ Cl	300

Table 3
Characteristics of model textile dye wastewater (MTDW).

Parameters	Unit	Theoretical values	Experimental values with standard deviation
pH			7.5 ± 0.5
COD	mg/L	2311	2367 ± 125
TOC	mg/L	863	847 ± 28
BOD ₅	mg/L		731 ± 80
Total N	mg/L	84	78 ± 8
Conductivity	mS/cm		6.6 ± 0.15

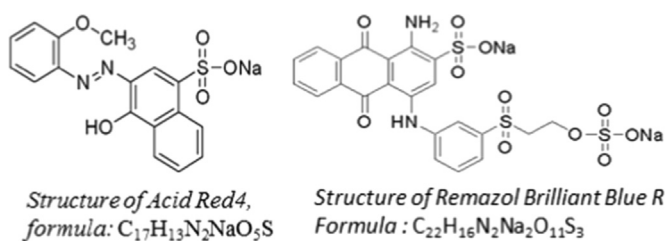


Fig. 3. Structure of the applied textile dyes.

3. Results and discussion

3.1. Effect of fouling regarding water permeability and COD removal efficiency

Water permeabilities of the three modules are presented in Fig. 4a. The average water permeability of PBM membrane is 38 L/(m² h bar) whereas the average value of Com1 is around 52 L/(m² h bar) (including the acclimation period at the beginning of the experiment). The obtained results indicate that the water permeability (WP) of PBM membrane reduced to 27% compared to

that of Com1. However, during the operation time of 105 days the Com1 membrane faced severe fouling problems on day 27 and the module needed replacement, since physical cleaning with pure water and chemical cleaning of 1% H₂O₂ could not regenerate them. The replaced Com1 membrane also faced lower permeate production on day 50 and day 64 due to lower HRT (25–57 h) and chemical cleanings with 1% H₂O₂ were needed to regenerate the permeability. The HRT was reduced (25–57 h) intentionally to check the response of Com1 but it was not stable at this HRT range. So, the operation with Com1 was resumed at operating HRT range as mentioned in Section 2.6. However, PBM membrane faced no fouling problem for the whole period of the experiments (105 days) and no cleaning was required. The lower cleaning frequency could reduce the MBR operation cost and contribute to ease of operation. The PBM membrane operation was very stable with almost no process fluctuation (Fig. 4). The WP of Com2 membrane module operated immediately after the PBM module was around 56 L/(m² h bar) which was almost similar to that of Com1. This shows that the biological process conditions in the MBR reactor during the different experimental sequences are almost similar.

The results show that PBM has a lower fouling propensity and consequently needed no membrane replacement within the

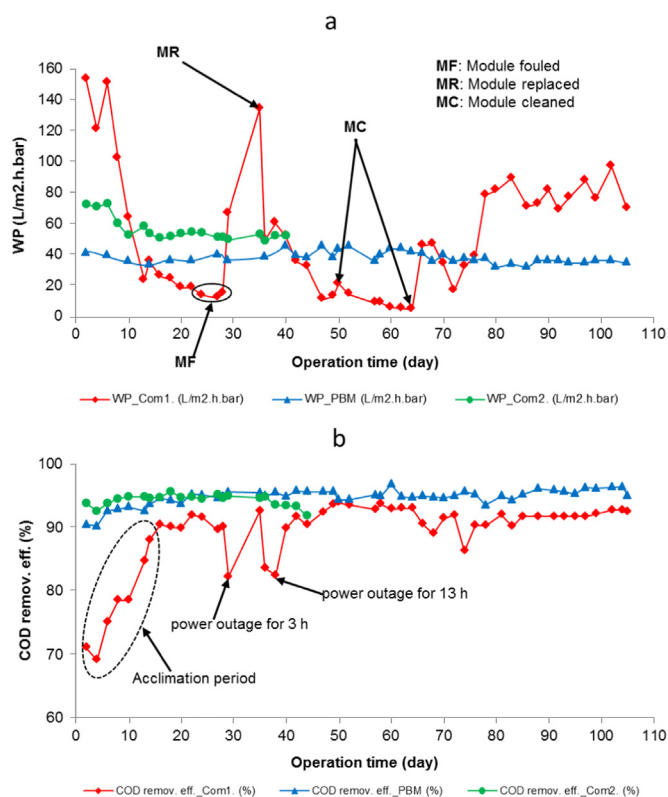


Fig. 4. (a) Water permeability and (b) COD removal efficiency of Com1, PBM and Com2 MBR experiments.

studied period. The antimicrobial properties, ensured by the cationic surfactant AUTEAB used for the PBM membrane preparation have contributed to an anti-biofouling effect preventing the growth of microorganisms at the membrane surface. This was confirmed by membrane resistance model analysis in Section 3.4. After 105 days of MBR experiments with the commercial PES (Com1) and novel coated PBM MBR module, it was noticed that the commercial module was densely covered with biological sludge (Fig. 5a) while the PBM module was comparatively cleaner (Fig. 5b). This is an indication that PBM membrane prevented microorganisms from creating bacterial colonies on the membrane surface.

The membrane replacement, caused by fouling, drives the operating costs higher. For this reason, PBM membranes could be economically viable due to longer operation periods despite a slightly lower flux.

As shown in Fig. 4b the COD removal efficiency with the novel PBM MBR module was very stable at $95 \pm 1\%$ (2367 ± 125 mg/L inlet COD fed to the membrane bioreactor) with a HRT in the range of 25–150 h and a MLSS of 8–12 g/L. Whereas the average COD

removal efficiency of the commercial module (Com1) was around $90 \pm 1\%$. It showed higher fluctuations at the beginning due to acclimation and power outages. The commercial module (Com2) which was directly run after the PBM module showed almost similar COD removal efficiency like the PBM MBR module as shown in Fig. 4b. However, it can be noticed that the COD removal efficiency of Com2 was tending towards down grading values at the end though there was almost no change in its water permeability. It can be concluded that the PBM MBR membrane module showed high and stable COD removal efficiency compared to Com1 and Com2 module as well as stable water permeability. However, long term operation with larger modules is imperative to study the effect of the novel PBM MBR module regarding COD removal and water permeability.

3.2. Effect of dye removal efficiency relating to permeate quality

The removal efficiency of the red dye with Com1 and the PBM was fluctuating in the range of 40–50%. Only Com2 directly tested after PBM trials showed lower fluctuation but lower red dye removal efficiency of 23% (Fig. 6a). The blue dye removal efficiency for PBM module increased to $55 \pm 1\%$ whereas for the commercial modules (Com1 and Com2) it fluctuated at around $45 \pm 1\%$ (Fig. 6b). Consequently, the PBM module showed $10 \pm 1\%$ higher blue dye removal efficiency than the commercial membrane. The red and blue dyes from MTDW are low biodegradable. The low biodegradability of the dyes (Red and Blue) was indicated by the low BOD₅/COD ratio of both dyes (BOD₅/COD ratio of Red: 0.33 and BOD₅/COD ratio of Blue: 0.35). Yigit et al. [5] discovered that the main mechanisms of dye removal in aerobic MBR system are mainly due to biodegradation and adsorption onto biomass. So, the dye rejections in this study might have occurred due to biodegradation and adsorption of dyes on sludge.

The permeate with higher dye removal efficiency indicates better permeate quality. In connection to this, PBM module showed $10 \pm 1\%$ higher permeate quality regarding blue dye content compared to commercial modules (Com1 and Com2). On the other hand, the red dye removal efficiency of Com2 module reduced significantly to 50% indicating the concern of permeate quality. In summary the permeate quality of the PBM module was comparatively stable and slightly higher in terms of COD (Fig. 4b) and blue dye removal efficiency (Fig. 6b), compared to commercial modules.

3.3. Effect of critical flux (CF) regarding membrane performances

The critical flux is generally regarded as the flux above which cake layer or gel layer formation by particles or colloids occurs rapidly. It has been reported that the critical flux has significant effects on membrane fouling and MBR operation [15]. In this study the critical flux was determined in order to analyze the performance of the Com1 and PBM modules. For determining critical

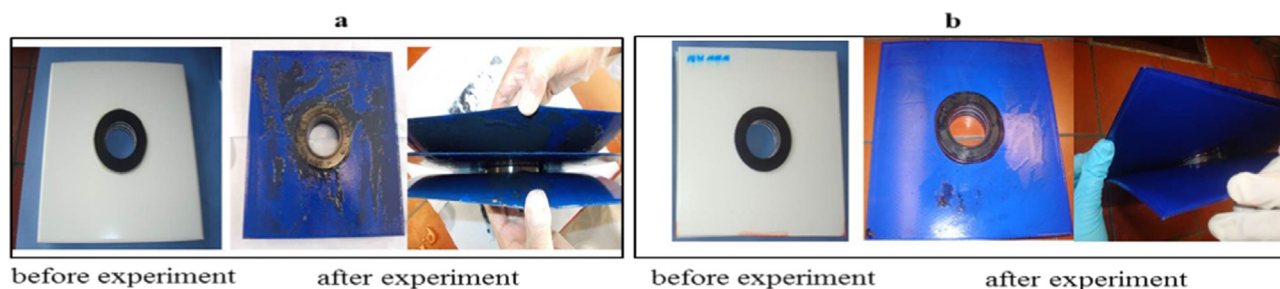


Fig. 5. (a) Com1 and (b) PBM MBR modules before and after pilot trials.

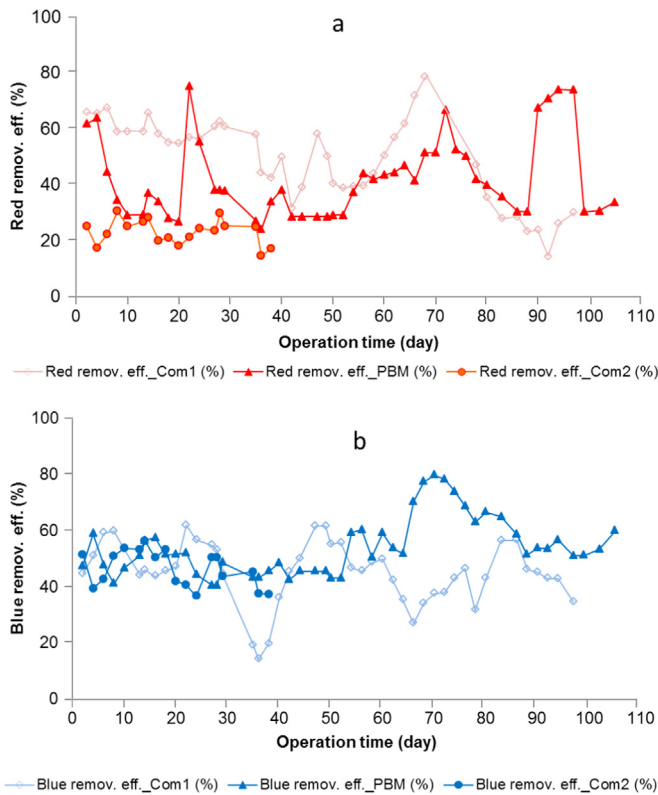


Fig. 6. Removal efficiency of (a) red dye and (b) blue dye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

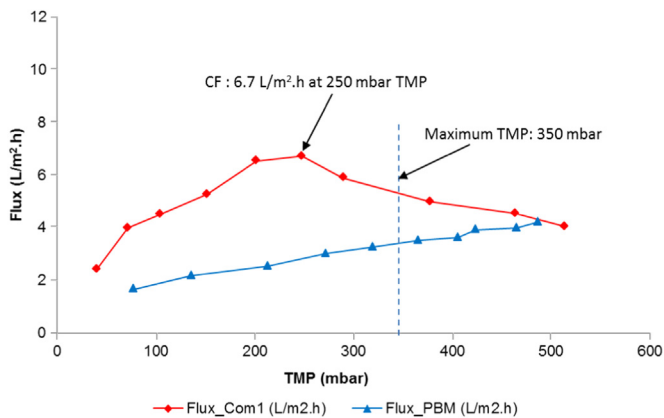


Fig. 7. Critical flux of Com1 and PBM membrane.

flux, the power of the suction pump was increased stepwise in order to increase water flux with corresponding transmembrane pressure (TMP). This method is in line with Bouhabila [28] where it is reported by plotting flux against TMP, it is possible to observe the transition between constant and non-constant permeability at the onset of fouling. The experiment was carried out with Com1 and PBM modules with activated sludge fed with MTDW. The maximum TMP limit for the applied membrane modules was 350 mbar as recommended by the Com1 module supplier (Microdyn-Nadir, Germany). The flux and TMP development, from critical flux experiment, are shown in Fig. 7.

Fig. 7 shows that for the Com1 module, after maximum flux of 6.7 L/(m² h) and TMP of 250 mbar, the flux decreased at higher

TMP indicating a severe membrane fouling. On the other hand, the PBM module flux still increased beyond the TMP of 250 mbar but it was crossing the maximum limit of TMP (350 mbar) recommended by Com1 module manufacturer. The maximum flux obtained experimentally with the PBM membrane was 3.5 L/(m² h) at TMP of 350 mbar and around 4 L/(m² h) at TMP of 500 mbar. This indicates that critical flux with PBM module has not been achieved yet which could be higher than that of Com1 at higher TMP and potentially could be used for longer MBR operation.

3.4. Effect of fouling propensity determined by membrane resistance model

The membrane resistance model is introduced to study systematically the effect of the fouling layers on membrane performances. For this study, two different foulants such as model textile dye wastewater (MTDW), the test media used for this study and MBR activated sludge which are responsible for creating fouling layers on the membrane surface, have been considered.

According to Darcy's Law, a relationship between TMP and flux can be developed as shown in Eq. (1).

$$J = \frac{TMP}{\mu R_t} \quad (1)$$

where, J is membrane permeate flux (L/m² h), μ is dynamic viscosity of permeate (N s/m²) and R_t total filtration resistance (1/m). R_t can be expressed as the sum of individual resistances, which can be varied based on the number and type of resistances considered (adapted from Jifeng et al. [30]). For this paper, the expression of R_t varied depending on the particular foulants and experimental set up. R_t for model textile dye wastewater and MBR activated sludge were defined as R_{t_mtdw} and R_{t_mbr} respectively and these are shown in Eqs. (2) and (3).

$$R_{t_mtdw} = R_m + R_{mtdw} \quad (2)$$

$$R_{t_mbr} = R_m + R_{mbr_activated\ sludge} \quad (3)$$

where, R_m is the constant resistance of the pristine membrane (1/m), R_{mtdw} is the fouling resistance due to MTDW (1/m) and $R_{mbr_activated\ sludge}$ is the fouling resistance due to MBR sludge deposited on the membrane surface (1/m). The resistance shown in Eqs. (2) and (3) is called the resistance in membrane series (RIS) model, which is applied to describe membrane fouling mechanisms (Jifeng et al. 2008). In this section, the RIS model has been

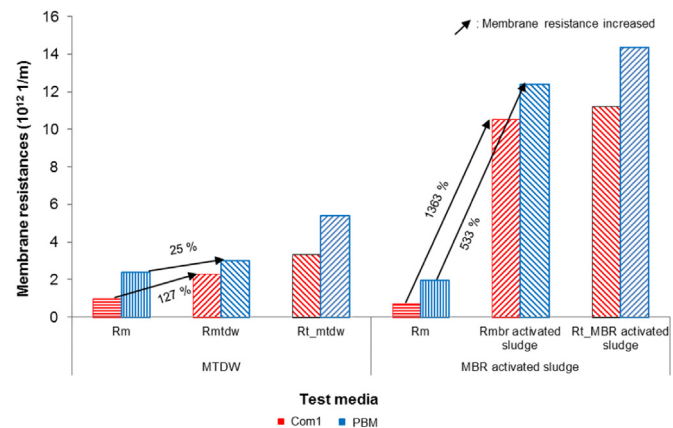


Fig. 8. Numerical values of membrane resistances with different foulants.

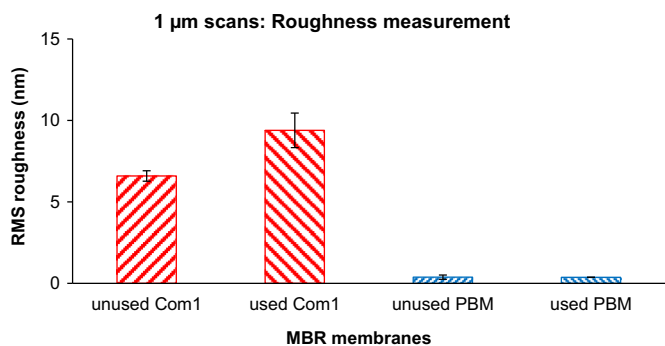


Fig. 9. RMS roughness values of the commercial and PBM membranes in MBR application.

adapted according to the experimental set ups and foulants. The respective resistances of both Com1 and PBM membranes were calculated using RIS model. The different resistances of Com1 and PBM modules with different foulants are shown in Fig. 8.

Fig. 8 indicates that pure membrane resistance for the PBM membrane is higher compared to the Com1 membrane due to the additional contribution of the PBM coating. However, the percentage increase of resistances for the Com1 membrane with MTDW and MBR activated sludge are much higher compared to those of the PBM membrane (Fig. 8). The resistance with Com1 increased to 127% with MTDW compared to its pure membrane resistance where PBM MBR in this case increased to 25% only. These extra resistances increased due to fouling layers on the modules governed by MTDW. Considering the resistance increment factors, the PBM module shows 5 times higher antifouling resistant compared to Com1 with MTDW. Similarly, PBM module shows 2.5 times higher antifouling propensity with MBR activated sludge experiment. These results confirm that PBM membranes have the higher antifouling resistances. Considering the individual

contribution of membrane resistances to their total values in respective experiments with the different foulants, the Com1 membrane contributes to 70% and 93% resistances to their total resistance values tested with MTDW and MBR activated sludge experiments respectively. In the case of the PBM membranes the fouling resistance is lower and it is 55% and 86% with MTDW and MBR activated sludge respectively. This suggests that MBR activated sludge is the most critical environment, with MTDW the least regarding fouling propensity and that the fouling propensity is less using the novel PBM membrane than the commercial ones.

3.5. Evaluation of stability of PBM coating after MBR experiments

After 105 days of operation of the Com1 and PBM membrane modules in MBR solution, surface analysis was carried out using AFM and SEM (Fig. 10) to verify if the PBM coating layer was still present on the membrane surface and to assess the relative amounts of fouling on the surfaces. Throughout the entire experimental period no chemical cleaning was conducted, only regular backflush with permeate was applied (every 9 min for 0.5 min, see Section 2.6). Roughness measurements for the Com1 membrane examined the initial RMS roughness values of 6.59 nm (± 0.32) rose to 9.39 nm (± 1.06) after use, with the increased roughness indicating the biofouling deposits on the surface. The PBM modified unused membrane showed lower surface roughness of 0.387 nm (± 0.13) than the unmodified membrane. After use the PBM membrane had a mean RMS roughness value of 0.374 nm (± 0.005), demonstrating that the surface morphology had not been significantly altered either by removal of the PBM layer or by biofouling (Fig. 9).

SEM imaging (Fig. 10) confirms this interpretation of the data, with bacterial colonies visible on the used PES membrane surface after operation (Fig. 10b), whereas the PBM membrane appear effectively unaltered after operation (Fig. 10d and e).

In addition, the antimicrobial activity of the used Com1 and

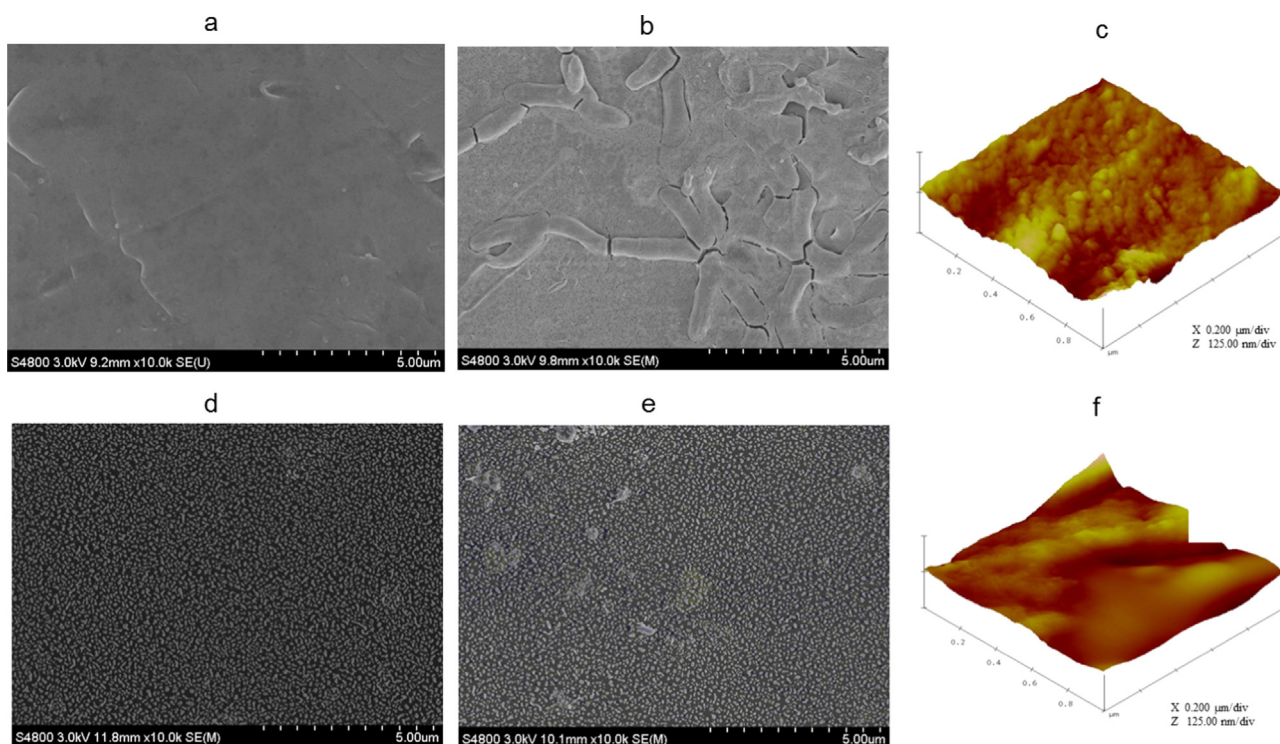


Fig. 10. SEM and AFM images of (a) unused Com1; (b) used Com1; (c) AFM surface images of used Com1; (d) unused PBM; (e) used PBM; (f) and used PBM MBR module.

PBM membranes were tested. 20 cm² area of the used membrane materials, both from Com1 and PBM modules, were subjected to 3 h of pre-incubation with 60 colony forming units (CFU) *E. coli* bacteria and then incubated overnight on Mueller Hinton agar plates at 37 °C. The next step involved swabbing samples from the membrane surface after 24 h incubation with *E. coli* bacteria and visualizing the collected sample on white cotton of the swab to determine whether bacterial growth had taken place. It was found that the presence of bacteria on the surface of the Com1 membrane was 60 CFU, suggesting no antimicrobial activity. Conversely, no accumulation of bacteria was observed on the surface of the used PBM membrane suggesting bacterial growth on the membrane surface had been retarded (see Fig. 5). This confirms that used PBM membrane has antibacterial properties like the pristine one due to the presence of cationic polymerisable surfactant and that the PBM coating is still present after its use.

4. Conclusions

A novel low fouling membrane based on a polymerisable bi-continuous microemulsion (PBM) process was prepared. To compare its performance to that of a commercial PES UF MBR membrane, the coated PBM membrane was formulated into a module called PBM MBR module and tested in an MBR reactor with an active membrane area of 0.33 m² using model textile dye wastewater as the feed solution. During the operation time of 105 days, the commercial PES MBR module faced severe fouling problem and the module replacement was needed since several physical and chemical cleanings could not regenerate the permeability. On the contrary, PBM MBR module faced no fouling problem for the same operational period due to its antifouling properties confirmed by analysis of resistance model, AFM and SEM techniques. The analysis of resistance model showed that PBM module has 2.5 times and 5 times higher antifouling effect with model textile dye wastewater and MBR activated sludge respectively compared to PES module. It was also visualized by physical observation that PES MBR module surface was densely covered by biofouling whereas the PBM module surface was comparatively clean. From the experiments, it was also discovered that the PBM MBR module has higher antimicrobial properties and lower membrane (used) surface roughness compared to the commercial PES MBR module, even after 105 days of experimentation. The antimicrobial properties of the PBM membrane contributed by cationic surfactant acryloyloxyundecyltriethylammonium bromide (AUTEAB) used for the membrane preparation guaranteed an anti-biofouling effect preventing the growth of microorganisms on the membrane surface. In particular, the MBR process with novel PBM module was stable, without fluctuations, smooth and did not require any membrane cleaning. However, water permeability was 27% lower than that of the PES membrane. From critical flux measurements, it has been observed that the flux with PBM module was around 4 L/m² h at TMP of 500 mbar and the ultimate critical flux could be higher if the applied TMP could be extended beyond the operational limit. The AFM and SEM imaging and antimicrobial analysis of the used PBM membranes in MBR confirm the continued presence of the PBM coating after 105 days of operation, demonstrating the robustness of the coating in the harsh MBR activated sludge environment. Moreover, the reduced requirement of cleaning frequency with the novel membrane based PBM MBR could lead to a decrease of the operation and maintenance costs of MBR process making it of high interest for large-scale industrial wastewater treatment. In order to increase the water permeability of the novel coated PBM membrane the thickness of the PBM layer can be reduced by decreasing the casting knife air gap what will be studied through further research.

Acknowledgements

This work was supported by European Union within BioNexGen project under grant agreement no. CP-FP-246039-2 EU-FP7/project.

References

- [1] M. Brik, P. Schoeberl, B. Chamam, R. Braun, W. Fuchs, Advanced treatment of textile wastewater towards reuse using a membrane bioreactor, *Process. Biochem.* 41 (2006) 1751–1757.
- [2] J. Hoinkis, V. Panten, Wastewater recycling in laundries - from pilot to large scale plant, *Chem. Eng. Process.* 47 (2008) 1159–1164.
- [3] S.J. You, R.A. Damodara, S.C. Hou, Degradation of Reactive Black 5 dye using anaerobic/aerobic membrane bioreactor (MBR) and photochemical membrane reactor, *J. Hazard. Mater.* 177 (2010) 1112–1118.
- [4] A. Spagni, S. Grilli, S. Casu, D. Mattioli, Treatment of a simulated textile wastewater containing the azo-dye reactive orange 16 in an anaerobic-biofilm anoxic-aerobic membrane bioreactor, *Int. Biodeterior. Biodegrad.* 64 (2010) 676–681.
- [5] N.O. Yigit, N. Uzal, H. Koseoglu, I. Harman, H. Yukseler, U. Yetis, G. Civelekoglu, M. Kitis, Treatment of a denim producing textile industry wastewater using pilot-scale membrane bioreactor, *Desalination* 240 (2009) 143–150.
- [6] J.A. Howell, H.C. Chua, T.C. Arnot, In situ manipulation of critical flux in a submerged membrane bioreactor using variable aeration rates, and effects of membrane history, *J. Membr. Sci.* 242 (2004) 13–19.
- [7] H.-Y. Yu, M.-X. Hu, Z.-K. Xu, J.-L. Wang, S.-Y. Wang, Surface modification of polypropylene microporous membranes to improve their antifouling property in MBR: NH₃ plasma treatment, *Sep. Purif. Technol.* 45 (1) (2005) 8–15.
- [8] H.-Y. Yu, Y.-J. Xie, M.-X. Hu, J.-L. Wang, S.-Y. Wang, Z.-K. Xu, Surface modification of polypropylene microporous membrane to improve its antifouling property in MBR: CO₂ plasma treatment, *J. Membr. Sci.* 254 (1–2) (2005) 219–227.
- [9] H.-Y. Yu, L.-Q. Liu, Z.-Q. Tang, M.-G. Yan, J.-S. Gu, X.-W. Wie, Mitigated membrane fouling in an SBR by surface modification, *J. Membr. Sci.* 310 (1–2) (2008) 409–417.
- [10] H.-Y. Yu, Z.-K. Xu, H. Lei, M.-X. Hu, Q. Yang, Photoinduced graft polymerization of acrylamide on polypropylene microporous membranes for the improvement of antifouling characteristics in a submerged membrane-bioreactor, *Sep. Purif. Technol.* 53 (1) (2007) 119–125.
- [11] A. Asatekin, A. Menniti, S. Kang, M. Elimelech, E. Morgenroth, A.M. Mayes, Antifouling nanofiltration membranes for membrane bioreactors from self-assembling graft copolymers, *J. Membr. Sci.* 285 (2006) 81–89.
- [12] A. Musolf, S. Leschik, M. Möder, G. Strauch, F. Reinstorf, M. Schirmer, Temporal and spatial patterns of micropollutants in urban receiving water, *Environ. Pollut.* 157 (11) (2009) 3069–3077.
- [13] T.-H. Bae, T.-M. Tak, Effect of TiO₂ nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration, *J. Membr. Sci.* 249 (1–2) (2005) 1–8.
- [14] T.-H. Bae, T.-M. Tak, Preparation of TiO₂ self-assembled polymeric nanocomposite membranes and examination of their fouling mitigation effects in a membrane bioreactor system, *J. Membr. Sci.* 266 (1–2) (2005) 1–5.
- [15] C. Zhao, X. Xu, J. Chen, G. Wang, F. Yang, Highly effective antifouling performance of PVDF/graphene oxide composite membrane in membrane bioreactor (MBR) system, *Desalination* 340 (2014) 59–66.
- [16] A. Figoli, J. Hoinkis, B. Gabriele, G. De Luca, F. Galiano, S.A. Deowan, Bi-continuous microemulsion polymerised coating for water treatment, patent application, 2013, PCT/EP2014/070603=WO2014/EP070603, filed on 27.09.2013.
- [17] F. Galiano, A. Figoli, S.A. Deowan, D. Johnson, S.A. Altinkaya, L. Veltri, G. De Luca, R. Mancuso, N. Hilal, B. Gabriele, J. Hoinkis, A step forward to a more efficient wastewater treatment by membrane surface modification via polymerizable bicontinuous microemulsion, *J. Membr. Sci.* 482 (2015) 101–114.
- [18] V. Kochkodan, D.J. Johnson, N. Hilal, Polymeric membranes: surface modification for minimizing (bio) colloidal fouling, *Adv. Colloid Interface Sci.* 206 (2014) 116–140.
- [19] D. Rana, T. Matsuura, Surface modifications for antifouling membranes, *Chem. Rev.* 100 (2010) 2448–2471.
- [20] T.D. Li, L.M. Gan, C.H. Chew, W.K. Teo, L.H. Gan, Hollow-fiber membranes coated with polymerizable bicontinuous microemulsions, *J. Membr. Sci.* 133 (1997) 177–187.
- [21] T.H. Chieng, L.M. Gan, W.K. Teo, Porous polymeric membranes by bicontinuous polymerization: effect of anionic and cationic surfactants, *Polymer* 37 (1996) 5917–5925.
- [22] J.H. Burban, M. He, E.L. Cussler, Organic microporous materials made by microemulsion polymerization, *AIChE J.* 41 (1995) 907–914.
- [23] J.H. Burban, M. He, E.L. Cussler, Silica gels made by bicontinuous microemulsions polymerization, *AIChE J.* 41 (1995) 159–165.
- [24] L. Shao, Z.X. Wang, Y.L. Zhang, Z.X. Jiang, Y.Y. Liu, S. Key, A facile strategy to enhance PVDF ultrafiltration membrane performance via self-polymerized polydopamine followed by hydrolysis of ammonium fluotitanate, *J. Membr. Sci.* 461 (2014) 10–21.
- [25] X.Q. Cheng, L. Shao, C.H. Lau, High flux polyethylene glycol based nanofiltration membranes for water environmental remediation, *J. Membr. Sci.* 476 (2015) 95–104.
- [26] D.J. Johnson, F. Galiano, S.A. Deowan, J. Hoinkis, A. Figoli, N. Hilal, Adhesion

- forces between humic acid functionalized colloidal probes and polymer membranes to assess fouling potential, *J. Membr. Sci.* 484 (2015) 35–46.
- [27] Microdyn-Nadir, Technical data, BIO-CEL[®] Membrane Material; (www.microdyn-nadir.com) accessed on (09.01.15).
- [28] E.H. Bouhabila, B.R. Aim, H. Buisson, Microfiltration of activated sludge using submerged membrane with air bubbling application to wastewater treatment, *Desalination* 118 (1998) 315–322.
- [29] S.I. Bouhadjar, S.A. Deowan, F. Galiano, A. Figoli, J. Hoinkis, M. Djennad, Performance of commercial membranes in a sidestream and submerged membrane bioreactor for model textile wastewater treatment, *Desalination water Treat.* 57 (2016) 5275–5285.
- [30] G. Jifeng, X. Siqing, W. Rongchang, Study on membrane fouling of submerged membrane bioreactor in treating bathing wastewater, *J. Environ. Sci.* 20 (2008) 1158–1167.