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ADVANCED OXIDATION PROCESSES FOR WATER/WASTEWATER TREATMENT

Fouling mitigation and cleanability of TiO_2 photocatalyst-modified PVDF membranes during ultrafiltration of model oily wastewater with different salt contents

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Abstract

In the present study, TiO_2-coated ultrafiltration membranes were prepared and used for oily water filtration (droplet size < 2 μm). The aim of this work was to investigate the effect of different salt contents on fouling and filtration properties of neat and TiO_2-coated membranes during oil-in-water emulsion filtration. The effect of the TiO_2 coating on the flux, surface free energy, and retention values was measured and compared with the neat membrane values. The cleanability of the fouled TiO_2-coated membranes by UV irradiation was also investigated by measuring flux recovery and contact angles, and the chemical changes during cleaning were characterized by ATR-IR. It was found that increasing the salt content of the model wastewaters, oil-in-water emulsions, increased the zeta potential and the size of the droplets. The presence of the TiO_2 coating decreases the membrane fouling during oily emulsion filtration compared to the neat membrane, due to the hydrophilicity of the coating regardless of the salt content of the emulsions. The neat and coated membrane oil retention was similar, 96 ± 2%. The coated membrane can be effectively cleaned with UV irradiation without additional chemicals and a significant flux recovery can be achieved. Monitoring of the cleaning process by following the membrane surface wettability and ATR-IR measurements showed that the recovery of flux does not mean the total elimination of the oil layer from the membrane surface.

Keywords TiO_2-coated membrane · PVDF · Salt content · Oil-in-water emulsion · Ultrafiltration · Fouling

Introduction

Waste thermal waters used for greenhouse heating often contain considerable amounts of oily impurities forming oil-in-water emulsions with additional dissolved organics and different amounts of dissolved salts. Stabilized oil droplets (< 10 μm) cannot be removed from emulsions by conventional water treatment techniques, but membrane filtration may be suitable to overcome this shortcoming (Fakhru'l-Razi et al. 2009; Dickhout et al. 2017). Oil-containing industrial wastewaters may vary significantly in their salt content: in case of produced waters from a few parts per million (ppm) up to about 300,000 mg L^{-1} (Fakhru'l-Razi et al. 2009). Ultrafiltration is an efficient method to treat these oil-in-water emulsions, without chemical additives and low energy cost compared to traditional separation methods (He and Jiang 2008; Kiss et al. 2013). Polymer membranes are the most commonly used type of membranes in water and wastewater treatment due to their low price and easy maintenance, but the main problem to be solved is fouling mitigation during membrane filtration processes. An appropriate fouling mitigation method could be to increase membrane hydrophilicity by modifying membranes with TiO_2 nanoparticles (Leong et al. 2014; Bai et al. 2010; Molinari et al. 2002). Photocatalyst-modified membranes proved to have good fouling mitigating properties in case of activated sludge filtration (Bae and Tak 2005) and photocatalytic bactericidal properties (Kim et al. 2003) and showed significant photocatalytic activity in case of model pollutants like methylene blue, humic acid, and 4-nitrophenol (Bai et al. 2010; Molinari et al. 2002). To our best knowledge, the feasibility of photocatalyst-modified membranes to treat real oil-in-water emulsions with high salt content has not been investigated. The emulsion properties (e.g., droplet size, ionic strength, temperature, pH, emulsifier

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concentration, and the volume ratio of oil to water phase) determine the interfacial interactions between the membrane surface and the emulsion and thus the fouling propensity of the membrane; in order to minimize fouling, better understanding of these effects is necessary (Fakhru'l-Razi et al. 2009; Dickhout et al. 2017).

For membrane coating and modification, TiO_2 is an appropriate photocatalyst due to its good physical and chemical properties, availability, high photocatalytic activity, and desirable hydrophilic properties (Bet-moushoul et al. 2016; Molinari et al. 2016; Yi et al. 2011; Hu and Scott 2008; Leong et al. 2014). The membrane material to be suitable for modification with TiO_2 must be resistant to UV irradiation and to the reactive species generated during the photocatalytic reaction (Bellobono et al. 2005; Chin et al. 2006); properties of PVDF membranes meet these requirements (Chin et al. 2006).

Fouling occurs when materials of colloidal size (with dimensions < 1 μm) are adsorbed on solid surfaces, which is determined by interactions between colloidal particles and membrane surface, which can develop, due to generally attractive van der Waals interactions, and generally repulsive electrostatic double-layer forces, due to the surface charges of the membrane and the colloidal particles. This DLVO theory can be extended by integrating the hydrophobic interactions taking into consideration the surface free energy of polar interactions. The net effect is a balance between all possible interactions (Oliveira 1997). Interactions of colloidal particles with polymeric membrane surfaces are influenced by membrane surface morphology (roughness). Earlier works (Hoek et al. 2003) show that the repulsive interaction energy barrier between a colloidal particle and a rough membrane is lower than the corresponding barrier for a smooth membrane, and it was suggested that the valleys created by the membrane surface roughness produce wells of low interaction energy in which colloidal particles may preferentially deposit, increasing the fouling. However, larger particles are not able to adhere, because gravitational and hydrodynamic forces are strong enough to remove them from the "peaks" of the rough surface—in this case, the fouling is decreasing with increased surface roughness (Oliveira 1997), which may occur by covering the surface with TiO_2. It should be clarified what is the resultant effect of the contradicting changes of the TiO_2-modified surface properties (increased hydrophilicity and increased roughness) (Kovács et al. 2017) on fouling propensity.

The aim of this work was to prepare TiO_2-coated PVDF membranes to be applicable for cleaning by heterogeneous photocatalysis after filtration of model oily wastewater containing 100 ppm crude oil and different salt concentrations. As oil-containing industrial wastewaters may vary significantly in their salt content, examined salt concentrations were chosen to cover three orders of magnitude from 250 to 25,000 mg L^{-1}. The effect of salt concentration on fouling and on filtration properties of neat and TiO_2-coated membranes during oil-in-water emulsion filtration was investigated. Furthermore, the cleanability of the fouled TiO_2-coated membranes by UV irradiation was investigated by monitoring the physical and chemical changes of the foulants on the membrane surface.

Materials and methods

Membrane and catalyst characteristics

Poly(vinylidene fluoride) membranes (PVDF 200 (New Logic Research Inc., USA)) with a 250-kDa molecular weight cutoff (MWCO) were coated with commercial TiO_2 Aeroxide P25 (Evonic Industries). Commercial Aeroxide P25 titanium dioxide has spherical shape with a primer particle size of ~ 25 nm (Veréb et al. 2012); however, it should be noted that in a suspension, it forms aggregates nearly 1 μm in diameter (Mogyorósi et al. 2010). This titania is a mixture of anatase (90%) and rutile (10%) phase, and it has a specific surface area of 49 $m^2 g^{-1}$.

Oil-in-water emulsions

The model wastewater (oil-in-water emulsion, $c_{oil} = 100$ ppm) was prepared from crude oil (Algyő-area, Hungary) and Milli-Q water (with no added salt, with 250, 2500, and 25,000 mg L^{-1} salt, respectively) by ultrasonication. The composition of the added salts and their mass ratios are given in Table 1. The pH of the oil-in-water emulsions with no added salt, with 250, 2500, and 25,000 mg L^{-1} salt, was 6.9, 8.5, 8.6, and 8.4, respectively. The 2500-mg L^{-1} composition of the model water represents an underground water composition characteristic in the southern part of the Great Hungarian Plain (Table 1).

The emulsion was prepared in two steps using crude oil (Algyő, Hungary) and distilled water. In the first step, 1 wt% emulsion was prepared by intensive stirring (35,000 rpm), then 5 mL of this emulsion was inoculated into 495 mL of distilled water (or the water with added salt content) directly below the transducer of an ultrasonic homogenizer (Hielscher UP200S) resulting in stable oil-in-water emulsion ($c_{oil} =$ 100 ppm). The duration of homogenization was 10 min, maximal amplitude and cycle were applied, and the emulsion was thermostated to 25 °C.

Membrane coating and filtration

The membrane preparation was carried out according to the method developed and described in our earlier work (Kovács et al. 2017): 100 mL of 0.4 g L^{-1} catalyst suspension was filtered through the membrane in a dead-end cell, at 0.1 MPa without stirring, at 20 °C. It results in 1.2 mg cm^{-2} TiO_2 coating that fully covers the membrane surface and

Table 1 Salt content and ratio of the model wastewaters

Salt content	wt%
$NaHCO_3$	91.61
NH_4Cl	2.17
$FeCl_3$	0.11
$CaCl_2$	0.77
$MgSO_4$	0.67
KCl	0.84
NaCl	3.79

forms a stable layer under operational conditions (Kovács et al. 2017). The filtration was carried out with a Millipore batch filtration unit (XFUF04701, Solvent-resistant Stirred Ultrafiltration Cell, Millipore, USA); after filtration, the membranes were removed from the cell, gently rinsed with distilled water, and kept wet until used.

The filtrations of the model solution were carried out at 0.3 MPa transmembrane pressure with 50 rpm stirring at 20 °C. Before every experiment, the membranes were immersed in water overnight and 1 L water was filtered through them to achieve a constant flux. The flux of the neat membrane was 820 ± 30 L m^{-2} h^{-1}. Relative fluxes are shown in the following that are all in proportion to this value. In each filtration experiment, 250 mL water or model solution was filtered to volume reduction ratio (VVR) 5. VRR [−] was defined as:

$$\mathrm{VRR} = \mathrm{VF}/(\mathrm{VF}–\mathrm{VP}) \tag{1}$$

where VF and VP are the volume of the feed and permeate (m^3) respectively at any time.

The UV cleaning of the fouled membranes was carried out in the filtration unit using a modified cap so that the UV light source could be fitted in it (Kovács et al. 2017). The UV light source was a mercury-vapor lamp, 40 W, $\lambda = 254$ nm (Germipak LightTech, Hungary). The UV irradiation of the fouled membranes lasted from 1 up to 6 h. Before and after each hour of irradiation, the membrane surface was rinsed with water, water flux measurements were carried out, parallel membranes were dried, and contact angles were measured. In the modified cell, 100 mL distilled water was over the membranes during UV irradiation, which was changed in every hour.

Analytical methods and calculations

pH of the emulsions was measured by a Consort C535 type multimeter. The size distribution and zeta potentials were determined by dynamic light scattering measurements using a Malvern ZetaSizer4 type equipment.

Determination of the chemical oxygen demand (COD) was based on the standard potassium-dichromate oxidation method; for the analysis, standard test tubes (Lovibond) were used. The digestions were carried out in a COD digester (Lovibond, ET 108) for 2 h at 150 °C; the COD values were measured with a COD photometer (Lovibond PC-CheckIt).

Membrane hydrophilicity was quantified by measuring the contact angle that was formed between the (neat and coated) dry membrane surface and distilled water. Ten microliters of distilled water was carefully dropped onto the membrane surface and immediately measured. Contact angles were measured using the sessile drop method (Dataphysics Contact Angle System OCA15Pro, Germany). The same steps were taken to measure the glycerol and the three different wastewater contact angles. Every measurement was repeated five times, and the average values were calculated and are presented in this work. The surface free energies of membranes were calculated by the Owens, Wendt, Rabel, and Kaelble (OWRK) method, using the OCA15 SCA21 software package (Dataphysics).

The neat, TiO_2-coated, fouled, and UV-cleaned membrane surfaces were also characterized by ATR-IR (attenuated total reflectance). The spectra were recorded with a BIO-RAD Digilab Division FTS-65A/896 FT-IR (Fourier-transform infrared) spectrophotometer with 4-cm^{-1} resolution. The 4000–1000-cm^{-1} wavenumber range was investigated. Two hundred fifty-six scans were collected for each spectrum.

The retention (%) values were calculated by the following equation:

$$R = \left(1 - \frac{c}{c_0}\right) \cdot 100\% \tag{2}$$

where c is the average COD of the permeate phase and c_0 is the COD of the feed.

The filtration resistances were determined according to the resistances in the series model, as membrane resistance (R_M) was calculated as follows:

$$R_\mathrm{M} = \frac{\Delta p}{J_\mathrm{W} \eta_\mathrm{W}} \quad \left[\mathrm{m}^{-1}\right] \tag{3}$$

where Δp is the transmembrane pressure (Pa), J_W is the water flux of the clean membrane ($m^3 \cdot m^{-2} \cdot s^{-1}$), and η_W is the viscosity of the water (Pa·s).

The irreversible resistance (R_Irrev) was determined by measuring the water flux on the used membrane after the filtration, followed by a purification step (intensive rinsing with distilled water):

$$R_{Irrev} = \frac{\Delta p}{J_\mathrm{WA} \eta_\mathrm{W}} - R_\mathrm{M} \quad \left[\mathrm{m}^{-1}\right] \tag{4}$$

where J_WA is the water flux after the cleaning procedure.

The reversible resistance (R_{Rev}—caused by not adhered oil layer and concentration polarization layer) can be calculated as follows:

$$R_{\mathrm{Rev}} = \frac{\Delta p}{J_{\mathrm{c}}\eta_{\mathrm{WW}}} - R_{Irrev} - R_{\mathrm{M}} \quad \left[\mathrm{m}^{-1}\right] \tag{5}$$

where J_{c} is the flux at the end of the filtration and η_{WW} is the viscosity of the emulsion. The total resistance (R_{T}) can be calculated as follows:

$$R_{\mathrm{T}} = R_{\mathrm{M}} + R_{Irrev} + R_{\mathrm{Rev}} \quad \left[\mathrm{m}^{-1}\right] \tag{6}$$

Results and discussion

Characterization of the o/w emulsions with different salt contents

In this study, first the effects of the salt content on the oil droplet size and zeta potential were investigated to determine the characteristics of the different emulsions. The same emulsion production method resulted in four emulsions with different average droplet size, depending on the salt content, but in every case, the droplets were smaller than 2 μm. With the increase of the salt content, the average droplet size (Fig. 1) and zeta potential increased (− 30, − 58, − 60, and − 15 mV, respectively), resulting in bigger droplets with increased negative surface charge except of the highest salt content. The increase in the droplet size and zeta potential may be the result of the too high cation concentration, suggesting that the ions do not take a part in zeta potential modification and can act as binders between the oil droplets (Yi et al. 2011; Hesampour et al. 2008). The zeta potential of crude oil droplets dispersed in saline water is dependent on the pH and ionic strength; the decrease in the magnitude of zeta potential of droplets is in accordance with other results (Kolltweit 2016; Mahani et al. 2015).

Characterization of neat and TiO_2-covered membrane surfaces

In order to characterize the neat and modified membrane surfaces, the wettability (Fig. 2) and surface free energy changes were measured. By coating the membrane with TiO_2, the surface free energy of the membrane increases from 30 to 48 m Nm^{-1}. The oil-in-water emulsions with different salt contents had no significant difference between their contact angles.

Membrane fouling

In the next series of experiments, the membrane resistances were investigated by means of the resistances-in-series method. It was found that TiO_2 forms a dense hydrophilic layer on the membrane surface (Bai et al. 2010; Kovács et al. 2017) that slightly increases the membrane resistance (Fig. 3). The catalyst layer reduces both the reversible and irreversible resistances compared to the neat membrane. The interactions according to DLVO theory and hydrophobic interactions determine the wettability and the surface free energy. According to earlier studies, lowering the surface free energy (which means lower polar interactions) and increasing the hydrophilicity may improve the fouling resistance of a membrane (Razmjou et al. 2011; Low et al. 2015). In our case, it was found that although the TiO_2 coating increased the surface free energy, but both reversible and irreversible fouling significantly decreased. This

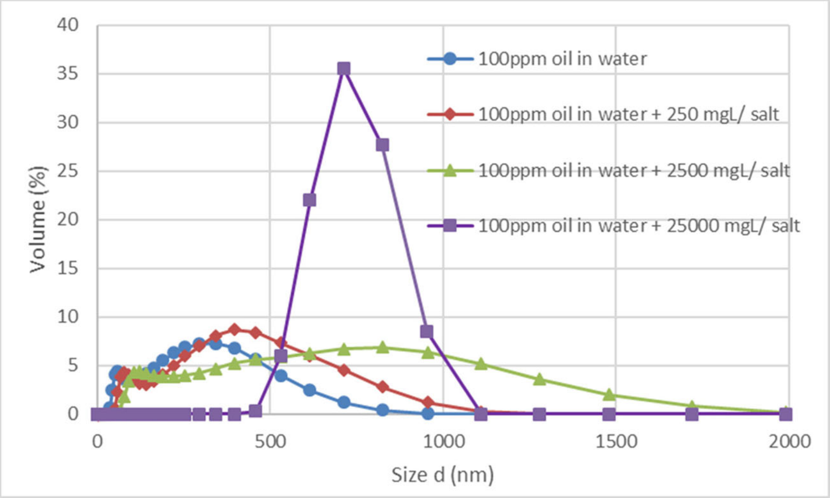

Fig. 1 Size distribution of oil droplets in emulsions with different (no added, 250, 2500, and 25,000 mg L^{-1}) salt contents

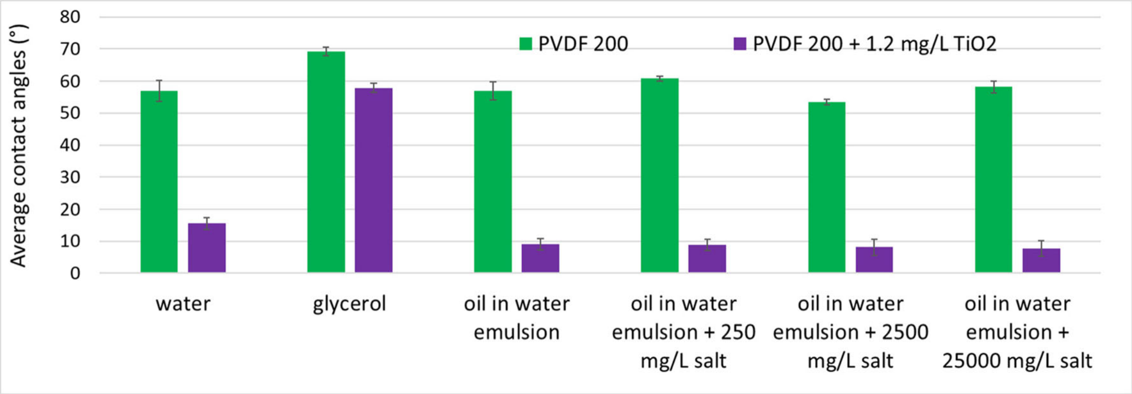

Fig. 2 Water, glycerol, and the four model wastewater average contact angles of the neat and TiO_2-coated PVDF 250-kDa membranes

means that the increased hydrophilicity (regarding to higher negative surface charge) of the surface leading to the repulsive electrostatic forces and/or the surface microroughness of the coating comes into prominence over the attractive van der Waals and hydrophobic interactions.

The effect of salt content on the filtration resistances was found to be contradictory; while in case of neat PVDF membrane, the salt content decreased the irreversible fouling, and in case of TiO_2-covered surfaces, it was observed that the increased salt content increased the irreversible fouling. Although decreased fouling could be expected due to higher magnitude of the zeta potential of the emulsion at higher salt content, the slightly increased irreversible (non-washable) resistances can be explained by the DLVO theory, as increase in ionic strength lowers the energy barrier and hence favors adhesion (Ruckenstein and Kalthod 1981). In case of TiO_2-covered surfaces, the lower salt concentration resulted in lower filtration resistances, probably due to increased surface zeta potential resulting in increased repulsive electrostatic forces. Furthermore, at higher salt concentrations, the magnitude of zeta potential of the surface may be decreased, as earlier studies showed (Luxbacher et al. 2014; Salgın et al. 2013), leading to increased role of the attractive van der Waals interactions, and thus the adhesion.

In case of 25,000 mg L^{-1} salt-containing oily water after the filtration by rinsing the fouled membrane surface with water, the TiO_2 coating washed off, together with the adsorbed oil layer causing lower filtration resistances. It means that high salt content may destabilizes the TiO_2 coating. This effect was than further examined at five different salt concentrations between 2500 and 25,000 mg L^{-1} (at 7500, 10,000, 12,500, 15,000, and 120,000 mg L^{-1}). In case of waters with salt contents higher than 12,500 mg L^{-1}, the TiO_2 layer destabilizes and washes off the membrane surface. This is the reason why the membranes fouled by 25,000 mg L^{-1} salt-containing oily waters were not included in further photocatalytic examinations.

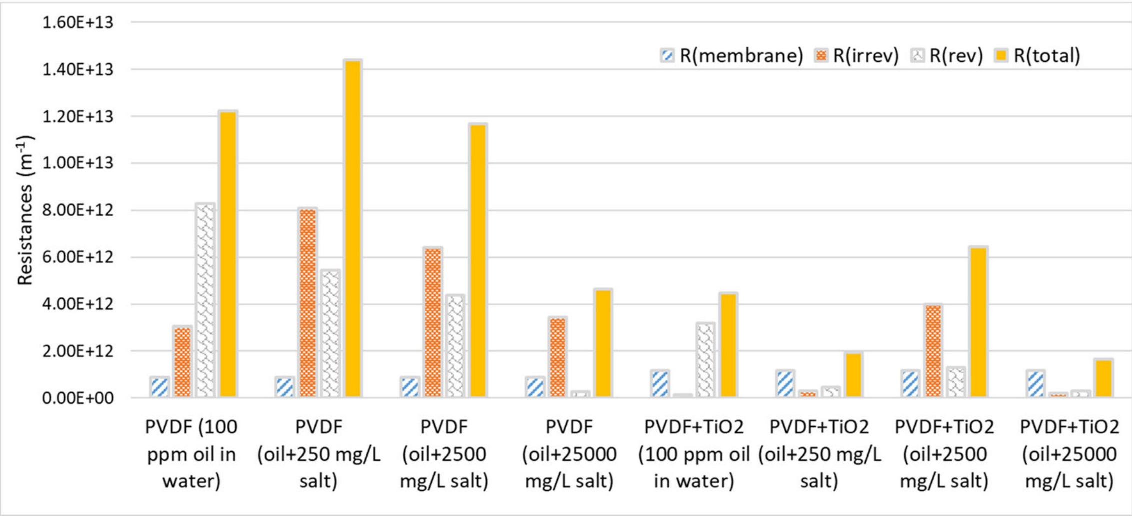

Fig. 3 Resistances of neat and TiO_2-coated PVDF 250-kDa membranes during the four model wastewater filtrations

The neat and TiO_2-coated membrane oil retention was similar, 96 ± 2%.

Cleanability of the fouled TiO_2-coated membranes by UV irradiation

After oil-in-water emulsion filtration, the membrane cleanability by means of photocatalysis (without any additional chemicals) was investigated. The fouled membranes were taken out of the cell and rinsed with distilled water to remove the oil layer if possible. Then, the membranes were put back in the cell filled with 100 mL distilled water and irradiated with UV light for 6 h. The contact angle and water flux changes were measured after every step and hourly during the UV cleaning process. This cycle was repeated in every case. To examine the cleaning efficiency, relative water fluxes and contact angles of the fouled and cleaned surfaces were compared (Fig. 4). It was found that the oil remaining on the TiO_2-coated membrane surface after filtration significantly increases the membrane surface hydrophobicity; the membrane surface hydrophilicity is in accordance with the filtration resistances (see Figs. 3 and 4).

During UV irradiation, the surface hydrophilicity was increased, and nearly total flux recovery was achieved, showing that the fouled membranes can be effectively cleaned with UV irradiation. It also was observed that the relative flux recovery was the most effective in case of the 2500-mg L^{-1} salt concentration. The efficiency of the heterogeneous photocatalysis is determined by several factors and these factors affect the degradation efficiency in a very complex way: besides the effect of water matrix (ionic strength, pH, inorganic salt content), the degradation is determined by the adsorption of the pollutants on the catalyst surface; in case of 2500 mg L^{-1} salt concentration, more oil was adsorbed on the TiO_2 surface (according to the contact angle and filtration resistance results) which may have been more easily available for photocatalytic degradation.

At the same time, the contact angle values and the ATR-IR spectra (Figs. 4a and 6) show that the oil layer does not decompose entirely during 6 h irradiation, which may cause more extended fouling in case of reusing the membranes

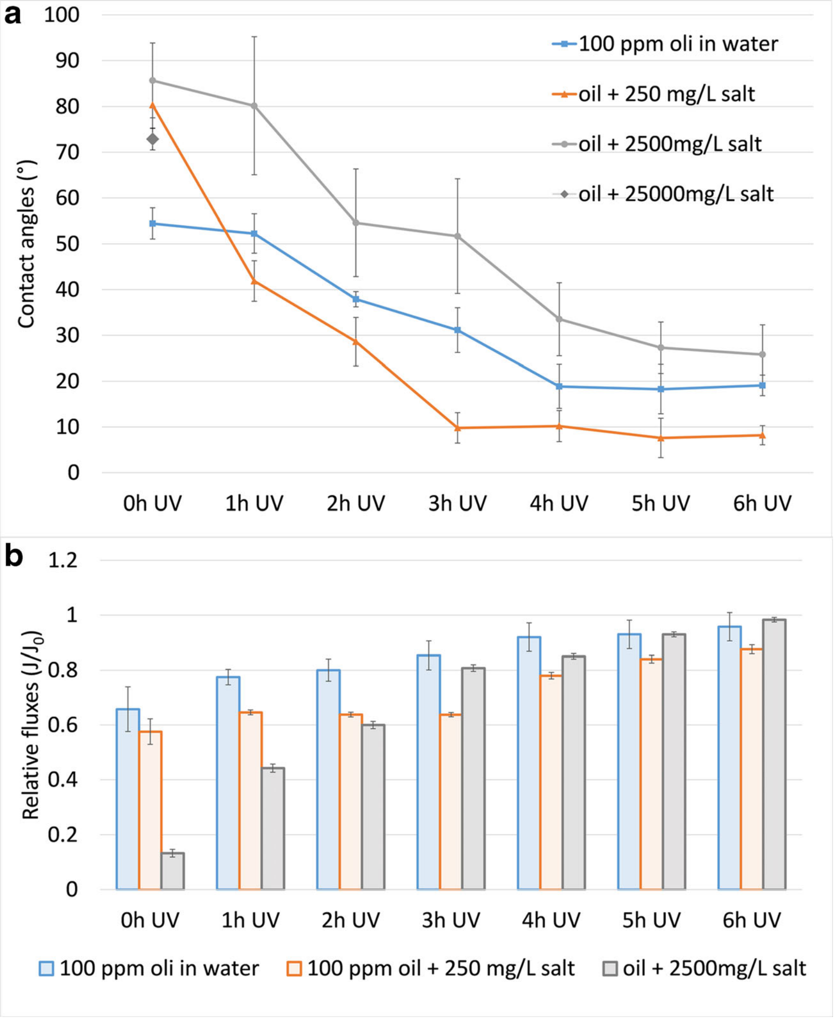

Fig. 4 Water contact angle (**a**) and relative water flux changes (**b**) of the three wastewater fouled 1.2-mg/cm^2 TiO_2-coated membranes during UV cleaning

(Luján-Facundo et al. 2015). In case of the oil-in-water emulsion with added salt, a less uniform oil layer forms on the membrane surface during filtration. These layers during irradiation contrary to the oil layer with no added salt do not faint in color gradually with the irradiation time; they break off in pieces, which can be attributed to the coagulation effect of the Ca^{2+} and Fe^{3+} ions present (Ríos et al. 1998). This effect is also in accordance with the increasing droplet size of the emulsions with the increased salt content (Fig. 1).

ATR-TIR measurements

At first, the spectra of neat and TiO_2-coated membranes were compared (Fig. 5). Typical absorption peaks of the PVDF membrane are at 1402 cm^{-1} overlapping with, 1382 cm^{-1} (bending vibration of $–CH_2$), 1210 cm^{-1} (wagging vibration of $–CH_2$), 1172 cm^{-1} (twisting vibration of $–CH_2$), and 1070 cm^{-1} (in plane wagging vibration of C–F). The TiO_2 coating also has the typical vibrations; the broad absorption band at around 3600–2800 cm^{-1} is related to the stretching vibration modes of the H_2O molecules. The broad band contains not only the components of the H_2O molecules with different numbers of hydrogen bonds but also the Fermi resonance attributed to the overtone absorption of the bending mode δ (H_2O) at 1637 cm^{-1} (Atitar et al. 2015). Comparing spectra, it can be stated that TiO_2 covers the membrane surface, overlying the membrane's vibrations.

The crude oil layer on the surface can be characterized by pronounced signatures at 2914 and 2850 cm^{-1} (CH stretching vibrations) and 1460–1377 cm^{-1} (CH bending vibrations). During heterogeneous photocatalytic reactions, this spectra change: typical absorption peaks of $–CH_2$ (at 1400 cm^{-1} and 1174 cm^{-1} can be observed instead of the characteristic peak of $–CH_3$ at 1460 cm^{-1} (Fig. 6)). The bands near 1200 cm^{-1} also could be assigned to the axial asymmetric stretching vibrations of the bonds pertaining to the CC(=O)-O functional group; those bands near 1170 cm^{-1} may correspond to the axial asymmetric stretching vibrations of bonds' characteristic to the O-C-C ester group, but the absence of an absorption band corresponding to stretching vibrations of the carbonyl (C=O) functional group in the region between 1700 and 1800 cm^{-1} denotes that the oxidized by-products as small acids and aldehydes cannot remain adsorbed in the surface, as they might be water soluble and can be washed of by the rinsing after the UV irradiation. The presence of salt did not affect these characteristics; however, in case of 2500 mg L^{-1} salt content, the oil layer covers the TiO_2 surface (covering the water absorption band around 1680 cm^{-1}), in accordance with the observed increased fouling of the membrane. Even after 6 h of irradiation, the presence of the oil layer was detectable, despite that the contact angles returned or closely correlated to the initial value of the clean TiO_2-coated membrane.

Conclusions

TiO_2-coated poly(vinylidene fluoride) (250 kDa) ultrafiltration membranes were prepared using the physical deposition method by filtering TiO_2 suspension through the membrane without stirring in order to be applicable for cleaning by heterogeneous photocatalysis after filtration of oily wastewater. Investigations were performed with oil-in-water emulsions with different salt contents. Characterization of emulsions shows that the droplet size and zeta potential of the droplets increase with increasing salt content. TiO_2-covered membranes were more hydrophilic than neat membranes, and according to ATR-IR measurements, the coverage was appropriate. During filtration, the TiO_2 coating significantly decreased both reversible and irreversible filtration resistances due to increased hydrophilicity (regarding to higher negative surface charge) of the surface leading the repulsive electrostatic forces and/or the surface microroughness of the coating to come into prominence over the attractive van der Waals and hydrophobic interactions. With increasing salt content of the emulsion,

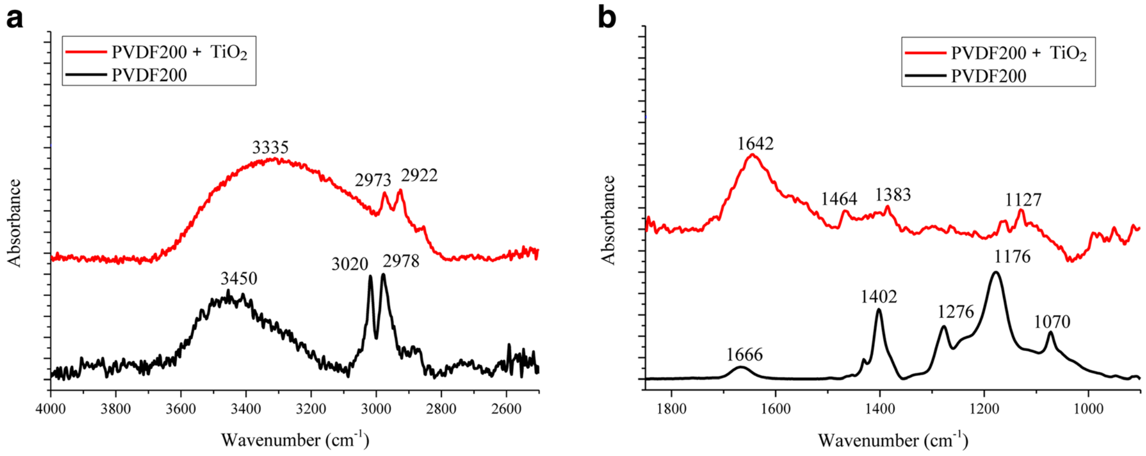

Fig. 5 ATR-IR spectra of neat and TiO_2-covered PVDF membranes

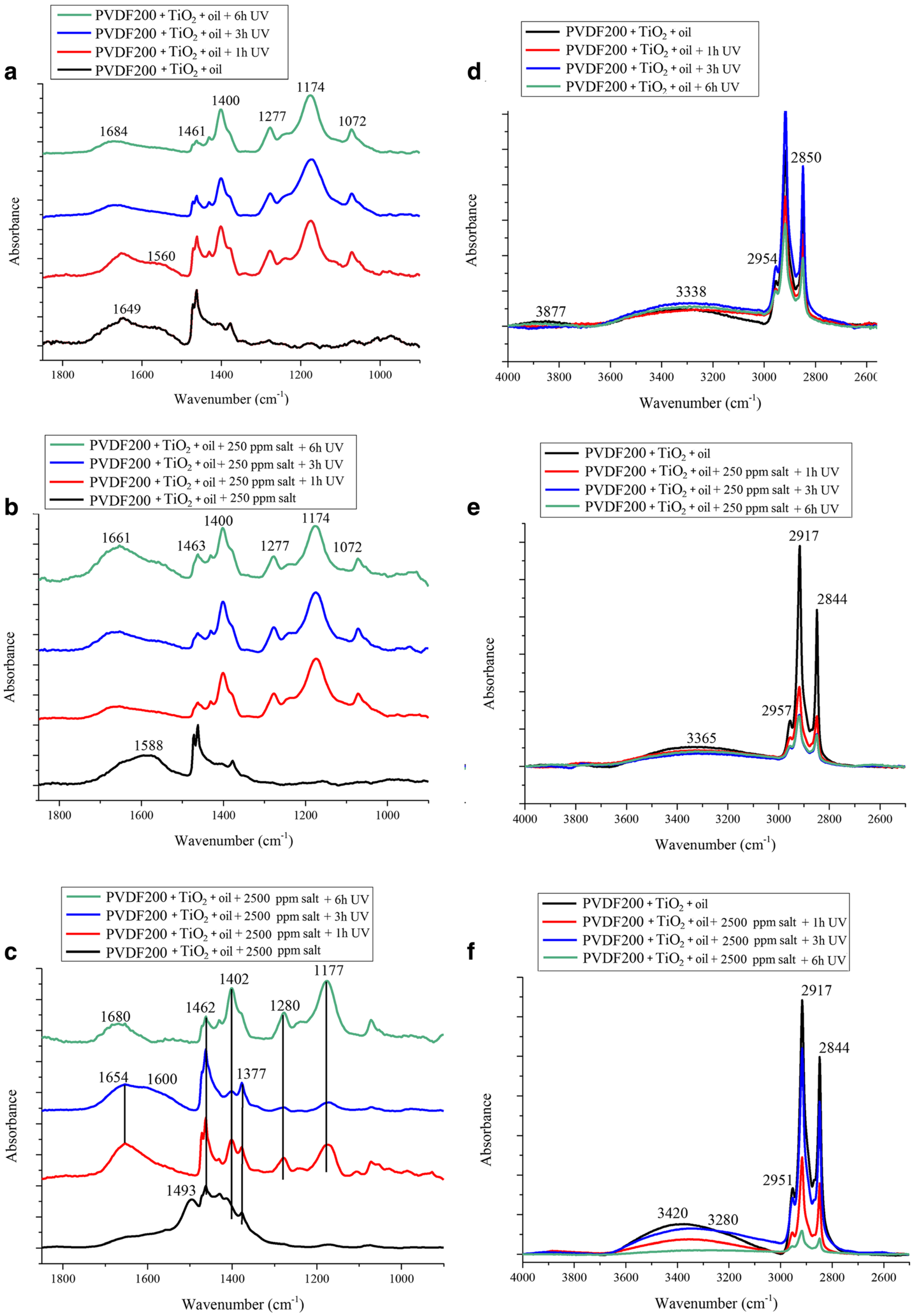

Fig. 6 ATR-IR spectra of membrane surface during UV cleaning in case of oil-in-water emulsion with no added salt (**a**, **d**) and with 250 mg L^{-1} (**b**, **e**) and 2500 mg L^{-1} added salt (**c**, **f**)

slightly increased irreversible (non-washable) resistances were observed, which can be explained by the DLVO theory, as increase in ionic strength lowers the energy barrier and hence favors adhesion. Cleaning the membrane with heterogeneous photocatalysis irradiating UVa significant flux recovery can be achieved, but the membrane surface wettability and ATR-IR measurements showed that the recovery of flux does not mean the total elimination of the oil layer from the membrane surface; however, the well-soluble oxidation by-products (e.g., small acids) cannot remain on the surface.

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References

Atitar MF, Belhadj H, Dillert R, Bahnemann DW (2015) The relevance of ATR-FTIR spectroscopy in semiconductor photocatalysis. In Larramendy ML, Soloneski S (ed) Emerging pollutants in the environment—current and further implications.doi: https://doi.org/10.5772/60887

Bae TH, Tak TM (2005) Effect of TiO_2 nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration. J Membr Sci 249(1-2):1–8. https://doi.org/10.1016/j.memsci.2004.09.008

Bai H, Liu Z, Sun DD (2010) Hierarchically multifunctional TiO_2 nanothorn membrane for water purification. Chem Commun 46(35):6542–6544. https://doi.org/10.1039/C0CC01143F

Bellobono IR, Stanescu R, Costache C, Canevali C, Morazzoni F, Scotti R, Bianchi R, Mangone ES, de Martini G, Tozzi PM (2005) Laboratory-scale photomineralisation of n-alkanes in aqueous solution, by photocatalytic membranes immobilising titanium dioxide. Int J Photoenergy 7(2):79–85. https://doi.org/10.1155/S1110662X05000127

Bet-moushoul E, Mansourpanah Y, Farhadi K, Tabatabaei M (2016) TiO_2 nanocomposite based polymeric membranes: a review on performance improvement for various applications in chemical engineering processes. Chem Eng J 283:29–46. https://doi.org/10.1016/j.cej.2015.06.124

Chin SS, Chiang K, Fane AG (2006) The stability of polymeric membranes in a TiO_2 photocatalysis process. J Membrane Sci 275(1-2):202–211. https://doi.org/10.1016/j.memsci.2005.09.033

Dickhout JM, Moreno J, Biesheuvel PM, Boels L, Lammertink RGH, de Vos WM (2017) Produced water treatment by membranes: a review from a colloidal perspective. J Colloid Interface Sci 487:523–534. https://doi.org/10.1016/j.jcis.2016.10.013

Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biak DRA, Madaeni SS, Abidin ZZ (2009) Review of technologies for oil and gas produced water treatment. J Hazard Mater 170(2–3):530–551. https://doi.org/10.1016/j.jhazmat.2009.05.044

He Y, Jiang ZW (2008) Technology review: treating oilfied wastewater. Filtr Separat 45(5):14–16. https://doi.org/10.1016/S0015-1882(08)70174-5

Hesampour M, Krzyzaniak A, Nyström M (2008) Treatment of wastewater from metal working by ultrafiltration, considering the effects of operating conditions. Desalination 222(1-3):212–221. https://doi.org/10.1016/j.desal.2007.01.155

Hoek EMV, Bhattacharjee S, Elimelech M (2003) Effect of membrane surface roughness on colloid−membrane DLVO interactions. Langmuir 19(11):4836–4847. https://doi.org/10.1021/la027083c

Hu B, Scott K (2008) Microfiltration of water in oil emulsions and evaluation of fouling mechanism. Chem Eng J 136(2-3):210–220. https://doi.org/10.1016/j.cej.2007.04.003

Kim SH, Kwak SY, Sohn BH, Park TH (2003) Design of TiO2 nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem. J Membr Sci 211:157–165. https://doi.org/10.1016/S0376-7388(02)00418-0

Kiss ZL, Kertész S, Beszédes S, Hodúr C, László Z (2013) Investigation of parameters affecting the ultrafiltration of oil-in-water emulsion wastewater. Desalin Water Treat 51(25-27):4914–4920. https://doi.org/10.1080/19443994.2013.795323

Kolltweit Y (2016) Relationship between crude oil composition and physical-chemical properties, Master Thesis, Department of Chemistry, Faculty of Mathematics and Natural Science, University of Bergen, June 2016

Kovács I, Kertész S, Veréb G, Papp IZ, Kukovecz Á, Hodúr C, László Z (2017) Membrane fouling control by means of TiO2 coating during model dairy wastewater filtration. Desalin Water Treat 73:415–421. https://doi.org/10.5004/dwt.2017.20689

Leong S, Razmjou A, Wang K, Hapgood K, Zhang X, Wang H (2014) TiO_2 based photocatalytic membranes: a review. J Membr Sci 472:167–184. https://doi.org/10.1016/j.memsci.2014.08.016

Low ZX, Wang Z, Leong S, Razmjou A, Dumée LF, Zhang X, Wang H (2015) Enhancement of the antifouling properties and filtration performance of poly(ethersulfone) ultrafiltration membranes by incorporation of nanoporous titania nanoparticles. Ind Eng Chem Res 54(44):11188–11198. https://doi.org/10.1021/acs.iecr.5b03147

Luján-Facundo MJ, Mendoza-Roca JA, Cuartas-Uribe B, Álvarez-Blanco S (2015) Evaluation of cleaning efficiency of ultrafiltration membranes fouled by BSA using FTIR–ATR as a tool. J Food Eng 163:1–8. https://doi.org/10.1016/j.jfoodeng.2015.04.015

Luxbacher T, Coday B, Cath T (2014) Does the surface zeta potential approach zero at high salinity? The 2014 Word Congress on Advances in Civil, Environmental, and Materials Research (ACEM14), Busan, Korea, 2014.08.24–28

Mahani H, Keya AL, Berg S, Bartels WB, Nasralla R, Rossen W (2015) Driving mechanism of low salinity flooding in carbonate rocks (SPE 174300). doi:https://doi.org/10.2118/174300-MS

Mogyorósi K, Balázs N, Srankó FD, Tombácz E, Dékány I, Oszkó A, Sipos P, Dombi A (2010) The effect of particle shape on the activity of nanocrystalline TiO_2 photocatalysts in phenol decomposition. Part 3: the importance of surface quality. Appl Catal B-Environ 96(3-4):577–585. https://doi.org/10.1016/j.apcatb.2010.03.007

Molinari R, Lavorato C, Argurio P (2016) Recent progress of photocatalytic membrane reactors in water treatment and in synthesis of organic compounds. A review. Catal Today 281:144–164. https://doi.org/10.1016/j.cattod.2016.06.047

Molinari R, Palmisano L, Drioli E, Schiavello M (2002) Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification. J Membr Sci 206(1-2):399–415. https://doi.org/10.1016/S0376-7388(01)00785-2

Oliveira R (1997) Understanding adhesion: a means for preventing fouling. Exp Thermal Fluid Sci 14(4):316–322. https://doi.org/10.1016/S0894-1777(96)00134-3

Razmjou A, Mansouri J, Chen V (2011) The effects of mechanical and chemical modification of TiO_2 nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes. J Membr Sci 378(1):73–84. https://doi.org/10.1016/j.memsci.2010.10.019

Ríos G, Pazos C, Coca J (1998) Destabilization of cutting oil emulsions using inorganic salts as coagulants. Colloid Surf A 138(2-3):383–389. https://doi.org/10.1016/S0927-7757(97)00083-6

Ruckenstein E, Kalthod DG (1981) Role of hydrodynamics and physical interactions in the adsorption and desorption of hydrosols or globular proteins. In Hallstrom B, Lund DB, Ch. Tragardh, (ed) Fundamentals and applications of surface phenomena associated with fouling and cleaning in food processing, Tylosand, Sweden, pp. 115–167

Salgın S, Salgın U, Soyer N (2013) Streaming potential measurements of polyethersulfone ultrafiltration membranes to determine salt effects on membrane zeta potential. Int J Electrochem Sci 8(1-3):4073–4084. https://doi.org/10.1016/S0927-7757(98)00828-0

Veréb G, Ambrus Z, Pap Z, Kmetykó Á, Dombi A, Danciu V, Cheesman A, Mogyorósi K (2012) Comparative study on UV and visible light sensitive bare and doped titanium dioxide photocatalysts for the decomposition of environmental pollutants in water. Appl Catal A-Gen 417–418:26–36. https://doi.org/10.1016/j.apcata.2011.12.018

Yi XS, Yu SL, Shi WX, Sun N, Jin LM, Wang S, Zhang B, Ma C, Sun LP (2011) The influence of important factors on ultrafiltration of oil/water emulsion using PVDF membrane modified by nano-sized TiO_2/Al_2O_3. Desalination 281:179–184. https://doi.org/10.1016/j.desal.2011.07.056