Investigation of surface and filtration properties of TiO$_2$ coated ultrafiltration polyacrylonitrile membranes

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ABSTRACT

In the present work, the surface and filtration properties of TiO$_2$ coated polyacrylonitrile ultrafiltration membranes were investigated. The membranes were coated using the physical deposition method. The appropriate TiO$_2$ coverage proved to be 0.3 mg/cm^2, which formed a hydrophilic cake layer on the membrane surface. The cleanability without chemicals and the retention of the coated membranes was compared to the neat membrane after model oily wastewater filtration.
The cleaning sustained of rinsing with distilled water and UV irradiation of the fouled membranes. The coated membranes have better antifouling properties; higher flux values during oily water filtration and by the mentioned cleaning process a significantly better flux recovery can be achieved. The amount of the catalyst and the irradiation time are limiting factors to the effectiveness of the cleaning process. The UV irradiation increases the wettability of the fouled membrane surface by degrading the oil layer. The coating, the continuous use, and the cleaning process do not affect significantly the membrane retention expressed in chemical oxygen demand.

Key words | coated polyacrylonitrile membrane, heterogeneous photocatalysis, hybrid process, membrane surface cleaning, oily wastewater, TiO$_2$ P25

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INTRODUCTION

The rapid growth of oil and gas, petrochemical, pharmaceutical, metallurgical and food industries resulted in large oily wastewater production. Physical and chemical wastewater treatment methods are widely investigated, taking into consideration their efficiency, cost, need of additives, equipment and infrastructure, process time, capacity, etc. (Padaki *et al.* 2015). Most of the traditional water treatment methods are not effective enough to treat stable oil in water emulsions containing micro sized or smaller oil droplets. Membrane filtration is an efficient process to treat oily wastewaters, without chemical additives and low energy cost compared to traditional separation methods (He & Jiang 2008; Hu & Scott 2008; Yi *et al.* 2011; Kiss *et al.* 2013, 2016). Ultrafiltration is the most effective treatment, among membrane processes for this purpose (He & Jiang 2008; Kiss *et al.* 2013). Polymer membranes are the most commonly used type of membranes in water and wastewater treatment. Despite their beneficial qualities, their separation performance, antifouling property and long-time stability need improvement (He & Jiang 2008; Hu & Scott 2008; Yi *et al.* 2011; Leong *et al.* 2014; Bet-moushoul *et al.* 2016; Molinari *et al.* 2016).

In membrane filtration, the membrane fouling is a key problem; in order to decrease it numerous different approaches were introduced during the last few decades. One of these approaches is to modify membranes with photocatalytic nanoparticles, therefore combining the advantages of membrane filtration (physical separation) and the advantage of photocatalysis (non-selective organic matter degradation). TiO$_2$ is one of the most commonly used photocatalyst due to its good physical and chemical properties, availability, high photocatalytic activity, and desirable hydrophilic properties (Hu & Scott 2008; Yi *et al.* 2011; Leong *et al.* 2014; Bet-moushoul *et al.* 2016; Molinari *et al.* 2016). Various techniques were used to modify the membrane materials with photocatalytic nanoparticles, to entrap them into the membrane material or to use the membrane as support for deposit. Photocatalyst can be supported on the membrane surface e.g. by dip coating (Kim *et al.* 2003; Bae & Tak 2005; Horovitz *et al.* 2016), photografting (Bellobono *et al.* 1992, 2006; Barni *et al.* 1995) and physical deposition of TiO$_2$ layer, by filtration of TiO$_2$ suspension through a polymer membrane (Molinari *et al.* 2002;

Bai *et al.* 2010). These modified membranes proved to have great fouling mitigation during treatment of real waters and wastewaters (Kim *et al.* 2003; Bae & Tak 2005), photocatalytic bactericidal properties (Kim *et al.* 2003) and they showed considerable photocatalytic activity using model pollutants like methylene blue, humic acid, 4-nitrophenol (Molinari *et al.* 2002; Bai *et al.* 2010), and recently oily wastewater (Ong *et al.* 2017), pharmaceutical compounds (Chakraborty *et al.* 2017). The membrane material must be resistant to UV irradiation and to the reactive species generated during the photocatalytic reaction (Bellobono *et al.* 2006). Polyacrylonitrile (PAN) is a commonly used polymer membrane material, which have a great stability under UV irradiation even after a longer exposure time (Molinari *et al.* 2002). Although PAN was claimed to be efficient in oily wastewater treatment retaining 97.2% of the oil/grease (Salahi *et al.* 2010), the flux decline caused by fouling remains a problem (Jhaveri & Murthy 2016).

In the present work, PAN ultrafiltration membranes were coated with TiO₂ in order to create a self-cleaning surface that is less prone to fouling during oily water filtration. To investigate the extent of fouling and the cleanability of fouled neat and TiO₂ coated membranes, flux changes were compared, resistances were calculated and fouling models were fitted. Wettability and surface free energy changes were measured to get a closer picture about the interactions between the membrane surface, the catalyst particles, and the oil layer.

MATERIALS AND METHODS

PAN ultrafiltration membranes (VSEP, New Logic Research Inc. USA) with 50 kDa cut off weight, and membrane surface area 0.00342 m² were used. Commercial TiO₂ (AEROXIDE P25, Evonik Industries) was suspended in distilled water, and was stirred for 30 minutes with 300 rpm and was used to coat the membrane surface. The model wastewater (oil in water emulsion) was prepared from crude oil (Algyő-area, Hungary) and distilled water. First a 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 directly below to the transducer of an ultrasonic homogenizer (Hielscher UP200S) resulting the oil in water emulsion (c_{oil} = 100 ppm). Time of homogenization was 10 minutes, maximal amplitude and cycle was applied while the emulsion was thermostated to 25 °C. In case of every filtration 250 mL oily water portion was filtered to volume reduction ratio (VVR) 5.

VRR [-], was defined as:

$$VRR = \frac{VF}{(VF - VP)} \tag{1}$$

where VF and VP is the volume of the feed and permeate [m³] respectively at any time.

The membranes were coated with TiO₂ by filtering through the membrane different amounts of the catalyst suspension in a dead-end cell, at 0.1 MPa with 300 rpm and without stirring. The quantity of the TiO₂ coating was measured by weighing the neat and the dried coated membranes that resulted in 0.3, 0.6 and 1.2 mg/cm² TiO₂ coating. The filtration was carried out with a Millipore batch filtration unit (XFUF04701, Solvent-resistant Stirred Ultrafiltration Cell, Millipore, USA). For the cleaning cycles with UV irradiation, its cap was modified so that the UV light source can be fitted in it. The UV light source was a low-pressure mercury-vapor-lamp (GERMIPAK Light-Tech, Hungary, 40 W, λ = 254 nm). Determination of the chemical oxygen demand (COD) was based on the standard potassium-dichromate oxidation method; for the analysis, standard test tubes (Lovibond, Belgium) were used. The digestions were carried out in a COD digester (ET 108, Lovibond, Belgium) for 2 hours at 150 °C; the COD values were measured with a COD photometer (PC-CheckIt, Lovibond, Belgium).

Contact angles were measured using the sessile drop method (Dataphysics Contact Angle System OCA15Pro, Germany). The surface free energies of membranes were calculated by the Owens, Wendet, Rabel, and Kaelble (OWRK) method, using the OCA15 software package (Dataphysics). Fouling mechanisms were described by using Hermia's model (complete pore blocking, gradual pore blocking, intermediate filtration and cake filtration) to determine the fouling mechanism of each membrane during filtration (Hermia 1982; Vela *et al.* 2008). Resistance-in-series model was applied to analyze resistances that lead to flux decline during the ultrafiltration process.

The membrane resistance (R_M) was calculated as (Chang *et al.* 2002; Cai *et al.* 2010):

$$R_M = \frac{\Delta p}{J_w \eta_w} \quad [m^{-1}] \tag{2}$$

where Δp is the transmembrane pressure (Pa), J_W is the water flux of the clean membrane and η_W is the viscosity of the water (Pa s).

The irreversible resistance (R_{Irrev}) was determined by re-measuring the water flux on the used membrane after the

filtration, followed by a purification step (intensive rinsing with distilled water):

$$R_{Irrev} = \frac{\Delta p}{J_{WA}\eta_W} - R_M \quad [m^{-1}] \tag{3}$$

where J_{WA} is the water flux after the cleaning procedure.

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

$$R_{Rev} = \frac{\Delta p}{J_c\eta_{WW}} - R_{Irrev} - R_M \quad [m^{-1}] \tag{4}$$

where Jc is the flux at the end of the filtration and η_{ww} is the wastewater viscosity (Pa s). The total resistance (R_T) can be evaluated from the steady-state flux by using the resistance-in-series model:

$$R_T = R_M + R_{Irrev} + R_{Rev} \quad [m^{-1}] \tag{5}$$

RESULTS

Surface properties of the TiO₂ layer

The surface and filtration properties of neat and TiO₂ coated PAN ultrafiltration membranes were investigated. The membranes were coated using the physical deposition method (Bai *et al.* 2010). The stability and evenness of the formed layer were investigated at different amounts of deposited catalyst.

Contact angle measurements were carried out to map the evenness of the coating and the wettability changes of the surface. The average contact angle for the neat membrane was $38° \pm 2.5°$ (Figure 1(a)), for the membrane coated by 0.3 mg/cm² TiO₂ without stirring was $6° \pm 2°$ (Figure 1(b)), and for the membrane coated while stirring (300 rpm) was $19° \pm 3.3°$ (Figure 1(c)). Commercial TiO₂ P25 has a primer particle size of ~0.025 μm (Veréb *et al.* 2012), in a suspension it forms aggregates nearly 1 μm in diameter (Mogyorósi *et al.* 2010), and the membrane pore size is ~0.006 μm (50 kDa). These facts, concerning size and contact angles, implicate that the TiO₂ on the surface of the membrane forms a hydrophilic layer, which increases the wettability of the surface. The difference between the wettability of the two membranes coated with or without stirring could be the result of non-homogeneous deposition of the catalyst on the membrane surface, by filtering the TiO₂ suspension through the membrane without stirring results in a homogeneous more even catalyst layer. The reason for this is that the shear stress inflicted on to the membrane surface as a result of stirring radially changes which causes the catalyst to deposit unevenly (Becht *et al.* 2008). For this reason, the non-stirring method was used in further experiments. The same tendencies were observed in case of the 0.6 and 1.2 mg/cm² TiO₂ coated membranes.

It was found that the hydrophilic TiO₂ layer on the PAN ultrafiltration membrane made with and without stirring does not change the surface free energy (neat membrane: 58 ± 6 mN/m, TiO₂ coated without stirring 62 ± 4 mN/m, with stirring 60 ± 8 mN/m) and the water flux (neat membrane: 420 ± 30 Lm⁻² h⁻¹, TiO₂ coated without stirring
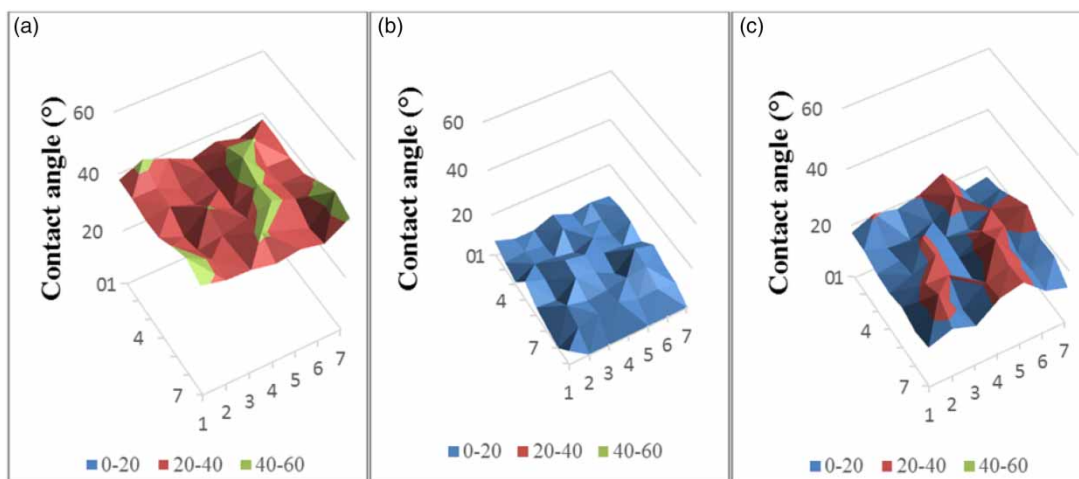

Figure 1 | Contact angles of the (a) neat, (b) 0.3 mg/cm² TiO₂ coated (without stirring during filtration, 0 rpm) and (c) 0.3 mg/cm² TiO₂ coated (stirring during filtration, 300 rpm) PAN50 membranes.

Table 1 | Water turbidity changes in case of 24 h 300 rpm stirring, flux changes in the presence of 0.3, 0.6 and 1.2 mg/cm² TiO₂ coated PAN membranes and 1 h UV irradiation

	Ratio of resuspended TiO₂ (%); after 24 h stirring, based on turbidity (NTU) changes)	water flux ($Lm^{-2} h^{-1}$) before 4 h of UV irradiation	water flux ($Lm^{-2} h^{-1}$) after 4 h of UV irradiation
neat PAN membrane		420 ± 30	422 ± 35
0.3 mg/cm² TiO₂ coated PAN	2.8	415 ± 28	419 ± 32
0.6 g/cm² TiO₂ coated PAN	2.1	409 ± 21	413 ± 24
1.2 mg/cm² TiO₂ coated PAN	1.4	406 ± 23	408 ± 22

$415 \pm 28 \, Lm^{-2} \, h^{-1}$, with stirring $413 \pm 35 \, Lm^{-2} \, h^{-1}$) values significantly.

To determine the stability of the membrane and the catalyst layer under operational conditions, initially the effects of the amount of the catalyst, UV irradiation, and stirring on the coated membrane water flux were investigated. In the first series of experiments the stability of the TiO₂ layer deposited on the membrane surface (0.3, 0.6, 1.2 mg/cm²) was investigated by means of stirring experiments: 100 mL distilled water with 300 rpm for 24 hours was stirred over the coated membranes in the cell during which the TiO₂ coating did not washed off, the water flux remained constant and the turbidity of the distilled water did not change significantly (Table 1), indicating that the catalyst did not resuspended. It means that the layer remains stable on the surface of the membrane during filtration too.

In another series of experiments, the coated membrane surface was UV irradiated for 4 hours after which the coated membrane water flux did not change significantly, showing that the membrane surface was not in this way noticeably (Table 1) damaged by the oxidative compounds produced by the catalyst during the photocatalytic reaction.

The effect of the TiO₂ layer on filtration properties in case of oily emulsion filtration

The difference between the fouling properties of the neat and TiO₂ coated membranes were investigated. The flux decline in case of the TiO₂ coated membrane was significantly lower compared to the neat membrane (Figure 2(a)). Reversible and irreversible resistances were calculated to obtain additional information using the resistances-in-series model. It was found that the filtration of oily water through the neat membrane results in lower constant fluxes due to the high reversible resistance caused by the oil deposition on the surface (Figure 2(b)). This layer can be removed by rinsing the membrane with water. The flux is higher and the reversible and irreversible resistances in case of the TiO₂ coated membrane are lower than in case of the neat membrane and lower than the membrane resistance, which makes them marginal. The TiO₂ coating on the membrane surface slightly increases the membrane resistance. The neat and TiO₂ coated membrane oil retention was similar, $96 \pm 2\%$, which is a similar value to that previously reported for 100 kD PAN membranes (97.2%) (Salahi *et al.* 2010).
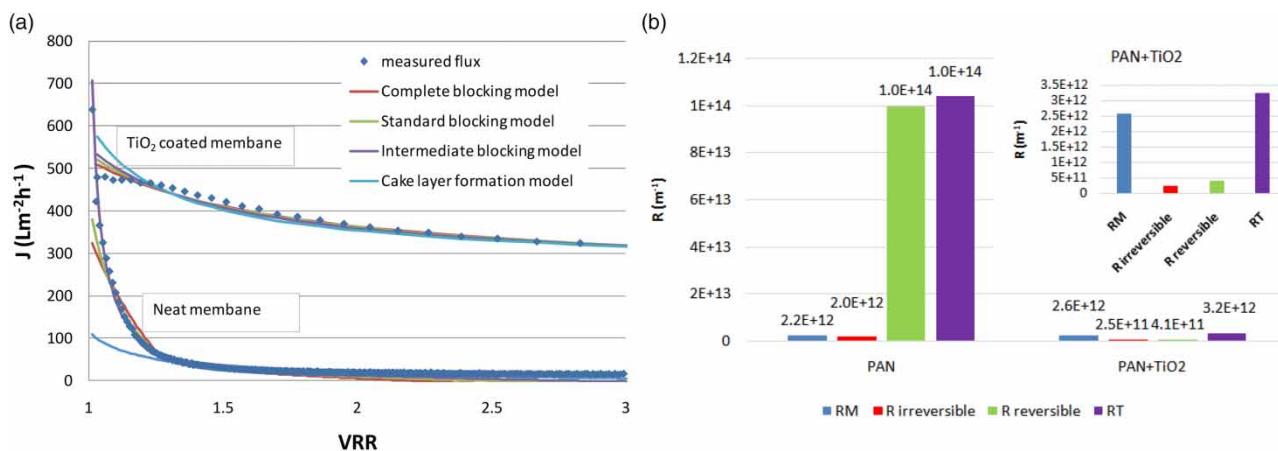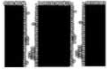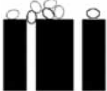

Figure 2 | (a) Flux decline and fitted fouling models during oily water filtration through the neat and TiO₂ coated PAN membranes in the function of VRR. (b) Resistances in case of oily water filtration through the 0.3 mg/cm² TiO₂ coated and neat PAN membranes.

Table 2 | Fouling mechanisms, in case of neat and 0.3 mg/cm² TiO₂ coated PAN membranes during oily water filtration

Fouling mechanism	Filtration law and constant pressure filtration (J_0A = const.)	Results of fitting	neat membrane	0.3 mg/cm² TiO₂ coated PAN membrane
Complete pore blocking	$J = J_0 e^{-k_b t}$ $\ln J = \ln J_0 - k_b \cdot t$	R^2 k (s⁻¹) J_0 (Lm⁻² h⁻¹)	0.909 $4.12 \cdot 10^{-3}$ 343	0.987 $1.2 \cdot 10^{-3}$ 517
Gradual pore blocking (standard pore blocking)	$J = J_0(1 + \frac{1}{2}K_S(A \cdot J_0)^{0.5} \cdot t)^{-2}$ $\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s \cdot t$ $k_s = 0.5 K_s A^{0.5}$	R^2 k (L⁻⁰·⁵·m·h⁻⁰·⁵s⁻¹) J_0 (Lm⁻² h⁻¹)	0.974 $1.88 \cdot 10^{-4}$ 425	0.982 $3.13 \cdot 10^{-5}$ 531
Intermediate filtration	$J = J_0 \cdot (1 + K_i \cdot A \cdot J_0 \cdot t)^{-1}$ $\frac{1}{J} = \frac{1}{J_0} + k_i \cdot t$ $k_i = K_i A$	R^2 k (m² L⁻¹·h·s⁻¹) J_0 (Lm⁻² h⁻¹)	0.995 $3.69 \cdot 10^{-5}$ 1,160	0.975 $3.26 \cdot 10^{-6}$ 546
Cake filtration	$J = J_0(1 + 2K_c(A \cdot J_0)^2 \cdot t)^{-0.5}$ $\frac{1}{J^2} = \frac{1}{J_0^2} + k_c \cdot t$ $k_c = 2K_c A^2$	R^2 k (m⁴ h²·L⁻²s⁻¹) J_0 (Lm⁻² h⁻¹)	0.96 $8.3 \cdot 10^{-7}$ 118	0.954 $1.79 \cdot 10^{-8}$ 602

In order to get a more sophisticated explanation about the fouling mechanism, Hermia's filtration models were fitted to the measured data. The fitting clearly shows that in case of the neat membrane the initial stage of the filtration is best descried by intermediate pore blocking (Figure 2(a), Table 2) that is followed by the cake layer formation in accordance with the high reversible resistance mentioned previously. In case of the TiO₂ coated membrane, all blocking models fit the measured data similarly (Figure 2, Table 2), for that the explanation lies in the extension of fouling, in the marginal reversible and irreversible resistance.

Cleanability of the TiO₂ coated oil fouled membranes

After oily water filtration, the membrane cleanability by means of photocatalysis (without any additional chemicals) was investigated. The fouled membrane was taken out of the cell and rinsed with 500 mL distilled water with a wash bottle to remove the oil layer if possible; chemical cleaning agents were avoided. Then, the membrane was left in the cell filled with 100 mL distilled water and irradiated with UV light for an hour, the water flux and contact angle changes were measured after every step. 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 (Figure 3). It was found

that the oil remaining on the TiO₂ coated membrane surface after filtration significantly increases the membrane surface hydrophobicity. In case of the neat membrane, contact angles remain constant after washing with water, while in case of the TiO₂ coating contact angles decrease. The surface hydrophilicity can be further increased and total flux recovery can be achieved within 1 hour of irradiation of the fouled TiO₂ coated membrane, showing that it can be effectively cleaned with UV irradiation, while UV irradiation of fouled neat membrane does not show any change neither in flux nor in wettability. Even though that 1 hour is sufficient time to achieve nearly total water flux recovery, which remains constant in case of extended time of UV irradiation, the contact angle values show that the oil layer does not decompose entirely (Figure 3), which may cause more extended fouling in repeated filtration/ cleaning cycles (Luján-Facundo *et al.* 2015). A way to improve the oil layer decomposition rate could be to increase the time, the intensity of the irradiation (Ku & Jung 2001), and the amount of the catalyst.

In order to investigate the importance of the hydrophilicity recovery, other than the flux recovery during cleaning, and to determine the extended effect of the TiO₂ coating even after repeated use and cleaning the previously described cycle was repeated three times in case of the neat and coated (0.6 and 1.2 mg/cm²) membranes; ten times in case of the
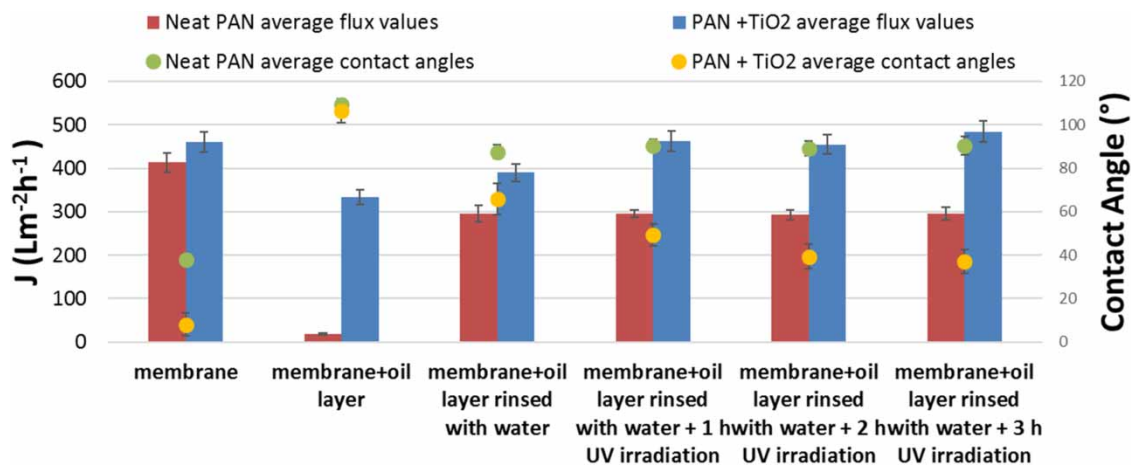
Figure 3 | Average contact angles and average flux values of the neat, 0.3 mg/cm² TiO₂ coated and then fouled and cleaned PAN membranes.

0.3 mg/cm² TiO₂ coated membrane. The flux of the neat membrane further decreased and both rinsing and irradiation had no significant effect on the membrane permeability, and the membrane was not further reusable. The results show (Figure 4) that by rinsing the membrane with distilled water does not have a consistent result on the flux recovery, regardless of the coating. The UV irradiation proves to be an effective cleaning method in case of the TiO₂ coated membranes, since even after numerous repetition of the process it results in a significant flux recovery. The difference between the relative water flux after rinsing and after UV irradiation state increases as the repetition goes on. The fouling mitigation during repeated cycles increased with increased amount of catalyst in case of 0.6 mg/cm² TiO₂, but no further increase was observed applying 1.2 mg/cm² TiO₂. The coated membranes had significantly higher relative

water flux and higher flux recovery than the neat membrane (Figure 6), the decreasing flux recovery during repeated cleaning processes indicate that the remaining oil on the surface hinders the total flux recovery. When comparing the coated membranes, appropriate flux recovery was obtained in case of the 0.3 mg/cm² TiO₂ coated membrane, thus higher amount of TiO₂ is not necessary (Figure 4(b)–4(d)).

CONCLUSIONS

TiO₂ coated PAN (50 kDa) ultrafiltration membrane was prepared using physical deposition method by filtering TiO₂ suspension through the membrane with and without stirring. Filtering the TiO₂ suspension through the membrane with stirring results in a less even catalyst layer, thus
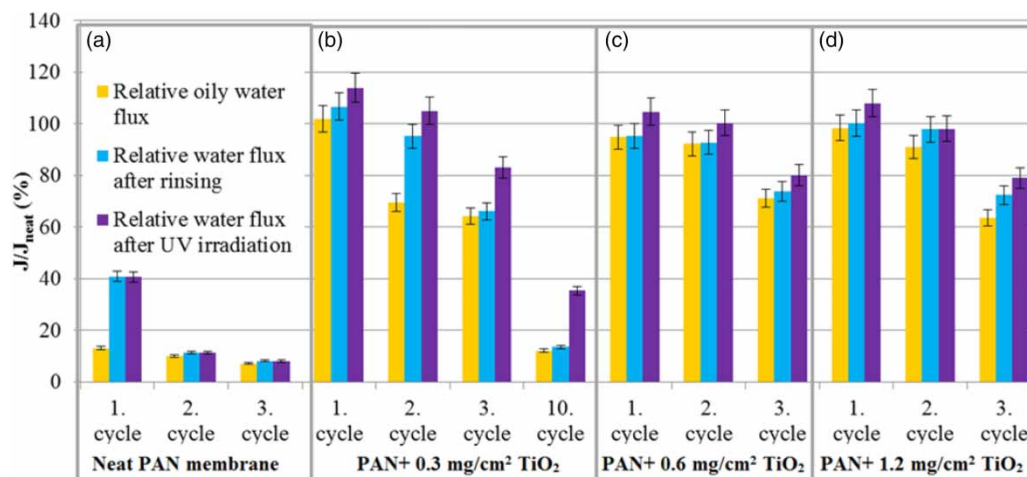

Figure 4 | Relative water fluxes after oily water filtration and rinsing the membrane with water and water fluxes of fouled membranes after 1 hour UV irradiation for the neat and different TiO₂ coated membranes.

only deposition without stirring results in appropriate even layer. TiO_2 forms a hydrophilic layer on the membrane surface, which stays stable during operation. 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. The neat and coated membrane oil retention was similar, $96 \pm 2\%$. 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 showed that the recovery of flux does not mean total decomposition of the fouling contaminants, and the remaining oil in the surface hinders the cleaning efficiency of the photocatalytic process in further filtration cycles.

ACKNOWLEDGEMENTS

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