Advantages of TiO₂/carbon nanotube modified photocatalytic membranes in the purification of oil-in-water emulsions

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ABSTRACT

For the effective purification of emulsified oil contaminated waters advanced treatment methods have to be applied, such as membrane filtration, which is able to eliminate macro-, and even nanoscale oil droplets, however, membrane fouling is still a major problem, which prevents economic utilization. Therefore, fouling mitigation is one of the most important aspects in the field of membrane separation developments. In the present study, solely TiO₂ and TiO₂/carbon nanotubes (CNT) composite modified PVDF membranes were prepared and used to purify oil-in-water emulsions. Achievable fluxes, reversible and irreversible filtration resistances, fouling models, filtration efficiencies and photocatalytic activities were compared in case of different nanomaterial covered and unmodified PVDF membranes. Applying either solely TiO₂ or solely CNT coating resulted in the significant reduction of total filtration resistance in both cases, but the combination of the two components (TiO₂ with 1 wt% CNT) resulted in by far the highest flux and lowest resistance, meanwhile, the enhanced photocatalytic efficiency of the composite was also achieved. To the best of our knowledge, this study demonstrates the beneficial effects of the combination of TiO₂ and CNT nanomaterials for the first time in the field of membrane separation of oil-in-water emulsions.

Key words | carbon nanotube, composite, enhanced flux, membrane, oil-in-water emulsion, titanium dioxide

INTRODUCTION

Purification of emulsified oil contaminated waters (d<sub>oil droplets</sub> < 5 μm) cannot be carried out by conventional water treatment methods (such as gravity separation, centrifugation, skimming, etc.), but membrane filtration can be a suitable method to eliminate macro- and even nanoscale oil droplets (Chakrabarty et al. 2010; Abadi et al. 2011; Yi et al. 2011). Microfiltration (Abadi et al. 2011; Shokrkar et al. 2012; Yang et al. 2014) ensures higher fluxes, meanwhile ultrafiltration (Chakrabarty et al. 2008, 2010; Masoudnia et al. 2014) results in higher purification efficiency, but membrane fouling is a major problem in both cases (Padaki et al. 2015), which causes flux reduction and increases the cost of these procedures, preventing the economical utilization. Therefore, the suppression of fouling is one of the most important aspects in terms of developing advanced membrane separation techniques.

Nanotechnology-based methods can be used to prepare highly hydrophilic and/or low-fouling membranes (Van der Bruggen 2009; Fischer et al. 2015; Yin & Zhou 2015; Islam et al. 2017; Kovács et al. 2018), moreover, in case of the
utilization of suitable semiconductor nanoparticles, contaminated membranes can be purified photocatalytically by UV (or even by solar) irradiation. Titanium dioxide (TiO$_2$) is one of the most investigated photocatalytic nanomaterial, because of its many favorable properties, such as non-toxicity, biocompatibility, chemical- and photostability, etc. (Vajda et al. 2011; Chang et al. 2014; Kertész et al. 2014). Carbon nanotubes (CNT) are also highly investigated both in composite photocatalytic material production (Woan et al. 2009; Vajda et al. 2011; Réti et al. 2016) and in the development of novel membrane surfaces (Smajda et al. 2007; Esfahani et al. 2015; Rashid & Ralph 2017).

Carbon nanotubes (as a composite component – e.g. in TiO$_2$/CNT) are able to enhance the photocatalytic efficiency of a semiconductor nanoparticle, due to the following two mechanisms (Gao et al. 2009; Woan et al. 2009): CNT can conduct the electron from the valence band of the activated TiO$_2$, resulting in extended electron-hole lifetime and, therefore, suppressed electron-hole recombination rate (Hoffmann et al. 1995). Moreover, CNT can act as a photosensitizer, if the photo-generated electrons of CNTs are able to migrate to the valence band of TiO$_2$, which can initiate redox reactions (Wang et al. 2005). The authors proved that both the physical mixture of TiO$_2$/CNT, and more likely, the synthesized composites had higher photocatalytic efficiency than pure TiO$_2$. Different weight ratios of CNT/TiO$_2$ composites were also widely investigated in the literature. Some authors (Wang et al. 2005; Yen et al. 2008) determined relatively high beneficial CNT/TiO$_2$ ratios (20 and 8 wt%, respectively) for phenol decomposition, however, other authors determined much lower optimal CNT contents. Gao et al. (Gao et al. 2009) investigated 1.5–20 wt% CNT contents and found that even 1.5 wt% significantly increased the activity, and no notable further increase was determined at higher CNT contents. Yu et al. (Yu et al. 2005) reported 3 wt% as optimal CNT/TiO$_2$ ratio, although this content was the lowest in the investigated composite series. Réti et al. (Réti et al. 2014) investigated the 1–10 wt% interval and measured the best photocatalytic activity in case of 1 wt% CNT content for phenol decomposition (and 5 wt% for oxalic acid degradation).

Due to the enhanced photocatalytic efficiency of TiO$_2$/CNT nanocomposites (and some other advantageous properties, such as increased mechanical and chemical stability, mesoporous characteristics, etc.), their utilization can be beneficial to create photocatalytic membranes, however, the hydrophobic surface property of CNT may cause disadvantageous effects during the membrane filtration of oil-in-water (o/w) emulsions. In the present study, TiO$_2$/CNT nanocomposites were prepared (with 1 wt% CNT content, which was chosen for the reasons detailed above) and used to modify the surface of a UV resistant polyvinylidene fluoride (PVDF) ultrafilter membrane. Self-prepared TiO$_2$/CNT/PVDF membranes were applied to purify 100 ppm crude oil containing o/w emulsions. Achievable fluxes, reversible and irreversible filtration resistances, fouling mechanisms, filtration efficiencies and photocatalytic activities were compared in case of solely TiO$_2$, CNT- and TiO$_2$/CNT composite-covered, and unmodified membranes.

**MATERIALS AND METHODS**

**Production of the nanomaterial modified membranes**

For the membrane surface modification, commercial titanium dioxide (TiO$_2$; Aeroxide P25, Germany, d = 25–39 nm, a_{BET} = 50.6 m$^2$ g$^{-1}$) and carbon nanotube (CNT; Nanothinx NTX1 multi walled carbon nanotube, Greece, l $\geq$ 10 μm; d = 15–35 nm) were applied. Nanomaterials (TiO$_2$ and CNT) by themselves or in composites (TiO$_2$ with 1 wt% CNT) were suspended in 2-propanol (c = 400 mg L$^{-1}$) by 1 min ultrasonic homogenization (Hielscher UP200S, Germany) at 25°C (maximal amplitude and cycle were applied). 40 mg of the given nanomaterial (suspended in 100 mL of 2-propanol) was immobilized on a PVDF membrane (New Logic Research Inc., USA, 100 kDa; ~1.0 mg cm$^{-2}$ catalyst coverage) by physical deposition method: the suspension was filtered through the membrane, applying 0.3 MPa transmembrane pressure in a batch-stirred membrane reactor (Millipore, XUF07601, USA), followed by drying in air at room temperature.

**Determination of contact angles**

For the description of the hydrophilicity of the membrane surfaces, the contact angles formed between the membrane
and ultrapure water were measured using the sessile drop method (Dataphysics Contact Angle System OCA15Pro, Germany) at room temperature. 10 μL water was carefully dropped onto the membrane surface and contact angles were immediately measured within 5 s (measurements were repeated 10 times and average values were calculated).

Production of the oil-in-water (o/w) emulsion

O/w emulsions (c_{oil} = 100 mg L^{-1}; d_{droplets} < 1.5 μm) were prepared in two steps, using crude oil (provided by MOL Nyrt.; Hungary), and ultrapure water (PureLab Pulse, ELGA Labwater, UK). Intensive stirring (35,000 rpm, 1 min) of crude oil and water was followed by 10 min ultrasonic homogenization (Hielscher UP200S, Germany) at 25 °C (using maximal amplitude and cycle). For the photocatalytic experiments 20 ppm oil concentration was set by the dilution of the emulsion.

Determination of the photocatalytic efficiencies

Photocatalytic experiments were carried out in a modified Millipore reactor, which was equipped with a UV-A fluorescence tube (Lightech, 10 W, λ_{max} ~ 365 nm; UV intensity: 24 mW m^{-2} – measured by an Optix UVTEX radiometer), and a magnetic stirrer. Photocatalytic efficiencies were determined by measuring the chemical oxygen demand (COD) and extractable oil content of a 20 ppm o/w emulsion during the irradiation of the photocatalytic membranes for 120 min. COD values were measured by a standard method, based on potassium dichromate oxidation, using standard test tubes (Hanna Instruments, USA), a Lovibond ET 108 type digester (t = 2 h, T = 150 °C), and a Lovibond COD Vario type spectrophotometer. Extractable oil content was measured by a Wilks InfraCal TOG/TPH type analyzer, using hexane as extracting solvent. Additionally, photocatalytic performances of the prepared membranes were determined by phenol decomposition. Changes in phenol concentration were followed using an Agilent 1100 series HPLC system equipped with Lichrospher RP 18 column applying methanol/water (35:65 vol%) mixture as eluent (the detection was carried out at λ = 210 nm).

Membrane filtration experiments

Filtration of o/w emulsions was carried out in a batch-stirred membrane reactor (Millipore XFUF07601, USA) equipped with the given membrane, using 0.1 MPa transmembrane pressure and 5.83 s^{-1} stirring speed (350 rpm). In all filtration experiments, 250 mL emulsion was filled into the reactor and filtered until the production of 200 mL permeate (volume reduction ratio: VRR = 5). Purification efficiencies were determined by measuring the COD and the extractable oil content of the permeates.

Filtration resistances and fouling models

The membrane resistance (R_M) was calculated as:

\[ R_M = \frac{\Delta p}{J_W \times \eta_W} [m^{-1}] \]  

(1)

where Δp is the applied transmembrane pressure [Pa], J_W is the water flux of the clean membrane [m^2 m^{-2} s^{-1}] and \( \eta_W \) is the viscosity of the water [Pa s]. The irreversible resistance (R_{Irrev}) was determined by remeasuring the water flux on the used membrane after the filtration, followed by a purification step (intensive rinsing with distilled water):

\[ R_{Irrev} = \frac{\Delta p}{J_{WA} \times \eta_W} - R_M [m^{-1}] \]  

(2)

where \( J_{WA} \) is the water flux after the cleaning procedure. The reversible resistance (R_{Rev}) can be calculated as:

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

(3)

where \( J_c \) is the flux at the end of the filtration and \( \eta_{WW} \) is the viscosity of the emulsion. The total resistance (R_T) can be calculated as the sum of the previously detailed resistances:

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

(4)

Hermia’s filtration law (Hermia 1982; Bowen et al. 1995; Zhao et al. 2016) can be applied as a mathematical model to...
characterize the fouling mechanism:

\[ \frac{d^2t}{dV^2} = k \left( \frac{dt}{dV} \right)^n \]  

(5)

where \( t \) is the filtration time, \( V \) is the volume of the permeate, \( k \) is the fouling constant and \( n \) is a value illustrating the different fouling mechanism (complete pore blocking: \( n = 2 \), intermediate pore blocking: \( n = 1 \), internal pore blocking: \( n = 1.5 \), cake layer formation: \( n = 0 \)). More details about the calculations can be found in other publications (Bowen et al. 1995; Aryanti et al. 2016; Veréb et al. 2018).

RESULTS

Description of the produced membrane surfaces

The photographs of the produced membranes are presented in Figure 1, which also demonstrates their hydrophilicity with the water droplets formed on the surfaces. Uncoated PVDF membrane was slightly hydrophilic, based on the measured \( 57.2 \pm 0.6^\circ \) contact angle. Meanwhile, both solely TiO\(_2\)-covered and TiO\(_2\)/CNT composite-covered surfaces were highly hydrophilic, since the droplets were immediately and totally spread on the surfaces. So, surprisingly, no measurable effect on the surface hydrophilicity was determined in case of 1 wt% carbon nanotube content. Solely CNT-covered membrane was also prepared as a control sample, which was highly hydrophobic as expected by the measured \( 125 \pm 1.2^\circ \) contact angle value.

Photocatalytic activities

In the first series of experiments, the photocatalytic efficiencies of TiO\(_2\), and TiO\(_2\)/CNT-coated membranes were compared to investigate the effect of the 1 wt% CNT content on the photocatalytic activity of the composite. First, the photocatalytic decomposition of phenol, as a widely used (Wang et al. 2005; Vajda et al. 2011; Réti et al. 2016) model organic contaminant was investigated. Phenol concentration was followed by HPLC (Figure 2), and the results proved the increased photocatalytic activity of the TiO\(_2\)/CNT composite-covered membrane.

After the increased photocatalytic activity was proven in the case of phenol model contaminant, 20 ppm crude oil containing o/w emulsion was treated photocatalytically for 120 min. Meanwhile, the COD and extractable oil content of the taken samples were measured. Figure 3 demonstrates that both COD and extractable oil content values decreased more intensively in the case of the TiO\(_2\)/CNT composite-covered membrane, compared to the solely TiO\(_2\)-covered membrane. As can be seen in Figure 3, the extractable oil content decreased slightly more than the COD, which can be explained by the production of water-soluble organic compounds during the photocatalytic decomposition, which are not extractable by hexane, but still contribute to the COD values. The improved activity can be beneficial...
during the photocatalytic regeneration of the contaminated self-cleaning photocatalytic membrane surfaces.

Membrane filtration of o/w emulsions

In the next series of experiments, the effects of different coatings on membrane filtration of 100 ppm crude oil containing o/w emulsions were investigated in detail. During the filtration of o/w emulsions with the uncoated membrane, quick and significant flux reduction (Figure 4(a)) was observed, therefore high total resistance (Figure 4(b)) was calculated, which was caused mainly by irreversible resistance. Coating with TiO₂ resulted in significantly higher flux (Figure 4(a)), and the considerable reduction of irreversible and total resistances (Figure 4(b)). Surprisingly, despite the hydrophobic surface property of the carbon nanotube, the TiO₂/CNT composite modified membrane resulted in by far the highest flux and lowest resistance. Moreover, the ratio of reversible and irreversible resistances (Figure 4(b)) was also the most beneficial in case of the composite-covered membrane. The very low flux reduction rate proved that this composite coating inhibited successfully the adhesion of the oil droplets on the surface. Lower amounts of accumulated hydrophobic contaminants resulted lower probability for the droplets to create a hydrophobic water barrier or to be pressed inside the composite layer during the filtration.

Unexpectedly, highly beneficial effect of the presence of CNT cannot be related to the surface hydrophilicity, since there was no measurable difference between the solely TiO₂, and the TiO₂/CNT-covered membranes (both was highly hydrophilic – see Figure 1). Additionally, 100% CNT-covered hydrophobic membrane also resulted higher flux than the uncoated membrane, but lower than the solely TiO₂-covered membrane. To get some explanation, the fouling mechanisms were investigated, to determine which fouling model (complete pore blocking, intermediate pore blocking, internal pore blocking, or cake layer formation) best describes the measured flux curves. The linearized forms of the models (Hermia 1982; Aryanti et al. 2016; Veréb et al. 2018) were fitted onto the measured flux...
curves, and the correlation coefficients were determined (Figure 5).

As can be seen in Figure 5, utilization of the uncoated membrane resulted in the formation of a cake layer on the surface – which was a significant barrier for water flow due to the hydrophobicity of the oil layer – and caused the observed intensive flux reduction during the filtration. In all other cases, cake layer formation was not dominant, resulting slower flux reduction, and the slightly fouled pores of the produced photocatalyst layers can be easily purified by UV or solar irradiation. For the confirmation, the photocatalytic cleanability of the modified membranes were also investigated. After 24 h of UV-A irradiation, the original water flux was entirely recovered both in case of TiO2-, and TiO2/CNT-covered membranes. From the point of the retention (during the filtration), in all cases, >98% purification efficiencies were measured for COD and extractable oil content as well, and there was no significant difference between the different membranes.

**DISCUSSION**

According to the literature, from the point of the photocatalytic efficiency, the optimal CNT content of TiO2/CNT composites is determined mostly as 1–20 wt% (Wang et al. 2005; Yu et al. 2005; Yen et al. 2008; Gao et al. 2009; Woan et al. 2009; Vajda et al. 2011; Réti et al. 2016, 2014), and is strongly dependent on the contaminants and several surface and structural properties of the composite components. Based on the observed significant beneficial effect of 1 wt% CNT content on membrane filtration and the wide literature of TiO2/CNT composite photocatalysts, different CNT contents, surface modification of the CNTs, or hydrothermally synthesized composites may lead to more effective o/w emulsion separation and/or advanced self-cleaning photocatalytic membranes. Detailed investigations of the optimisation of TiO2/CNT ratio, the utilization of modified/functionalyzed CNT, and the incorporation of the composites into membrane materials are also highly promising in the field of o/w emulsion separation, as similar investigations already resulted improved properties in case of other kind of water contaminants (Bai et al. 2015; Esfahani et al. 2015; Irfan et al. 2015). Additionally, it must be noted that, in long-term utilization,
the widely used polymeric membrane materials (even the UV resistant membranes) can be damaged by highly reactive hydroxyl radicals, which are produced during photocatalytic applications. For example, Dzinun et al. recently published (Dzinun et al. 2017) that UV irradiation slightly decreased the stability of the TiO<sub>2</sub>/PVDF membrane after 30 days' exposure, which was mainly attributed to the formation of surface cracks. However, there was no Ti leaching from the membrane. On the basis of these considerations, highly chemical resistant membranes, such as polytetrafluoroethylene or ceramic membranes also have potential for future investigations.

CONCLUSIONS

Both TiO<sub>2</sub> and CNT coatings resulted in significant reduction of total resistances during the ultrafiltration of oil-in-water emulsions. Surprisingly, the TiO<sub>2</sub>/CNT composite modified membrane resulted in far the highest flux and therefore the lowest total resistance; moreover, the ratio of reversible and irreversible resistances was also the most beneficial in the case of the composite covered membrane. In addition, the composite had increased photocatalytic activity (both for oily and water-soluble contaminants), which is beneficial from the point of regeneration properties of the contaminated membranes. Based on the presented results, detailed investigations about the utilization of TiO<sub>2</sub>/CNT modified membranes in o/w emulsion separation are highly promising.

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