TiO$_2$ COATED MEMBRANE SURFACE CHARACTERISATION WITH CONTACT ANGLE MEASUREMENTS

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Abstract
In this work a neat polyacrilonitrile ultrafiltration membrane performance was compared to a same but TiO$_2$ coated membrane during oily water filtration. The fouling mechanisms of the two membranes and the resistances were determined and calculated.It was found that in case of the neat membrane initially intermediate pore blocking occurs that is followed by cake layer formation. The TiO$_2$ coating proved to be beneficial due to its fouling mitigating effect. With contact angle measurements the membrane wettability changes were monitored,whichoccurred as a result of the TiO$_2$ coating, oily water filtration and cleaning of the membrane surface by UV irradiation. After 3 hours of UV irradiationthe water flux reached the neat membrane flux, but the residual oil layer on the surface still had a significant effect on the surface wettability.

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. [4], but most of them are not effective enough to treat stabile oil in water emulsions. Membrane filtration is an efficient process to treat oily wastewaters, without chemical additives and low energy cost compared to traditional separation methods [1, 2, 5]. Ultrafiltration is the most effective treatment, among membrane processes for this purpose [5]. 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 [1-4].

As the membrane fouling is a key problem; in order to minimize it membrane surfaces can be modified with photocatalytic nanoparticles. One way of modifying the membrane is to deposit the particles on the membrane surface [6–8]. TiO$_2$ is the most commonly used photocatalyst due to its good physical and chemical properties, availability, high photocatalytic activity and desirable hydrophilic properties [6–9]. Increasing the membrane hydrophilicity can increase the membrane fouling resistance [9].Contact angle measurements are commonly used to determine the wettability of a surface. Contact angles also can show an accordance with the surface roughness [10].

The aim of this work was to investigate the effect of TiO$_2$ coating on a polyacrilonitrile ultrafiltration membrane performance during oily water filtration compared to the neat membrane. Furthermore, to characterize the membrane surface wettability changes by contact angle measurements after TiO$_2$ coating, oily water filtration, and a cleaning process which consisted of rinsing the membrane surface with water and then irradiating it for 1,2 and 3 hours with UV light.

Experimental

The membrane was a polyacrylonitrile membrane (VSEP, New Logic Research Inc. USA) with 50kDa cut off weight, and membrane surface area 0.00342 m^2. Commercial TiO$_2$ (AEROXIDE P25, Evonik Industries) was used to coat the membrane surface. The membranes were coated with TiO$_2$ by filtering through the membrane 25mL, 0.4 g/L catalyst suspension in a dead end cell, at 1 MPa without stirring, that resulted in 0.3mg/cm^2 TiO$_2$ 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. This way a photocatalytic membrane reactor was set up. The UV light source was a low pressure mercury-vapor-lamp (GERMIPAK LightTech, Hungary, 40W, λ=254nm). The filtrations of the model wastewater were carried out at 0.3 MPa transmembrane pressure, without stirring at 20°C.

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 (35000 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 (coil=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:

$$VRR = VF / (VF – VP) \hspace{4cm} (1)$$

where VF and VP is the volume of the feed and permeate [m^3] respectively at any time.

Hermia's model was applied to determine the fouling mechanism of each membrane during filtration [11,12]. Resistance-in-series model was applied to analyze resistances that lead to flux decline during the ultrafiltration process[11].

Membrane hydrophobicity was quantified by measuring the contact angle that was formed between the (neat, TiO$_2$ coated and oily contaminated) membrane surface and distilled water. 10μL water was carefully dropped on the top of the membrane surface. Contact angles were measured using the sessile drop method (Dataphysics Contact Angle System OCA15Pro, Germany). In every case the membrane was sliced up and the entire surface was characterized.

Results and discussion

In the first series of experiments the difference between the fouling propertiesof the neat and TiO$_2$ coated membranes were investigated. The flux decline in case of the TiO$_2$ coated membrane was significantly lower compared to the neat membrane(Fig. 1). In the initial stage of the filtration the intermediate pore blocking describes the best the measured data which is followed by the cake layer formation (Fig. 1.a). In case of the TiO$_2$ coated membrane all blocking models fit the measured data similarly (Fig. 1.b), for that theexplanation lies in the resistances. The calculated resistances give additional information aboutthe mechanism of the fouling. Filtration of oily water through the neat membrane results in a high reversible resistance and irreversible resistance, compared to the TiO$_2$ coated membrane (Fig. 2), meaning that first complete pore blocking occurs and that is followed by the oil cake layer forms on the membrane surface which can be removed by rinsing the membrane with water. The reversible and irreversible resistances in case of the TiO$_2$ coated membrane are lower than the membrane resistance, which makes them marginal and explains why the blocking models fit the measured data so closely because none of them occurs to a significant extent (Fig. 1.b and 2).
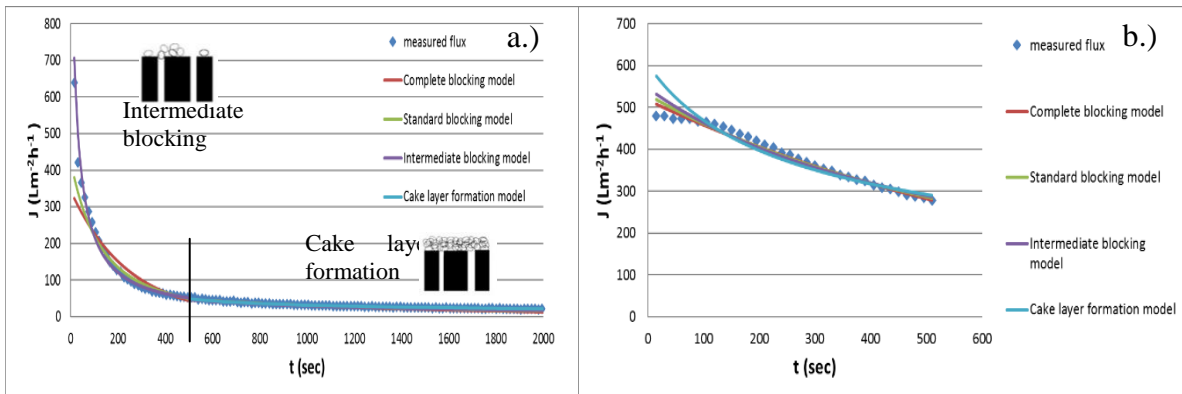
Figure 1. Flux decilne and fitted fouling modells during oily water filtration throught the neat (a) and TiO$_2$ coated (b) PAN membranes
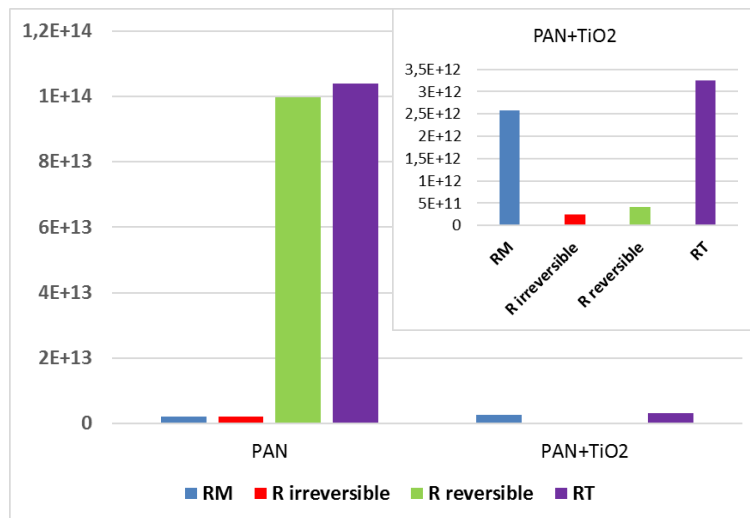

Figure 2. Resistances in case of oily water filtration throught the TiO$_2$ coated and neat PAN membranes

In the second series of experiments the wettability changes of the membrane during coating, oily water filtration, and UV cleaning were measured to determine if the cleaning process of the surface can be monitored with contact angel measurements. By coating the membrane with TiO$_2$ the surface wettability increases (Fig. 3), the catalyst forms a hydrophilic layer on the membrane surface.
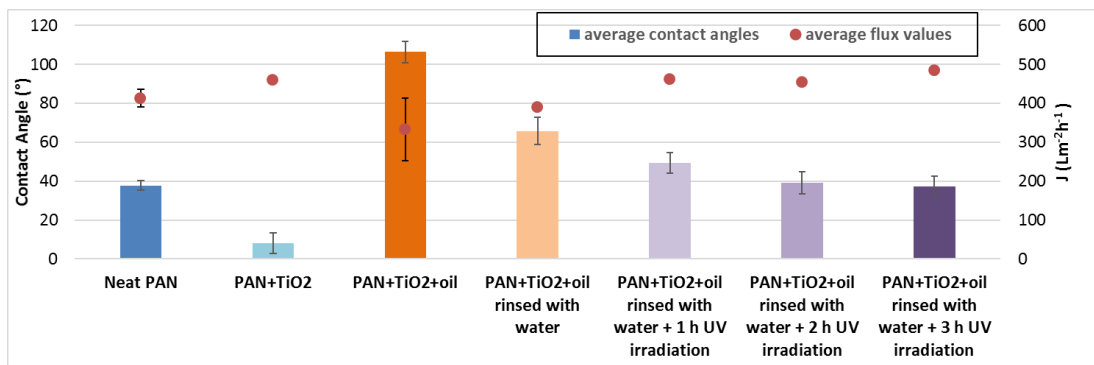

Figure 3. Average contact angles and average flux values of the neat, TiO$_2$ coated and than fouled and cleaned PAN membranes

The TiO$_2$ layer does not change the water flux significantly (Fig. 3). During the filtration of

the oily water a hydrophobic oil layer forms on the surface, which results in the decrease of the flux (Fig. 3). By rinsing the membrane surface with water the oil layer can be removed to an extent that results in a flux and hydrophilicity increase (Fig. 3). The wider error bar on the flux of TiO_2 coated membraneduring oily water filtration represents the extent of fouling during filtration.The UV irradiation of the membrane surface with time results in higher flux and hydrophilicity (Fig. 3). After 3 hours the water flux reached the neat membrane flux(Fig. 3). The average hydrofilicity of the membrane after 3 hour is nearly the same as the neat membrane hydrofilicity, but to recover the hydrofilicity of the TiO_2 coated membrane a longer irradiation time is needed. The hydrofilicity increase indicates the degree of the decomposition of the oil layer.

Conclusion
During oily water filtration on the neat polyacrilonitrile membraneinitially intermediate blocking occurs that is followedby cake layer formation, that results in a rapid flux decline. This means that the oil layer acts as an additional filtration layer. By coating the membrane surface with TiO_2, the membrane becomes more resistant to fouling, and does not come to oil cake layer formation. The flux decline during oily water filtration is moderate compared to the neat membrane. The reversible and irreversible resistances are negligible compared to the membrane resistance. The oil that is on the TiO_2 coated membrane surface after filtration significantly increases the membrane surface hydrophobicity that can be reduced by rinsing the membrane surface with water, which results in significant flux recovery. By UV irradiation the surface hydrophilicity can be further increased and total flux recovery can be achieved within 3hours.

Acknowledgements

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