Doctoral (Ph. D.) Theses

Investigation of the properties and applicability of TiO_2 modified polymeric membranes

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1. INTRODUCTION

The rapid growth of the human population results in increased environmental pollution due to transportation and industrial activity. Protecting water quality, ensuring drinking water supplies worldwide, and treating polluted waters are key issues. Compliance with ever-stricter legislation on wastewater discharge into water bodies and drinking water quality requires continuous development of water treatment technologies.

A significant amount of the global wastewater is made up of oil-containing wastewater, which is contributed by the oil and gas industry, petrochemical, pharmaceutical, metallurgical and food industries. Effective treatment of the resulting wastewater is an inevitable task. One solution to this problem is water reuse, which requires the use of advanced technologies. There are many methods for doing this, including traditional physical and chemical treatment methods. Physical treatments include adsorption (activated carbon, copolymers, zeolites and resins), sand filtering, hydrocyclones and evaporation; Chemical treatments include oxidation, electrochemical processes, photocatalytic treatment, Fenton reaction, ozone treatment, ionic liquids and the use of demulsifiers. However, conventional methods have their own drawbacks such as high cost, chemical demand, large space requirements and the generation of secondary pollutants. This gives rise to membrane filtration as a state-of-the-art, continuously evolving process that can provide a solution for treating oil-polluted waters. Pressure driven membrane filtration techniques such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis are suitable for separating particles of different sizes. Depending on membrane technology, they can be used from suspended solids to retention of monovalent ions. The advantages of membrane filtration over conventional methods are a more efficient separation, easy to integrate in existing technologies and relatively simple operation. The membrane technology market is in a rapid growth phase due to continuous research and development. However, there are still several problems that need to be addressed in order to produce membranes with better retention and stability, but with a lower fouling propensity, than commercially available membranes. Research concerning the decrease of membrane fouling propensity focuses primarily on the development and optimization of membrane materials and design.

2. OBJECTIVES

The aim the doctoral dissertation was to investigate the modification of micro- and ultrafiltration polymeric membranes by physical deposition of TiO_2 to reduce membrane fouling and to investigate the possibility of chemical-free membrane cleaning by UV irradiation.

In the application of membrane separation, it is extremely important to reduce membrane fouling and the extension of membrane lifespan, to this goal the effects of a membrane modification by photocatalyst nanoparticles were investigate. Model oil-containing wastewaters were prepared to investigate the applicability of photocatalyst nanoparticle-modified membranes for filtration of oil-in-water emulsions and their re-use after purification.

Therefore, during the research work, the following goals were set:

- Characterization of applied photocatalyst nanoparticles
- Investigation of the photostability of the polymer membranes used
- Preparation and surface characterization of membranes modified by physical deposition of photocatalyst nanoparticles, confirmation of photocatalytic activity
- The applicability of layers formed by nanoparticles of different geometry on the surface of polymeric membranes
- Comparison of filtration characteristics of modified and original membranes by determining flux changes, resistances, fouling mechanisms during oil-in-water emulsion filtration,
- Characterization of oil in water emulsions with different salt concentrations
- Testing UV-light-cleanability of oil fouled membranes
- Investigation of the effect of oil-in-water emulsions with different salt concentrations on membrane fouling and cleanability

3. EXPERIMENTAL

During the experiments the nanoparticles used for membrane modification, commercially available Aeroxide P25 titanium-dioxide (TiO2 P25) and synthesized TiO_2 nano-rods (TiO2 NR) were characterized. The geometry of the particles was analysed by electron microscopy (Hitachi S-4700 Type-II Cold Field Emission Scanning Electron Microscope, Philips CM10 Type TEM), Rigaku Miniflex II X-ray diffractometer was used to determine crystalline structure of the TiO_2 particles and the specific surface area was investigated by BET method with Micromeritic gas adsorption meter (Gemini Type 2375).

Physical deposition of the catalysts to the polymeric membranes was accomplished by TiO2 suspensions filtration using a batch filtration unit (XFUF07601, Solvent-resistant Stirred Ultrafiltration Cell, Millipore, USA). The same membrane filtration unit was used for the filtration experiments and with a modified lid for the photocatalytic purification of the membrane with UV irradiation.

To investigate the fouling propensity and cleanability of unmodified and TiO2 modified polymer (PES (0.2 µm), PAN (50 kDa), PVDF (250 kDa) membranes 100 ppm oil-in-water emulsions whit different salt concentrations (0, 250, 2500 and 25000 mg dm^{-3}) were filtered. Membrane fouling was determined by measuring the flux decline and by calculating fouling resistances and fitting the measured data with fouling mechanism models. The wettability and surface free energy of clean and modified membranes were determined by sessile drop method (Dataphysics Contact Angle System OCA15Pro, Germany). For the determination of droplet size and zeta potential of oil in water emulsions, a ZetaSizer 4 (Malvern, UK) instrument was used.

The surface of un-used TiO_2 modified, clogged and UV irradiated membranes was characterized by ATR-IR (attenuated total reflection) spectrometry. The spectra were recorded on a BIO-RAD Digilab Division FTS-65A / 896 FT-IR (Fourier Transform Infrared) spectrophotometer with a resolution of 4 cm^{-1} at a wavelength range of 4000-1000 cm^{-1}.

4. SUMMARY OF NEW SCIENTIFIC RESULTS

1. New scientific results obtained during TiO_2 modification of polymeric membranes:

(III) It was proven that the TiO_2 layer remains stable on the membrane surface under operational conditions in a batch filtration unit. It was found that the total coverage of polymeric sheet membranes by physical deposition can be achieved with 1.2 mg cm^{-2} of TiO_2 P25 or TiO_2 NR catalyst.

TiO_2 P25 and TiO2 NR catalysts form a hydrophilic layer on the surface of PES, PAN and PVDF polymeric membranes, the hydrophilicity of the layer increases with the amount of catalyst until full coverage is achieved. In case the catalyst does not provide even coverage and the wettability is determined by the nature of the membrane material. TiO_2 layers resulted in increased surface free energy values with increased hydrophilicity. These results have also shown that contact angle measurement can be a suitable method for testing the quality of the catalyst layer. Based on my experiments, 50% less (0.6 mg cm^{-2}) catalyst amount do not provide complete coverage, while 50% more (1.8 mg cm^{-2}) do not provide a stable TiO_2 layer on the membrane surface.

Experiments with Acid red 1 dye solution showed that the modified membranes have photocatalytic activity.

2. New scientific results obtained during the TiO_2-modified membrane filtration of oil-in-water emulsions:

(I, II) It was found that as a result of TiO_2 modification of both PAN and PVDF membranes, the flux reduction during the filtration of oil-in-water emulsions is drastically lower compared to the unmodified membranes; the modification results in at least one order of magnitude reduction in total filtration resistance.. By detailed examination of the filtration mechanisms, it was proven that the TiO_2 layer prevents the formation of an oil layer on the membrane surface, which would act as a cake layer resulting in high filtration resistance.

In the case of unmodified PAN and PVDF membranes, during filtration of the oil-in-water emulsion, initially gradual pore blocking occurs, which is followed by cake layer formation as the filtration progresses. Modification of PAN membranes with TiO_2 P25 layer results in lower reversible and irreversible resistances during the oil-in-water emulsion filtration and significantly lowers reversible and irreversible resistances compared to the unmodified membranes, thus no significant membrane fouling occurs. The slower fouling of TiO_2 P25 modified PVDF membranes, according to the fitted fouling mechanisms is not due to the formation a uniform oil layer on the membrane surface, rather is caused by oil droplets adhering to the surface.

3. **New scientific results obtained during the purification of oil-fouled TiO_2 modified membranes:**

(I, II) It was proven that the surface of the polymer membrane modified with TiO_2 P25 catalyst layer fouled during the filtration of oil-in-water emulsion can be cleaned by UV irradiation and the initial flux of the membrane can be restored.

By increasing the UV exposure time, the initial contact angle values of the fouled membranes can be restored. However, infrared spectroscopy of the surface showed that this does not mean complete degradation and removal of contaminants. The degradation by-products and oil residues may remain on the membrane surface after cleaning but does not prevent re-use of the membrane. Repeating several successive filtration and purification cycles, it was proven that the photocatalytic purification step can significantly extend the lifespan of the modified membrane.

4. **New scientific results obtained during TiO_2 modified membrane filtration of oil-in-water emulsions with different salt concentrations:**

(I) It was proved that even in the case of high salinity oil-in-water emulsions the membrane fouling propensity is reduced by TiO_2 P25 modification of the membrane. Salinity also has no significant negative effect on the photocatalytic cleanability of the membrane.

The surface charge of unmodified PVDF membrane is increased due to the high salt concentration, thereby increasing the electrostatic repulsion between the droplets and the surface, reducing the reversible resistance. As the salinity increases, the average droplet size of the oil droplets increases, reducing irreversible membrane fouling.

The increased hydrophilicity of the surface due to the TiO_2 layer, reduces both the reversible and irreversible resistances compared to the unmodified membrane resistances during the filtration of salt containing (0, 250, 2500, 25000 mg dm^{-3}) oil-in-water emulsions.

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