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 TiO₂ 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 TiO2 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 TiO2 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 with 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 TiO2 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\textsubscript{2} modification of polymeric membranes:

(III) It was proven that the TiO\textsubscript{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\textsuperscript{-2} of TiO\textsubscript{2} P25 or TiO\textsubscript{2} NR catalyst.

TiO\textsubscript{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\textsubscript{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\textsuperscript{-2}) catalyst amount do not provide complete coverage, while 50\% more (1.8 mg cm\textsuperscript{-2}) do not provide a stable TiO\textsubscript{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\textsubscript{2}-modified membrane filtration of oil-in-water emulsions:

(I, II) It was found that as a result of TiO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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.
5. PUBLICATIONS RELATED TO THE PRESENT THESIS

I. Fouling mitigation and cleanability of TiO$_2$ photocatalyst-modified PVDF membranes during ultrafiltration of model oily wastewater with different salt contents
Ildikó Kovács, Gábor Veréb, Szabolcs Kertész, Cecilia Hodúr, Zsuzsanna László

II. Investigation of surface and filtration properties of TiO$_2$ coated ultrafiltration polyacrylonitrile membranes
I Kovács, G Veréb, Sz Kertész, S Beszédes, C Hodúr, Zs László
WATER SCIENCE AND TECHNOLOGY 77:(4) p. 931-938. (2018) IF$_{2018}$: 1,624

III. Investigation of titanium-dioxide coatings on membrane filtration properties
STUDIA UNIVERSITATIS BABES-BOLYAI CHEMIA 62:(1) p. 249-259. (2017) IF$_{2017}$: 0,305

OTHER PUBLICATIONS

1. Membrane fouling control by means of TiO2 coating during model dairy wastewater filtration
Ildikó Kovács, Szabolcs Kertész, Gábor Veréb, Ibolya Zita Papp, Ákos Kukovecz, Cecilia Hodúr, Zsuzsanna László

2. Effects of shear rate on membrane filtration
Szabolcs Kertész, Péter Bor, Cecilia Hodúr, József Csanádi, Gábor Veréb, Ildikó Kovács, Gábor KeszthelyiSzabó, Zsuzsanna László

3. Ultrasound membrane hybrid processes for dairy wastewater treatment: pilotscale analysis
Szabolcs Kertész, Ildikó Kovács, Cecilia Hodúr, Gábor KeszthelyiSzabó, Gábor Veréb, Zsuzsanna László

4. Treatment of model oily produced water by combined preozonation– microfiltration process
Zsolt László Kiss, Ildikó Kovács, Gábor Veréb, Cecilia Hodúr, Zsuzsanna László
5. Surface analysis of a modern silver coin: SEM/EDS measurements
   Papp Z, Kovács I
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CONFERENCE PRESENTATIONS RELATED TO THE PRESENT

1. THESIS Dielectric Constant Measurements in Wastewater Treatment Processes
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   9th Eastern European Young Water Professionals Conference

2. Investigation of Surface and Filtration Properties of TiO2 Coated Ultrafiltration
   Polyacrylonitrile Membranes
   Kovács I, G Veréb, Sz Kertész, S Beszédes, C Hodúr, Zs László
   9th Eastern European Young Water Professionals Conference

3. Effects of preozonation in case of microfiltration of oil contaminated waters using
   polyethersulfone membrane at various filtration conditions
   Gábor Veréb, Mihály Zakar, Ildikó Kovács, Katalin Pappné Sziládi, Szabolcs Kertész, Cecília Hodúr, Zsuzsanna László
   Desalination for the Environment Clean Water and Energy

4. Purification of oil contaminated water by different advanced oxidation processes
   combined with membrane filtration
   Gábor Veréb, Renáta Bozóki, Mihály Zakar, Ildikó Kovács, Cecília Hodúr, Zsuzsanna László
   International Conference on Science and Technique Based on Applied and Fundamental Research (ICoSTAF’16)

5. Purification of model dairy wastewater by advanced oxidation processes combined with
   membrane filtration
   Ildikó Kovács, Sándor Beszédes, Szabolcs Kertész, Gábor Veréb, Cecilia Hodúr, Zsuzsanna László
   International Conference on Science and Technique Based on Applied and Fundamental Research (ICoSTAF’16)
6. **Effects of heterogeneous photocatalysis on membrane filtration properties using TiO\textsubscript{2} coated membranes**

   Ildikó Kovács, Szabolcs Kertész, Gábor Veréb, Cecília Hodúr, Zsuzsanna László

   Desalination for the Environment Clean Water and Energy


7. **TiO\textsubscript{2} coated membrane surface characterisation with contact angle measurements**

   Ildikó Kovács, Szabolcs Kertész, Gábor Veréb, Cecília Hodúr, Zsuzsanna László

   22nd International Symposium on Analytical and Environmental Problems. 438 p.


8. **Surface characteristics of TiO\textsubscript{2} coated ultrafiltration membranes**

   Ildikó Kovács, Gábor Veréb, Szabolcs Kertész, Cecília Hodúr, Zsuzsanna László

   III. Soós Ernő Tudományos Konferencia – Víz és szennyvízkezelés az iparban


9. **TiO\textsubscript{2} coated poliacrylonitrile membranes application to treat oily wastewater**

   I Kovács, G Veréb, S Beszédes, Sz Kertész, C Hodúr, Zs László

   PERMEA International Conference on Membrane Processes


10. **TiO\textsubscript{2} réteg vastagságának optimalizálása, és hatása a membránszűrés paramétereire**

    Kovács Ildikó, Dr Beszédes Sándor, Dr Kertész Szabolcs, Dr Veréb Gábor, Prof Dr Hodúr Cecília, Dr László Zsuzsanna

    XXII. Nemzetközi Végyszékonferencia


11. **Applying ozonization as pretreatment combined with membrane filtration for the purification of oil contaminated waters**

    Mihály Zakar, Gábor Veréb, Ildikó Kovács, Cecília Hodúr, Zsuzsanna László

    International Conference on Science and Technique Based on Applied and Fundamental Research (ICoSTAF'16)


12. **Ultrafiltration of dairy wastewater using vibration module**

    Péter Bor, Cecilia Hodúr, József Csanádi, Gábor Veréb, Ildikó Kovács, Gábor KeszthelyiSzabó, Zsuzsanna László, Szabolcs Kertész
13. **Effects of shear rate on membrane filtration**

Szabolcs Kertész, Péter Bor, Cecília Hodúr, József Csanádi, Gábor Veréb, Ildikó Kovács, Gábor KeszthelyiSzabó, Zsuzsanna László

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Róma, Olaszország, 2016. p. 57.

14. **Treatment of oil contaminated waters by (photo) fenton reaction and their effects on membrane filtration**

Veréb Gábor, Bozóki Renáta, Kovács Ildikó, Kertész Szabolcs, Hodúr Cecília, László Zsuzsanna

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15. **Purification of oil contaminated waters by coagulation/flocculation, membrane filtration and combined methods**

Veréb Gábor, Nagy Lilla, Kovács Ildikó, Kertész Szabolcs, Hodúr Cecília, László Zsuzsanna

XXII. Nemzetközi Vegyészkonferencia

16. **Removal of Acid red 1 by TiO2 nanoparticles coated polyethersulfone membrane under UV irradiation**

Ildikó Kovács, Szabolcs Kertész, Sándor Beszédes, Cecília Hodúr, Ibolya Zita Papp, Ákos Kukovecz, Zsuzsanna László

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17. **Combination of ultrasonication and ultrafiltration for dairy wastewater treatment**

Sz Kertész, Kovács I, Hodúr C, G KeszthelyiSzabó, Zs László

IV. International Conference of CIGR Hungarian National Committee and the Szent István University Faculty of Mechanical Engineering and the XXXVII R&D Conference of Hungarian Academy of Sciences Committee of Agricultural and Biosystems Engineering Gödöllő, Magyarország, 2015. p. 82. (ISBN:9789632695051)

18. **Effect of Fenton reaction pretreatment on membrane filtration parameters of dairy wastewater**

Kovács Ildikó, Kertész Szabolcs, Beszédes Sándor, Veréb Gábor, Hodúr Cecília, László Zsuzsanna

21st International Symposium on Analytical and Environmental Problems

20. Olajszennyezések ózonsos előkezeléssel kombinált membránszűrése desztillált vízben és modell termálvízben

Veréb Gábor, Filus Erik Sándor, Kovács Ildikó, Kertész Szabolcs, Beszédes Sándor, Hodúr Cecília, László Zsuzsanna


21. Olajszennyezett Vizek Tisztítása Ózonsos Előkezeléssel Kombinált Membránszűréssel

Veréb Gábor, Sulumán Ádám, Kovács Ildikó, Kertész Szabolcs, Beszédes Sándor, Hodúr Cecília, László Zsuzsanna

21st International Symposium on Analytical and Environmental Problems

22. Treatment of model oily produced water by combined preozonationmicrofiltration process

Zsolt László Kiss, Ildikó Kovács, Gábor Veréb, Cecília Hodúr, Zsuzsanna László

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23. Effect of advanced oxidation pretreatment on membrane filtration parameters of dairy waste water

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