Highly fouling resistant ultrafiltration membranes for water and wastewater treatments

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ABSTRACT

Control of fouling is a critical issue to increase the competitiveness of ultrafiltration (UF) membranes for drinking water and wastewater treatments. Highly fouling resistant UF membranes synthesized by photo-graft copolymerization of a water soluble monomer, poly(ethylene glycol) methacrylate (PEGMA), onto a polyethersulfone UF membrane have been evaluated with respect to the adsorptive as well as the ultrafiltration fouling. Protein, humic substance and polysaccharide solutions were used as the model for foulants occurring in the water sources for drinking water as well as in wastewater effluents. The results show that the modified membranes exhibited a much higher fouling resistance for all foulants than the unmodified membranes. Their combined high fouling resistance and high rejection suggests that the obtained modified membranes are very promising as a new generation of thin-layer composite low fouling UF membranes for drinking water and wastewater treatment applications.

Key words: fouling, natural organic matter, polysaccharide, protein, ultrafiltration, surface modification

INTRODUCTION

Nowadays, along with the increasing demand of ultrafiltration (UF) for various other applications, the use of UF for drinking water and wastewater treatments has become more and more interesting (Glucina et al. 2000; Atkinson 2006). UF not only can produce a high product (water) quality but can also reduce the cost for treatment. However, fouling – resulting in loss of performance of a membrane – is the major limitation. Consequently, it reduces the process economics and restricts a more widespread applicability of UF. Many studies have been devoted to overcome the problem of fouling. Basically, those studies include foulant identification/characterization, investigation of fouling mechanisms and minimizing or control of fouling. Control of fouling seems to be the most important aspect from the practical point of view. Thus, many methods have been proposed to control the fouling. Process conditions (e.g., adjusting operation conditions, pre-treatment and back-flushing) have been intensively developed in order to achieve better control of membrane fouling, but in most cases, the permeate fluxes are clearly determined by membrane itself. Therefore, it would be desirable having available high-performance membranes with a pronounced and stable resistance towards fouling by all foulants present in drinking water resources and wastewater effluents. Surface modification was then proposed as an important strategy for control of fouling (Ulbricht 2006). Charge-based modification to reduce the fouling during natural organic matter (NOM) removal was reported (Wei et al. 2006). However, such modification is strongly dependent on the pH and ionic content of the solution. Recently, we have started to modify a polyethersulfone (PES) membrane for UF of aquatic humic substances by a hydrophilization approach, which is not limited with respect to a general use of the obtained membranes (Susanto & Ulbricht 2006). However, to be practically useful, the resulting membrane performance must further be improved with respect to...
fouling resistance, permeate flux as well as rejection. In addition, it is important to be evaluated with other potential foulants occurring in drinking water sources (e.g., surface water and ground water) and wastewater effluents.

During application of UF for drinking water and wastewater treatments, two big issues have been identified from past studies: NOM is considered to be primary contributor to membrane fouling in drinking water treatment (e.g., Maartens et al. 1999; Hilal et al. 2004; Kweon & Lawler 2005), whereas soluble extracellular polymeric substances (EPS), which are mainly composed of polysaccharides, are considered as one of the important biofoulant components during wastewater treatment (Rosenberger et al. 2005; Ye et al. 2005). In addition, protein, an already very well known foulant, was also reported as one of the main components in the effluents of a membrane bioreactor (Jarusutthirak et al. 2002; Jin et al. 2004; Rosenberger et al. 2005). Asatekin et al. (2006) used proteins, polysaccharides and NOM as models for foulants in a membrane bioreactor.

In this work, novel thin-layer polymer hydrogel composite PES-based UF membranes are evaluated for water and wastewater treatment applications. Those membranes were synthesized by photo-grafting of a monomer for a hydrogel polymer, poly(ethylene glycol) methacrylate (PEGMA), onto commercial PES UF membranes (Susanto & Ulbricht 2007). The evaluation was done by investigation of membrane-solute interactions (adsorptive fouling) and membrane-solute-solute interactions (ultrafiltration). Myoglobin, humic acid and dextran solutions were used as the models for protein, NOM and polysaccharide components, respectively.

**METHODS**

**Materials**

Commercial PES UF membranes with a nominal cut-off of 100 kg/mol (PES-SG100) and 10 kg/mol (PES-SG10) obtained from Sartorius, Germany, were used. A PES-SG100 membrane was used as the base membrane for modification. Prior to use for experiments, the membranes were washed with ethanol by shaking at 100 rpm on a mechanical shaker for 1.5–2 hours and then equilibrated with water. Only membrane samples that had initial water permeability in the range +15% relative to the average values (5.71 + 0.85 L/m² h kPa) were used for modifications (cf. Susanto & Ulbricht (2005) for membrane selection). Poly(ethylene glycol) methacrylate (PEGMA 400, the number indicating PEG molar mass in g/mol) was purchased from Polysciences Inc., Warrington, USA. N,N’-methylenbisacrylamide (MBAA), myoglobin from horse skeletal muscle (95–100% purity) and humic acid (HA) were purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Potassium dihydrogen phosphate (KH2PO4) and disodium hydrogen phosphate dihydrate (Na2HPO4·2H2O) were purchased from Fluka Chemie AG, Buchs, Germany. Nitrogen gas purchased from Messer Griesheim GmbH, Krefeld, Germany, was ultrahigh purity. Water purified with a Milli-Q system from Millipore was used for all experiments.

**Membrane modification**

A UVA Print system (Hoenle AG, Gräfelfing, Germany) equipped with a high-pressure mercury lamp with wavelengths more than 300 nm, providing homogenous illumination of up to 100 cm² area with an intensity of 35 + 5 mW/cm² (measured with a UVA meter, Hoenle AG) was used. Circular PES membrane samples (PES-SG100) with a diameter of 25 mm were immersed into monomer solutions in a Petri dish. A second smaller glass Petri dish was used to cover the membranes and also as another deep-UV filter. Thereafter, the samples were subjected to UV irradiation for various time periods. Then, the membranes were taken out, immediately rinsed with water and then washed with excess of water to remove any unreacted monomer or physically adsorbed polymer. The washing was sequentially done at room temperature for 30 min, at 50 + 2°C for 2 hours and again at room temperature for 30 min.

**Static adsorption, ultrafiltration procedure and solute analyses**

All experiments were conducted with a dead-end stirred cell filtration system. The system consisted of a filtration cell (Amicon model 8010, Millipore) connected to a reservoir
(~450 or 1850 mL). It was pressurized by nitrogen. To avoid the effects of membrane compaction on the interpretation of modification and fouling data, each sample was firstly compacted by filtration of pure water at pressure of 450 kPa for at least 0.5 hours. Thereafter, the pressure was reduced to the desired pressure for water flux measurement. For static adsorption experiments, the water flux was initially measured and then a test solution (myoglobin (1 g/L; pH 7 in phosphate buffer) or humic acid (100 mg/L, pH 7.2, 1 mM Ca$^{2+}$, conductivity 1100 mS/cm) or dextran (T10, 10 g/L in water)) was added to the cell (before use, the myoglobin as well as HA solution was pre-filtered through a 0.45 µm microfilter from Sartorius, Germany, to remove undissolved material). Thereafter, the outer membrane surface was exposed for certain time (2 h, 18 h and 3 h, for myoglobin, HA and dextran solutions, respectively) without any flux at a stirring rate of 300 rpm. Then, the test solution was removed and the membrane surface was rinsed two times by filling the cell with pure water (5 mL) and shaking it for 30 seconds. Water fluxes before and after exposing were compared. The evaluation of membrane performance was expressed in term of adsorptive fouling resistance (cf. Equation (1)). An adsorptive fouling resistance of 1 means no adsorptive fouling occurred. Ultrafiltration of myoglobin (1 g/L, pH 7.2) and dextran (1 g/L in water) solutions were conducted at the same transmembrane pressure (100 kPa) for all membranes, whereas ultrafiltration of humic acid solution (50 mg/L, pH 7.2, 1 mM Ca$^{2+}$ added, conductivity 1100 µS/cm) was done at similar initial water flux (92 L/m²h). In these experiments, the balance was connected to the PC and weight of permeate was online recorded. Profiles of permeate flux and apparent solute rejection over time were investigated. Myoglobin and humic acid concentrations were determined by measuring UV absorbance at 230 and 255 nm, respectively. The dextran concentration was analyzed by gel permeation chromatography (HP-GPC) using RI detector (cf. Susanto & Ulbricht 2005).

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R_{ads} = \frac{J_{ads}}{J_o}
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where \( R_{ads} \) is adsorptive fouling resistance, \( J_o \) and \( J_{ads} \) are water fluxes before and after exposing to the test solutions, respectively.

**RESULTS AND DISCUSSION**

First of all, it is important to note that the two modified membranes, which were evaluated in detail, are PES-g-PEGMA (PES grafted from 40 g/L of PEGMA and by using 5 min UV irradiation) and PES-g-PEGMA/MBAA (PES grafted from a solution with 40 g/L of PEGMA and 0.4 g/L MBAA and by using 4 min irradiation). The modification created thin polymer hydrogel layers on the surface of base PES UF membrane. Therefore, the modified membranes are considered as composite membranes (cf. Susanto & Ulbricht 2007). Those modified membranes had similar rejection curve as compared with the unmodified PES membrane with nominal cut-off of 10 kg/mol (PES-SG10) indicating similar pore size as well membrane cut-off, but had much lower contact angle (cf. Susanto & Ulbricht 2007). In addition, the surface chemistry and wettability of those composite membranes did not change after incubating in sodium hypochlorite solution for a period of 8 days. In order to consider the effects of flux-rejection trade-off during the evaluation, the PES-SG10, which had similar cut-off, was used as the reference during performance analysis.

**Membrane-solute interactions (adsorptive fouling)**

The adsorptive fouling resistance of the composite membranes was investigated and compared with unmodified membrane. The results are presented in Figure 1. It is clearly observed that
the composite membranes showed higher adsorptive fouling resistance than unmodified membranes meaning that water flux after adsorptive fouling was higher. For example, the modification could increase the $R_{ads}$ caused by protein from 0.45 (for PES-SG10) to around 0.93 and the $R_{ads}$ caused by HA could be increased from 0.67 to $\sim$ 0.93. The more hydrophilic character of the surface of the composite membranes (as evidenced by their much lower contact angle) is the most probable reason for this phenomenon.

**Ultrafiltration of model of drinking water and wastewater foulants**

In this study, the membrane-solute-solute interactions are evaluated by ultrafiltration of the potential foulant solutions. The results are presented in term of either permeate flux/initial water flux ratio or permeate flux over the filtration time.

Interestingly, during evaluation using myoglobin both composite membranes had a much higher flux ratio than both unmodified membranes indicating that they are much less prone to fouling (Figure 2). The unmodified membranes had a permeate flux of only $\sim$ 20% (for nominal cut-off of 100 kg/mol) and $\sim$ 30% (for nominal cut-off of 10 kg/mol) relative to the initial water flux, whereas both composite membranes had more than 80%. As already evoked above, this much lower fouling of composite membranes was most probably due to the much more hydrophilic character. It should be noted that the charge-based interactions should not be involved (the pH of the protein solution was at the isoelectric point). A common phenomenon during fouling study was also observed in this work. Even though membranes with larger pore size leading to higher flux had smaller flux loss in the beginning of operation, after operating of more than 10 min a more severe fouling was observed (indicated by higher flux loss relative to the water flux) than for membranes with smaller pore size (cf. PES-SG10 vs. PES-SG100). The unmodified PES membrane with nominal cut-off of 10 kg/mol had the highest protein rejection ($\sim$ 70%) whereas the unmodified PES membrane with nominal cut-off of 100 kg/mol had the lowest rejection ($\sim$ 16%). The composite membranes had slightly lower protein rejection than the 10 kg/mol PES membrane, i.e. $\sim$ 58% and $\sim$ 61% for PES-g-PEGMA and PES-g-PEGMA/MBAA, respectively.

Second evaluation was done by using HA solution as the feed. Results in Figure 3 show that both composite membranes had higher permeate flux than both unmodified membranes. The PES-g-PEGMA and PES-g-PEGMA/MBAA showed permeate fluxes approximately 80% and 72% of their initial water flux, respectively, whereas the unmodified PES membranes showed permeate flux only approximately 51% for nominal cut-off of 10 kg/mol and
39% for nominal cut-off of 100 kg/mol. Similar apparent rejections were observed, i.e. ~95%, ~86%, ~92% and ~92% for PES-SG10, PES-SG100, PES-g-PEGMA and PES-g-PEGMA/MBAA, respectively. It was also observed that the water fluxes after external cleaning were significantly higher for composite membranes than for unmodified membranes. External cleaning by using pure water (with shaking) could recover the initial water fluxes to approximately 90% and 86% for PES-g-PEGMA and PES-g-PEGMA/MBAA, respectively. By contrast, the same cleaning procedure for unmodified membranes yielded ~65% and ~47% recovery for PES-SG10 and PES-SG100, respectively. Then, similar to the experiments using protein, even though UF was done at similar initial water flux (~92 L/m²h) in order to minimized effects of hydrodynamic conditions, the membrane with larger pore sizes showed more severe fouling (cf. PES-SG10 vs. PES-SG100). This observation agrees well with previously reported studies (Cho et al. 1999; Yuan & Zydney 2000).

Finally, the composite membranes were evaluated with the polysaccharide foulant. The use of dextran as model for polysaccharides is supported by our previous study, which showed that dextran could significantly foul the PES UF membranes (Susanto & Ulbricht 2005). A parallel study by Kweon & Lawler (2005) also supports this argument. As presented in Figure 4, both composite membranes show higher relative flux ratio (permeate flux/initial water flux) than the unmodified membrane with nominal cut-off of 10 kg/mol. The flux ratio was increased by 10% by modification. It is important to note that both composite membranes had similar rejection of dextran T-10 compared with unmodified PES membrane with nominal cut-off of 10 kg/mol (all data between 74 and 82%). Further, the relative water fluxes after external cleaning with water were higher for both composite membranes than for the unmodified membrane (i.e., 83%, 96% and 94% for PES-SG10, PES-g-PEGMA and PES-g-PEGMA, respectively).

Overall, in all evaluations with different types of potential foulant solutions, both composite membranes showed significantly higher fouling resistance and water flux recovery than both unmodified membranes. This higher fouling-resistance could be attributed to the hydrogel character of grafted polymer layer, which increased the hydrophilicity of the membrane surface. Further, the differences between composite membranes without and with chemical cross-linking in the hydrogel layer (slightly higher rejection for the cross-linked at same flux – except for humic acid – and same resistance to adsorptive fouling) suggest that the internal structure of the grafted thin polymer layer could be used to “fine-tune” the membrane performance. However, a contribution of membrane pore structure to membrane-solute interactions was also clearly observed as evidenced by the fact that no composite membrane, which is absolutely inert during adsorption experiments and by the difference in fouling behaviour for membranes with different pore structure (cf. PES-SG10 vs. PES-SG100). Finally, their combined high fouling resistance and high rejection (similar to unmodified PES membrane with 10 kg/mol) suggests that the obtained modified membranes are very promising as a new generation of thin-layer composite low fouling UF membranes for drinking water and wastewater treatment applications.

**CONCLUSIONS**

The fouling resistance of novel thin-layer polymer hydrogel composite PES-based UF membranes, synthesized by photo-grafting of PEGMA onto commercial PES UF membranes, has been evaluated for water and wastewater treatment applications. The results suggest that the resulting composite membranes had much higher adsorptive as well as ultrafiltration fouling resistance than unmodified
membranes, when examined using protein, NOM and polysaccharide solutions. Much higher recovery of water flux after cleaning was another interesting result. Considering their higher fouling resistance and water flux recovery and their similar solute rejection compared to commercial unmodified PES membranes, these composite membranes should be considered as low fouling UF membranes with great potential for water and wastewater treatment applications.

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REFERENCES


