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Ultrafiltration of polysaccharide–protein mixtures: Elucidation of fouling mechanisms and fouling control by membrane surface modification

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ABSTRACT

This work describes the fouling behavior of polysaccharide–protein mixture solutions by investigation of adsorptive and ultrafiltration fouling. Alginate, dextran, myoglobin and bovine serum albumin were used as model foulants. Three commercial poly(ether sulfone) (PES) ultrafiltration (UF) membranes with nominal cut-off of 10, 30 and 100 kg/mol and a PES-based thin layer hydrogel composite (TLHC) membrane, synthesized by photo-initiated graft copolymerization of poly(ethylene glycol) methacrylate (PEGMA) and having a cut-off of 10 kg/mol were used. The effects of pH, foulant concentration, ionic content and proportion of protein to polysaccharide in the solution on fouling were investigated. The results showed that significant water flux reductions and changes in membrane surface property were observed after static adsorption for PES membranes for all feed solution conditions. This water flux reduction decreased with increasing the pH of the solution. Addition of monovalent ions could either increase or decrease the water flux reduction. Synergistic effects between polysaccharide and protein with respect to forming a mixed fouling layer with stronger reduction of flux than for the individual solutes under the same conditions have also been verified for PES UF membranes. UF experiments using a stirred dead-end UF suggested that both reversible and irreversible fouling have contributed to the overall fouling. The antifouling efficiency of the TLHC membrane with respect to both adsorptive and ultrafiltration fouling has been demonstrated for the strong foulant alginate as well as for polysaccharide–protein mixtures.

1. Introduction

Because membrane processes are increasingly used for separations of mixtures with high complexity, the focus of fouling studies in ultrafiltration (UF) has also been shifted from using well-studied foulants such as proteins to more complicated and less-defined substances such as humic acids or polysaccharides. In the last years, polysaccharides have been used as models for effluent organic matter to be treated with reverse osmosis [1,2], but they are also relevant for fouling in wine microfiltration (MF) [3]. Interactions of ultrafiltration membranes with polysaccharides have been investigated during processing of bioproduct or food streams [4–6], and also as model for marine biofouling [7]. However, the strongest motivation is certainly based on the success of membrane separations and membrane bioreactors (MBR) for water and wastewater treatment [8]. MBR has proven as a more efficient technique for wastewater treatment compared to other conventional (biological) processes. MBR delivers a better product quality of treated water, meeting the need for saving water, and contributing to less volume-demand for a treatment plant. However, beside the obvious advantages of MBR, further improvement of its performance is now challenging researchers. The complex characteristics of the feed and the high solid content including biomass promote to exacerbate the problem of membrane fouling [9,10]. Many attempts have been devoted to overcome these problems and can be generally classified into: (1) foulant identification and characterization, (2) investigation of fouling mechanisms, and (3) minimizing or control of fouling.

With respect to foulant identification, it has been reported that exctracellular polymeric substances (EPS) are the key components affecting fouling in MBR [6,9,11,12]. Polysaccharide, protein and natural organic matter have been identified as the main constituents of EPS [6,11–16]. Wang et al. [17] also reported that the organic matter in the supernatant and the EPS of the bulk sludge and the cake sludge consist mainly of polysaccharides, proteins and humic acid.

Numerous fouling mechanism studies have been performed using various foulant models to describe fouling in MBR. Beside protein, an already very well known foulant, polysaccharides have

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nowadays gained a great deal of attention to be used as model for an important foulant in MBR [18,19]. Alginate, which is an unbranched binary copolymer, consisting of (1 → 4) linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues with varying sequences [20], could be used as representative model for the polysaccharides of EPS [21]. The group of Chen has then intensively used alginate for describing fouling behavior of MBR system [22–24]. They observed that alginate clearly fouled both UF and MF membranes, and cake models appeared to fit the entire range of UF membranes, while the consecutive standard pore blocking and cake models were more applicable to MF membranes [22]. Furthermore, they reported that the properties of the fouling layer formed (reversible vs. irreversible) were influenced by filtration time and hydrodynamic conditions. Long-term subcritical flux operation resulted in irreversible fouling layer, while short-term dead-end constant pressure or flux-stepping experiments yielded reversible fouling layer [23]. This fouling of alginate on MF membranes has also been visualized [24]. In sum, alginate has been frequently used as a model of EPS for describing fouling phenomena in UF as well as MF. Several fouling mechanisms have been proposed; however, considerable disagreement can be found in previous reported literature. For example, it was reported that the extent of fouling corresponded to the concentration of EPS [25]. Nevertheless, such phenomenon was not observed in a later study [26]. Differences in feed characteristics, membrane properties and experimental conditions may be the reasons.

Backwashing or backflushing has been used for controlling alginate fouling [27,28]. This technique could reduce the amount of accumulated particles on and in the membrane to some extent and hence increased the resulting flux. However, decrease of flux with increasing filtration time was still observed. Control of fouling by adjusting process parameters such as permeate flux has also been proposed [28].

Surface modification of the membranes is gaining increasing importance for minimizing membrane fouling; an overview on the various chemical strategies applied to polymer membranes can be found in a recent review [29]. Very recently, new thin layer hydrogel composite (TLHC) UF membranes, based on commercial polyethersulfone (PES) membranes, have been prepared via photo-initiated graft copolymerization of monomers containing side groups with "kosmotropic" properties along with controlled chemical crosslinking during grafting. The antifouling properties of those new membranes have been evaluated using a limited set of adsorption and UF experiments with the model foulants myoglobin and humic acid [30]. TLHC membranes with adjusted surface chemistry had also shown promising performance in UF of NOM-containing water [31].

Overall, previous studies indicated that the polysaccharide alginate significantly fouled state-of-the-art membranes and consequently resulted in severe flux decline. To relate these findings to application processes, several other factors such as variable composition of feed to the MBR as well as different membrane characteristics including pore size and surface chemistry, must further be investigated. In addition, different alginate sources may also have different characteristics with respect to membrane fouling. The objectives of this research are to study the fouling behavior of alginate on PES-based unmodified and TLHC UF membranes with the same cut-off, with focus on alginate mixtures with protein. In addition, the effect of pH and ionic content on the fouling behavior is also presented. In this work, fouling studies for both single polysaccharide and polysaccharide–protein mixtures were performed by investigation of membrane–solute interactions (adsorptive fouling) and membrane–solute–solute interactions (ultrafiltration). Although, recent studies concerning the effect of ionic environment on alginate fouling can be found [1,27,28], differences in membrane characteristics as well as the experimental approaches used in this study will complement those previous publications.

2. Materials and methods

2.1. Materials

Three commercial PES UF membranes donated by Sartorius, Germany, were used. The membrane nominal cut-offs obtained from manufacturer are 10 kg/mol (SG 10), 30 kg/mol (SG 30), and 100 kg/mol (SG 100); this data has been experimentally confirmed by sieving analyses with PEG/PEO mixtures [30]. Prior to use for experiments, the membranes were washed by soaking overnight in water to remove impurities left over from the manufacturing process or additives used for stabilization. In addition, a TLHC membrane with a cut-off of 10 kg/mol, prepared by photo-graft copolymerization of poly(ethylene glycol) methacrylate (PEGMA) on the PES membrane SG 100 was also used (cf. membrane modification). Alginic acid sodium salt from brown algae was purchased from Fluka BioChemical. Dextran T-10 (the number indicates molar mass in kg/mol) was purchased from Pharmacia Fine Chemical Uppsala, Sweden. Myoglobin from horse skeletal muscle (95–100% purity) and bovine serum albumin (BSA) were purchased from Sigma–Aldrich Chemie GmbH, Steinheim, Germany and ICN Biomedicals, Inc. (California, US), respectively. PEGMA was purchased from Polysciences Inc. Warrington. Potassium dihydrogen phosphate (KH_2PO_4), disodium hydrogen phosphate dihydrate ($Na_2HPO_4{\cdot}2H_2O$) and calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$) were purchased from Fluka Chemie AG (Buchs, Germany). Potassium chloride (KCl), potassium hydroxide (KOH), and hydrochloric acid (HCl), all of p.a. quality, were purchased from Bernd Kraft GmbH, Duisburg, Germany. Sulfuric acid was from J.T. Baker, Holland. Water purified with a Milli-Q system from Millipore was used for all experiments.

2.2. Alginate and protein analyses

Fig. 1 shows the molar mass distribution of alginic acid, obtained from gel permeation chromatography (conducted in 0.01 M sodium azide solution using a column PSS Suprema, PSS, Mainz, Germany, coupled in series with a column MZ Hema 40, MZ Analytic, Mainz, Germany). That GPC was also used to analyze concentration of dex-

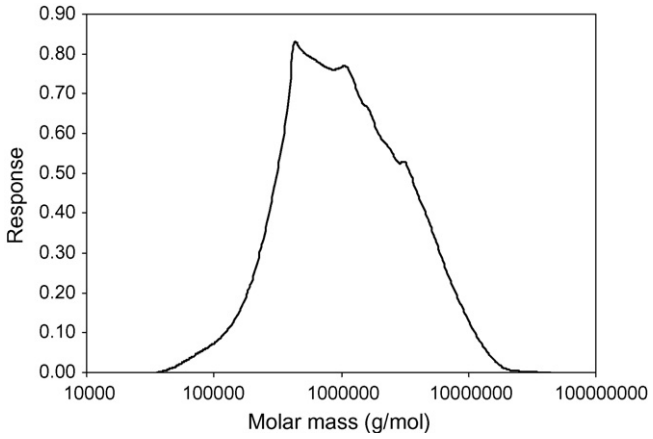

Fig. 1. Molar mass distribution of alginate used in this study, obtained from gel permeation chromatography: number average of molecular weight, M_n = 600 kg/mol, weight average of molecular weight, M_w = 1900 kg/mol, polydispersity index PDI = M_w/M_n = 3.2.

tran. Analysis of particle size by dynamic light scattering was done using a ZetaSizer (Malvern). Alginate concentration was measured by colorimetric test developed by Dubois using phenol-sulfuric acid method (cf. [32]). The sample was firstly reacted with phenol in acid medium forming an orange-yellow color and its absorbance at 480 nm was measured via UV-spectroscopy (CARY-50 Probe, Varian, Germany). The concentration of myoglobin was determined from its UV absorbance at 230 nm measured using the UV–vis spectrophotometer CARY-50 Probe (Varian, Germany), while BSA concentration was analyzed using the BCA protein assay (from Pierce [33]).

2.3. Membrane modification

The method for the preparation of TLHC membranes followed earlier reported work [30]. Briefly, a UVA Print system (Hoenle AG, Gräfelfing, Germany) equipped with a high-pressure mercury lamp, emitting wavelengths >300 nm and providing homogenous illumination of up to 100 cm^2 area with an intensity of 35 ± 5 mW/cm^2, was used. Circular PES membrane samples (with diameter of either 25 or 44 mm) were immersed into 40 g/L of PEGMA solution in a Petri dish. A second smaller glass Petri dish was used to cover the membranes and also as another deep-UV filter. The samples were then subjected to UV irradiation for 5 min. Thereafter, 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 h and again at room temperature for 30 min. It had been found that TLHC membrane obtained from 40 g/L of PEGMA and 5 min irradiation yields the best performance for protein and humic acid ultrafiltration [30].

2.4. Water flux measurement, adsorptive fouling and ultrafiltration procedures

The experiments were carried out by using a dead-end stirred cell filtration system (Amicon cell models 8010 and 8050, Millipore, for adsorptive fouling and UF experiments, respectively). Pure water flux (J_0) was measured first for each membrane sample. For static adsorption experiments, a solution of either polysaccharide, protein or polysaccharide–protein mixture was added to the cell and the outer membrane surface was exposed for 3 h without any flux at a stirring rate of 300 rpm (our preliminary adsorptive fouling studies had shown that 3 h were sufficient to achieve saturation of the surface adsorption capacity for polysaccharides and proteins used in this study). Afterwards, the 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 s. Pure water flux (J_a) was measured afterwards. The UF of feed solutions was conducted at a constant pressure (100 kPa) for ~2 h. Amicon cell model 8050 connected to a feed reservoir (~450 mL) was used. The concentration factor varied (1.2–1.5), depending on the feed solution and membrane used. The flux profile over time was monitored online gravimetrically. Thereafter, the solution was removed, and the membrane surface was externally rinsed two times by filling the cell with pure water (25 mL) and shaking it for 30 s. Pure water flux was measured afterwards. Relative flux reduction (Eq. (1)) was calculated from the water fluxes at the same pressure before and after fouling experiments.

$$\mathrm{RFR} = \frac{J_0 - J_a}{J_0} \times 100\% \quad (1)$$

2.5. Contact angle (CA)

CA was measured using an optical contact angle measurement system (OCA 15 Plus; Dataphysics GmbH, Filderstadt, Germany). The static captive bubble method, which is preferred for porous membrane surfaces, was chosen [34]. Membranes were inverted (active layer to the bottom) in pure water at a temperature of 21 ± 1 °C. An air bubble (5–10 μL) was injected from a syringe with a stainless steel needle onto the sample surface water. At least seven measurements of bubbles at different locations were averaged to obtain CA for one membrane sample.

2.6. Zeta potential (ZP)

The membrane surface charge before and after adsorptive fouling were investigated by outer surface streaming potential measurement. Experiments were carried out in a flat-sheet tangential flow module described in previous study in detail [34]. Before measurement, the membrane was equilibrated by soaking in 0.001 mol/L KCl solution. The streaming potentials of membranes were measured using 0.001 mol/L KCl solution, in the range of pH 3–10 and at a temperature of 25 ± 1 °C. Fouling was performed by slow circulation of foulant solution in the cell for 3 h. The foulant solution was then replaced step-wise by water and 0.001 mol/L KCl solution, respectively. The ZP, ζ, was calculated using the Helmholtz–Smoluchowski equation.

3. Results and discussion

3.1. Membrane–solute interactions (adsorptive fouling)

Membrane–solute interactions were investigated by exposing the outer membrane surface to either single-solute feed solution or binary solute feed solution. The relative water flux reduction (RFR) was used to identify the membrane–solute interactions. Because fouling of PES UF membranes with dextran and protein as single solutes has already been well explained in previous literature [35], only alginate was used for detailed investigations using single solute feed solution (Section 3.1.1). Selected data for single protein solutions were measured as the reference for the binary-solute feed experiments (Section 3.1.2). In most of the experiments, a high concentration of solute (10 g/L) was used due to the fact that the concentration of solute on the membrane surface will during UF gradually increase as consequence of solute rejection by the membrane.

3.1.1. Single-solute feed solution (alginate)

3.1.1.1. Effect of membrane characteristics and pH value of solution on adsorptive fouling. As presented in Fig. 2, it can be clearly seen that the effect of adsorptive fouling of alginate on water flux was influenced by the membrane nominal cut-off. In all pH solutions, RFR increased with increasing cut-off, indicating that membranes with larger pores were more susceptible to adsorptive fouling than those with smaller ones. This observation can be explained as follows: Considering the molar mass distribution of alginate (cf. Fig. 1), and the apparent diameter in aqueous solutions (pH 5–8) measured with dynamic light scattering (45–60 nm), it is reasonable that for membrane SG 10 adsorption occurred only on the outer membrane surface, whereas for membrane SG 30 a small fraction of alginate could penetrate into the membrane pores (it should be remembered that there is a distribution of pore sizes). The possibility of alginate to access membrane pores became even higher for membrane SG 100, and, consequently, both external and internal fouling could occur for SG 100 and SG 30. Such phenomena are in agreement with previously reported results [24,34,35]. The alginate used

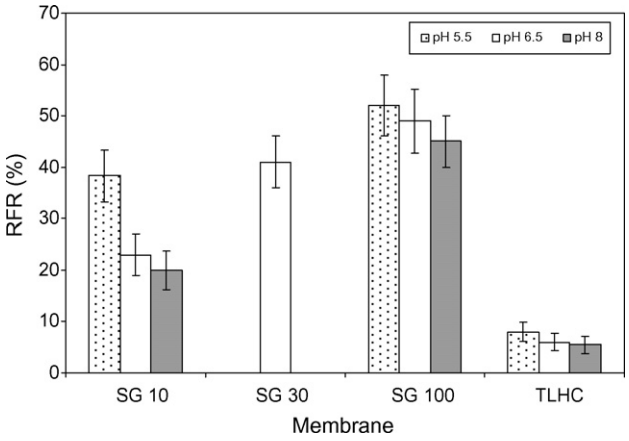

Fig. 2. Effects of membrane characteristics and pH value of solution on relative flux reduction during adsorptive fouling (alginate concentration 10 g/L, adsorption time 3 h). For study of pH effect, the alginate was dissolved in phosphate buffer (0.05 M); thereby the total ionic content could be kept almost constant. The error bars represent standard deviation.

in this study had a much larger size compared to alginate used in other studies [27,28], but it was similar in size to the EPS used by Frank and Belfort [7]. However, the hydrophobic character of the PES surface, which leads to a negative free energy for adsorption of any, even a very hydrophilic solute [36], is the main reason for the adsorption of alginate on the membrane surface. That is similar to the fouling of PES UF membranes by dextrans [35], but the effects observed for alginate were much larger. This may be related to the higher molar mass of alginate, with the effects of solution chemistry onto the size of the molecule and the tendency to form aggregates will be even more important.

As the pH of the solution was increased, the resulting RFR values decreased, indicating that alginate adsorption was more significant at lower pH. By decreasing the pH of the solution, carboxyl groups of the alginate will be protonated. This has consequences for the structure of the solute and its interactions with the surface: The electrostatic repulsion between alginate and the membrane surface will be reduced at lower pH, and protonation will also result in a smaller size of the alginate molecule due to lower intramolecular electrostatic repulsion [37]. As a result, accessing the membrane pores by alginate molecules would become easier leading to higher adsorbed amounts. This finding supports previous results reported by Lee and Elimelech [1], who observed higher flux decline in acidic than in alkaline alginate solution even though the acidic pH in the present study was higher. The pH of the alginate solution could not be decreased to values lower than 5 because then precipitation took place. The alginate used in the present study probably contained a more block-like structure (polyM and polyG), because for alginate containing a larger content of an alternating structure (polyMG), precipitation will occur at lower pH value [37] (cf. also Section 3.3).

Interesting results were obtained in adsorption experiments with the composite membrane. The effects of adsorptive fouling on RFR for TLHC membrane were significantly smaller compared to all unmodified PES membranes for all pH values. It is important to mention that this TLHC membrane had a cut-off and pore size distribution similar to the PES membrane SG 10 (cf. [30] for more details on characteristics of TLHC membranes). This observation indicates that the interaction between alginate and the surface-modified membrane was significantly less compared to the unmodified PES. The grafted poly(PEGMA) layer on the membrane surface resulted in a hydrophilic character, leading to a strong binding of water, and thus hindering the adsorption of solutes including alginate on the membrane surface. The mechanism of this antifouling behavior has been discussed in detail in our previous paper [30].

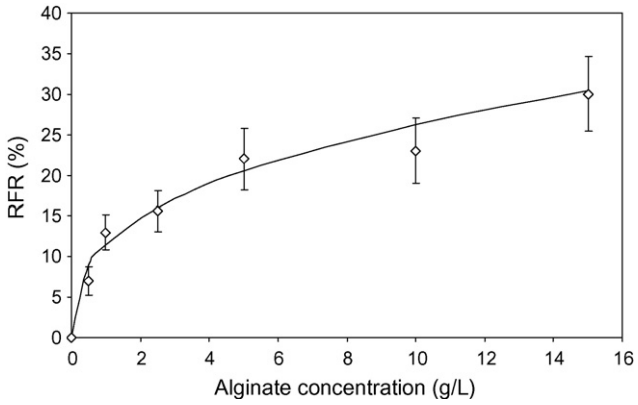

Fig. 3. Influence of alginate concentration on relative flux reduction after static adsorption (membrane SG 10, pH 6.5, adsorption time 3 h). The error bars represent standard deviation.

3.1.1.2. Effect of alginate concentration on adsorptive fouling. The extent of fouling during UF of alginate was reported to be very much influenced by its concentration [38]. In this work, the effect of concentration on adsorptive fouling was further investigated. The study was performed by varying the alginate concentration within the range 0–15 g/L using PES membrane SG 10.

As shown in Fig. 3, with increasing concentration of alginate, the RFR would first rise steeply reaching a quasi-plateau condition beyond the concentration of 5 g/L, but RFR increased slightly with further increase of concentration. This indicates that monolayer adsorption has the dominating effect, but effects of solute–solute interactions in contact with the membrane surface could also be observed (note that in this case, diffusion of alginate through the membrane pores seemed impossible because the alginate molar mass was much larger than the membrane cut-off).

3.1.1.3. Effect of ionic content on adsorptive fouling of alginate. Previous studies had indicated that the fouling during ultrafiltration of alginate solution was largely influenced by ionic concentration as well as ion type [1,28]. In this study, ion effects on adsorptive fouling were studied. The experiments were conducted by varying both ionic concentration and ion type.

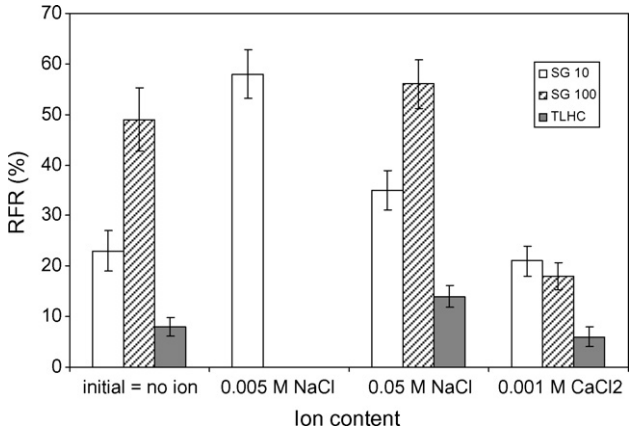

Fig. 4. Relative flux reduction of three different membranes after static adsorption (3 h) by using alginate (10 g/L) in aqueous solutions with different ionic environments. The error bars represent standard deviation.

Fig. 4 shows the effects of ionic environment on RFR with different membranes. It was observed that the addition of small amount of sodium chloride (NaCl) to the alginate solution increased the RFR. However, if the concentration of NaCl was further increased to 0.05 M, the RFR decreased but was still higher than that without added ions. An increase of ion concentration in alginate solution reduced the molecular size of alginate due to shielding of electrostatic forces [37]. For the same reason, the shielding of negative net charge of the alginate molecule, lead to reduced electrostatic repulsion with the membrane. This behavior is analogous data by Frank and Belfort [7], who found that the hydrodynamic radius of the anionic EPS was 30 nm at KCl concentration less than 0.001 M and down to 15 nm at KCl concentrations beyond 0.001 M. With the alginate used in this study, it has been observed that with the addition of NaCl (containing a non-gelling cation) to yield a concentration beyond 0.05 M, "salting out" started as indicated by the formation of visible gel particles. Such particles may have formed in a fouling layer on the membrane surface, but the pore blocking may have been less efficient than with alginate molecules leading to decreasing RFR.

At the first glance it was surprising, the addition of calcium chloride ($CaCl_2$) to the alginate solution did not increase the RFR compared to that of ion-free solution. No effect on RFR was observed, even though the addition of calcium ions can cause chelating of carboxylic groups of alginate, resulting in aggregation of alginate molecules [39]. Such behavior has been noticed by visible gel formation in this experiment (this is also the reason why $CaCl_2$ concentration could not be increased beyond 0.001 M). The larger size of alginate aggregates probably reduced the effects of adsorption on flux reduction. Interestingly, this is in close agreement with the result obtained with addition of NaCl at higher concentration (cf. above). In addition, aggregation might yield a more loose structure of the fouling layer on the membrane surface, and this can effectively be removed by the external cleaning conducted after the adsorption experiments.

Similar results as already shown and discussed above (cf. Fig. 2), namely the effect of membrane pore size and surface modification could also be observed in these experiments (cf. Fig. 4). The TLHC membrane clearly showed much smaller RFR than both unmodified PES membranes.

3.1.2. Mixed solute feed solution (polysaccharide–protein mixtures)

Feed streams containing various different dissolved components are common in liquid filtration using membranes. In these experiments, two binary feed solutions, i.e., dextran–myoglobin (DEX–MYO) and alginate–bovine serum albumin (ALG–BSA), were used. Adsorptive fouling was conducted by varying proportions of protein to polysaccharide in the solution (at pH ~7). The polysaccharide concentration was maintained at 10 g/L. The relative flux reduction after adsorptive fouling with different membranes is compared in Fig. 5.

The results for unmodified PES membrane (SG 10) clearly showed that the addition of protein to the polysaccharide solution changed the extent of fouling. A more severe flux reduction was observed with increasing protein content in the solution. One could certainly claim that this increase in RFR may be caused by increasing total dissolved solid amount in the solution. However, comparing with the results presented earlier on the effect of solute concentration on RFR (cf. Fig. 3), it becomes clear that this marked increase in RFR should be due to polysaccharide–protein interactions. As protein content was increased, the trend toward such "synergistic" fouling effects became more evident. For the ALG–BSA system, the observed RFR values were 34% and 53%, using added 0.1 and 1 g/L BSA, respectively. These values were higher

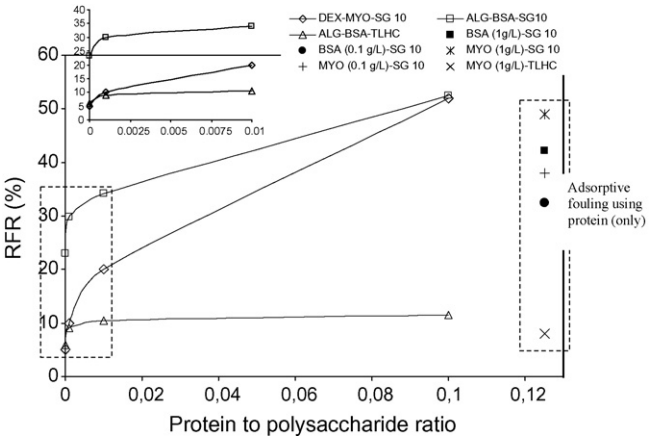

Fig. 5. Influence of protein/polysaccharide ratio on relative flux reduction for unmodified and THLC membranes with a cut-off of 10 kg/mol. Polysaccharide concentration was fixed at 10 g/L and adsorption time was 3 h. RFR data for after static adsorption using protein (only) solution (either 1 or 0.1 g/L) are included for comparison.

than the RFR for the solution containing only BSA with the same concentration, i.e., 32% and 42% for 0.1 and 1 g/L BSA, respectively. For the DEX–MYO system, such synergistic effect was only observed at added 1 g/L MYO (at 0.1 g/L, RFR for MYO alone was still higher than RFR for DEX–MYO mixture). These results strongly support a finding in a previous study by Ang and Elimelech [2], who had observed increased fouling during reverse osmosis when two organic foulants (e.g., protein and polysaccharide) were present in the solution as compared to single-solute feeds. One possible explanation would be that both biopolymers can interpenetrate each other forming a network structure. Intermolecular binding can be due to ionic bonds (for ALG and BSA) or multiple hydrogen bonds (for both systems). In fact, it had been reported that alginate has the ability to adsorb proteins [40]. Such network structure would result in a layer with higher hydraulic resistance than one from the single substances and, consequently, decreasing water flux. With increasing protein concentration, the degree of cross-linking would increase, leading to higher RFR. Finally, the effects in mixtures with dextran were significantly smaller than with alginate, and this can be well explained because this polysaccharide has no acidic or basic (potentially charged) functional groups, and it is therefore well known to behave like a (bio)inert hydrophilic substance.

Interestingly, the RFR for the surface-modified membrane did not show any significant effect of protein addition on adsorptive fouling (all RFR data were in the range of 10%). The protein solution by itself also yielded very low RFR, i.e. less than 10% (cf. Ref. [30] in more detail). All these results imply that the first interaction between membrane and foulant was very important. In this case, because of the hydrophilic and neutral character of the grafted polyPEGMA layer such first interactions were only weak (for alginate and protein) or even negligible (for dextran). Consequently, even though both different biopolymers could interact with each other, they would not be deposited on the membrane surface, or they would easily be removed with external washing. This is a very promising result since it shows a strong antifouling potential (at desired membrane molecular weight cut-off) by using the membrane modification evaluated in this work.

3.2. Effect of adsorptive fouling on membrane characteristics

The effect of adsorptive fouling on membrane characteristics was studied by using solutions containing alginate, BSA, and a mixture of both. Changes in contact angle (CA) and zeta potential (ZP)

Table 1
Static contact angles, measured with the captive bubble technique (air in water), of PES-based UF membranes before and after adsorptive fouling (data are presented as contact angle ± standard deviation, in °)[a]

Treatment	Membrane SG 10	Membrane SG 100	TLHC membrane
Without	60.5 ± 2.6	47.9 ± 4.2	40.2 ± 4.3
Fouled by alginate (10 g/L)	48.9 ± 3.2	38.2 ± 3.6	39.2 ± 3.9
Fouled by BSA (1 g/L)	54.6 ± 3.8	53.1 ± 4.1	42.1 ± 3.6
Fouled by alginate and BSA mixture (10 ± 1 g/L)	51.6 ± 2.7	50.3 ± 3.9	41.6 ± 4.1

[a] Contact angle of fresh membranes was measured first. The membranes were then soaked in the foulant solution for 3 h, rinsed, and then the contact angle was again measured.

after adsorptive fouling, given in Table 1 and Fig. 6, respectively, were used to investigate these effects.

The differences in CA for the two PES membranes are due to the differences in pore size [35,36], and the TLHC membrane war clearly more hydrophilic (cf. Table 1). It can be clearly seen in Fig. 6 that the surface of a fresh PES membrane had a negative charge over the entire pH range studied and the absolute values decreased towards acidic pH values (the reasons for this phenomenon had been discussed in our previous study [34]). In contrast, the effective surface charge of the TLHC membrane was much smaller than that of PES, i.e. close to neutral.

In general, exposing the unmodified PES membranes to the foulant solutions changed the CA and the ZP indicating that a change in surface properties has occurred. While the CA of PES did not change significantly (<2°) after exposure to the water under identical conditions, the reduction of CA was larger after exposure to the alginate solution than after exposure to the BSA solution. First, the apparent hydrophilization of the PES surface strongly indicates that solute adsorption has occurred. The differences for the two solutes are probably due to the more hydrophilic character of alginate than BSA. Exposing the PES membrane to all different foulant solutions changed the surface charge of the membrane significantly, also indicating adsorption of solute on the membrane surface has taken place. It should be noted that the ZP data represent the effects of (macro)ion adsorption from solution as well as of dissociation of acidic or basic groups of (macro)ions on the surface. The protein BSA will change its net charge from positive to negate in the range of the isoelectric point (~4.7). At neutral pH value, the deprotonation of carboxylic groups of sodium alginate

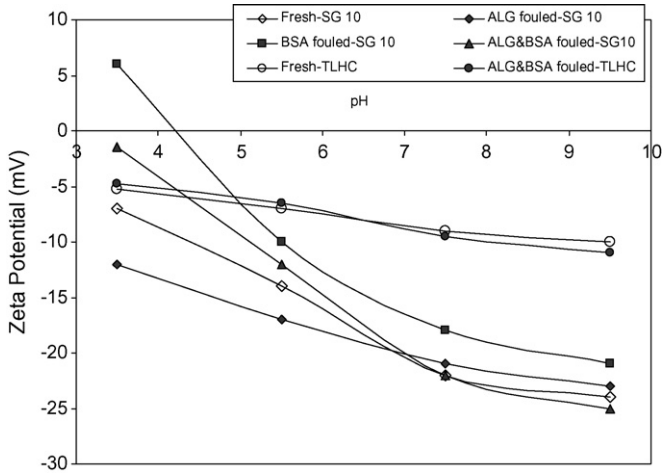

Fig. 6. Zeta potentials as a function of pH (at 0.001 mol/L KCl) for membrane SG 10 and TLHC membranes, before and after exposing for 3 h to protein (1 g/L), polysaccharide (10 g/L), or polysaccharide–protein (10/1 g/L) mixture solution.

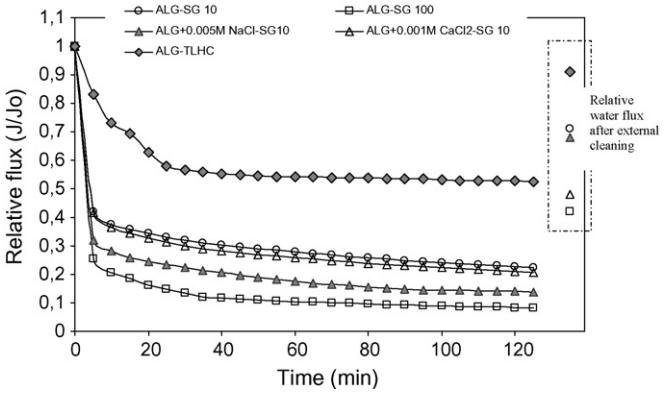

Fig. 7. Normalized flux during ultrafiltration of alginate solutions using PES-based UF membranes at a trans-membrane pressure of 100 kPa (initial alginate concentration 1 g/L in water, NaCl and $CaCl_2$ were added in two experiments as indicated). Water fluxes after external cleaning with water, relative to initial water flux are also included.

will be complete, resulting in a high negative surface charge. The ZP data for PES membranes fouled with BSA and alginate alone in comparison with the data for the fresh PES confirm that the two different biopolymers were indeed adsorbed to the membrane surface. Interestingly, both CA and ZP data for the PES membranes after exposure to alginate and BSA mixture solutions were between the respective values of the PES membranes fouled by alginate and BSA alone. This result implies that both alginate and BSA existed in the adsorbed layer on the membrane surface.

Clearly, CA and ZP data for the surface-modified PES membrane did not change after exposure to all solutions, indicating that no significant adsorption occurred on the membrane surface. These results do further prove the previous interpretations with respect to the antifouling character of the TLHC membrane.

3.3. Membrane–solute–solute interactions studied in dead-end stirred ultrafiltration

To investigate membrane–solute–solute interactions, dead-end stirred ultrafiltration was performed with constant trans-membrane pressure (100 kPa). The results are presented in terms of permeate flux relative to initial water flux for UF of alginate (Fig. 7), alginate–BSA mixture (Fig. 8), and dextran–myoglobin mixture (Fig. 9) solutions. Rejection measurements showed that the

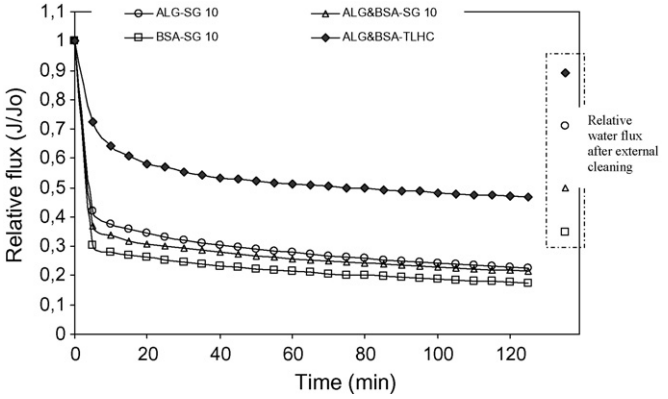

Fig. 8. Normalized flux during ultrafiltration of alginate–BSA mixture solution (single-solute solutions for comparison) using PES-based UF membranes at a trans-membrane pressure of 100 kPa (alginate concentration 1 g/L, BSA concentration 0.1 g/L, pH ~7). Water fluxes after external cleaning with water, relative to initial water flux are also included.

unmodified PES (SG 10) and the TLHC membrane had rejection of more than 99% and 74% for alginate and dextran T-10, respectively, whereas the PES membrane SG 100 had still a rejection for alginate of 94%. This implies that the alginate size was much larger compared to the membrane barrier pore size, even for the membrane with nominal cut-off 100 kg/mol.

Overall, it can be clearly seen that the fluxes through all UF membranes dropped rapidly in the beginning of filtration for all solutions. Lower UF permeate fluxes compared to the water fluxes seemed to indicate that the concentration polarization at the membrane surface was significant during UF. However, the fluxes after longer times were much different, and relatively high values for the PES membrane SG 10 and DEX solution as well as the TLHC membrane and DEX–MYO solution (around 0.75; cf. Fig. 9) in comparison the other values which were as lower than 0.2 (for PES SG 10 and ALG with 0.001 M NaCl; cf. Fig. 7) indicate that fouling was significant in many experiments. Water flux measurements after external cleaning with water indicated that reversible fouling significantly contributed to the overall fouling on the one hand and that irreversible fouling has also taken place in several cases on the other hand. External cleaning could increase water flux after ultrafiltration in all cases. Because the membrane pore size was too small compared to alginate size (cf. rejection data), pore narrowing as well as pore blocking should not occur for SG 10 and only slightly for SG 100. Apparently, solute adsorption on the membrane surface as confirmed in adsorptive fouling experiments has taken place. However, higher water flux after external cleaning (with water) in ultrafiltration experiments compared to water fluxed measured after adsorptive fouling indicates that there was addition of hydraulic resistance caused by an additional solute layer during ultrafiltration. Therefore, fast cake or gel formation on the membrane surface seemed to be the dominant mechanism under UF conditions.

It was observed that addition of calcium chloride did not significantly change alginate fouling compared to no addition of ions (ALG-SG 10; cf. Fig. 7). In contrast, addition of sodium chloride tended to increase fouling. Similar phenomenon was also observed by van de Ven et al. [28]. The possible reason would be that even though addition of calcium and sodium ions could increase alginate size, yielding aggregation of macromolecules, the differences in compactness of deposited layers resulted in different hydraulic resistances (with addition of higher concentration of calcium and sodium, the gelation phenomenon was clearly visible, cf. Section 3.1.1). These results are in good agreement with previous adsorptive fouling data (cf. Section 3.1.1). More details of the effect of ionic content including concentration and type in dead-end ultrafiltration experiments with PES membranes have been well documented and explained [28]. Nevertheless, a different phenomenon had also been reported by another group, i.e., the addition of calcium caused more severe fouling due to foulant–foulant interaction [1]. This finding could be attributed to differences in the properties of alginate used. An alginate can consist of three different blocked, i.e., homopolymeric blocks of mannuronate (MM) and guluronate (GG) and blocks with an alternating sequence [37,41,42]. The differences in block content especially GG block content and molar mass result in different behavior in responding to ionic surrounding, swelling, shrinking and mechanical strength [42].

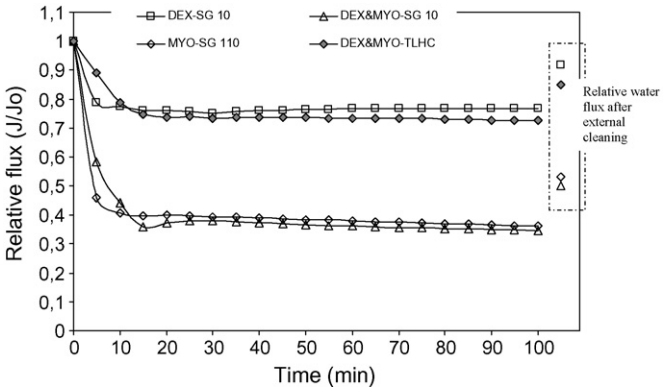

Fig. 9. Normalized flux during ultrafiltration of dextran–myoglobin mixture solution (single-solute solutions for comparison) using PES-based UF membranes at a trans-membrane pressure of 100 kPa (dextran concentration 1 g/L, MYO concentration 0.1 g/L, pH ~7). Water fluxes after external cleaning with water, relative to initial water flux are also included.

For UF with unmodified PES membranes, the relative fluxes for the single protein solutions were lower (in case of alginate, cf. Fig. 8) or almost identical (in case of dextran, cf. Fig. 9) to the permeate fluxes for the binary solutions containing a ten-fold higher polysaccharide concentration. Hence, surprisingly, the "synergistic" effect between the two different biopolymers observed for adsorptive fouling (cf. Section 3.1.2) was clearly not found during ultrafiltration. The possible reason is that the high molar mass of alginate (which is completely rejected by the 10 kg/mol cut-off membranes, cf. above) might hinder penetration of protein into the membrane pores and, as a result, internal fouling can not occur (note that during ultrafiltration, the driving force for penetration of foulant into membrane pores is much higher than in diffusion-driven adsorption experiments). This explanation is supported by the higher rejection for BSA in a feed containing alginate and BSA than for a feed containing BSA only (BSA rejections were 98% and 91%, for ALG–BSA and BSA, respectively; the latter data proves that internal fouling of the PES membrane by BSA is indeed possible). These results also suggest that the RFR tests by static adsorption are useful for the investigation of UF fouling by feed solutions containing single solutes, but that such tests can be less useful for more complex multi-components systems. Nevertheless, with respect to a more qualitative evaluation of the overall fouling potential of the solutions this test has still been valid for both single- and binary-solute systems.

The outcome was different for the surface-modified membranes: Similar to the data on adsorptive fouling, the TLHC membrane showed much higher fouling resistance compared to the unmodified PES membrane as can be seen by its much higher permeate flux for all three feed solutions (ALG, cf. Fig. 7; ALG–BSA, cf. Fig. 8; and DEX–MYO, cf. Fig. 9). Although a decrease in flux over filtration time was observed, the external washing using water could recover about 90% of the initial water flux. A tentative explanation for the differences in permeate fluxes after 2 h (DEX–MYO $\gg$ ALG > ALG–BSA) can also be given using the arguments developed above (cf. Section 3.1.2): The hydraulic resistance of the (cake) fouling layer ontop of the poly(PEGMA) layer of the composite membrane will be lower with the uncharged "bioinert" dextran than with the charged alginate having a strong tendency toward aggregation, and the network formation between ALG and BSA would further increase the hydraulic resistance of the cake layer. The weak adhesion between cake layer and poly(PEGMA) hydrogel was the basis for the efficient removal without chemical cleaning. Furthermore, combination of backwashing techniques and surface modification of the membrane may result in even more effective methods for fouling control.

4. Conclusions

The importance of solute adsorption on the membrane surface for fouling of ultrafiltration membranes has been clearly demon-

strated for feeds and membranes which have great relevance for performance of wastewater treatment and MBR systems. Relative water flux reduction after static adsorption, driven by solute diffusion to the membrane surface, can be used to investigate the mechanism of fouling, i.e., the roles of solution chemistry (here demonstrated with the effects of pH and salt onto alginate fouling), interactions between different foulants (here in mixtures of polysaccharides and proteins), as well as the surface chemistry of the membrane. Surface analytical methods such as contact angle and zeta potential measurements can provide valuable additional evidence for the extent of solute adsorption on the membrane surface. By combining RFR, CA and ZP data, synergistic effects between polysaccharide and protein with respect to forming a mixed fouling layer with stronger reduction of flux than for the individual solutes under the same conditions have been verified for PES UF membranes. As in previous studies, correlations between the RFR values and the flux during UF have been found for single-solute solutions (here new data have been provided for alginate). However, for more complex solutions of foulant mixtures (polysaccharide and protein), the fouling under UF conditions may be dominated by different boundary layer conditions caused by the convective flux to and through the membrane. Under those conditions, effects of adsorptive fouling can even be larger than fouling under ultrafiltration conditions. Finally, the antifouling efficiency of a new PES-based composite membrane with a thin grafted PEGylated hydrogel layer, with the same cut-off as the reference PES membrane, has been demonstrated for the strong foulant alginate as well as for polysaccharide–protein mixtures: No solute adsorption could be detected with CA and ZP, and RFR values were less than 10%, UF fluxes were much higher than with the unmodified PES membrane, and about 90% of the initial water flux could be restored after UF just by external washing with water. Such TLHC membranes will be further evaluated for UF applications with complex feeds.

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