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Fouling Reduction by Graft-Modification with Hydrophilic Polymers

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Abstract: Flat sheet polypropylene microfiltration membranes were successfully graft-modified with acrylic acid using the macroinitiator method. The surface modification induced a change in the course of fouling. Unmodified membranes showed the strong form of critical flux during filtration of protein solution, while for the surface modified membranes the weak form of critical flux was determined. Although the critical flux could be shifted towards higher values (from ca. $20\,\mathrm{l/m^2h}$ to > 40 $\mathrm{l/h^2m}$) by the surface modification, the permeability decreased by a factor of 6.

Keywords: Microfiltration, surface modification, fouling, critical flux

INTRODUCTION

Despite great efforts that have been made in the past, fouling is still a serious problem in membrane filtration. Besides other mechanisms, fouling is caused by attractive interactions such as hydrophobic, Van der Waals, or electrostatic interactions between the feed components and the membrane surface. Surface modification of membranes is a well-established technique to alter the surface properties of membranes and the interactions between feed components and the membrane surface and therefore to reduce membrane fouling.

Often, irradiation based methods like UV-irradiation, γ-ray irradiation, electron beam irradiation or plasma techniques are used to graft hydrophilic polymers onto the membrane surface. However, these techniques bear the risk of damaging the membrane material irreversibly (1–6).

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On the other hand, several cleaning methods are used to maintain the membrane performance including backflushing, air sparging, or chemical cleaning. The concept of critical flux was introduced by Howell and coworkers in the mid-nineties (7, 8) and has been subject of a recently published review (9). This concept describes a permeate flux below which no deposition of colloids and therefore no irreversible fouling occurs. In an early paper, Field et al. defined two types of critical flux: the strong form, where the transmembrane pressure (TMP) deviates from a certain value on from the (linear) pure water line and the weak form, where already at the starting point fouling occurs and the TMP-flux relationship is still linear but below the pure water line (Fig. 1) (7). At the critical flux $J_{crit.}$ the TMP-flux relationship becomes non-linear.

In general the movement of a feed component is determined by several forces directing towards the membrane surface or away from it as expressed in equation (1).

$$N = JC - D\frac{dC}{dy} + p(\zeta) + q(\tau) \tag{1}$$

where D is the Brownian diffusion coefficient, p(ζ) represents the force induced by electrostatic interactions and q(τ) the effect of local hydrodynamics on mass transport, respectively.

The effect of surface charge on colloidal fouling and the "critical flux" has been exploited by several authors (10–12). In previous papers we showed that fouling of polypropylene membranes with BSA could be reduced substantially by the surface modification with polyelectrolytes and polyelectrolyte multilayers (4, 13). However the effect of surface modification on the critical flux has not been investigated so far. It is supposed that repulsive electrostatic

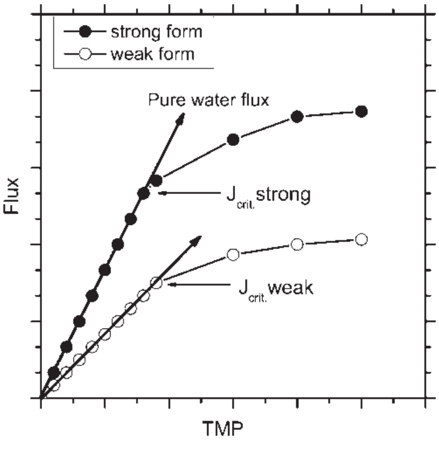

Figure 1. Forms of critical flux as originally defined by Field et al. (7).

interactions between feed components and the membrane surface might have a positive effect on the critical flux.

Here we report on the modification of polypropylene microfiltration membranes by covalent bonding of a so-called macroinitiator and simultaneously grafting of charged monomers onto the membrane surface. The macroinitiator consists of an olefin-maleic anhydride copolymer containing ca. 10 mol% perester groups. The perester groups decompose upon thermal treatment forming radicals, which can react with the substrate thus leading to a covalent bonding. Furthermore, the radical sites were successfully used to initiate the grafting of hydrophilic and/or charged polymers onto the membrane surface (14). The filtration and fouling behaviour was tested by pure water filtration and filtration of protein solutions (Bovine Serum Albumin, BSA). Certain focus was set on the influence of the surface modification on the critical flux. All results are discussed in comparison to the non-modified base membranes.

EXPERIMENTAL

Celgard 2400 polypropylene flatsheet membranes with a pore size of 40 x 120 nm^2 (specification of the manufacturer, verification by SEM (15, 16)) were used throughout this study. The porosity was 37%.

The protein retention R was calculated from the protein concentrations in the feed (c_{feed}) and permeate (c_{perm}) using equation (2).

$$R = \frac{c_{feed} - c_{perm}}{c_{feed}} \cdot 100(\%) \tag{2}$$

The protein concentrations were determined from UV/vis spectroscopic measurements at a wavelength of 288 nm (absorption maximum in the UV spectrum of aqueous BSA solution). The obtained absorption intensities were converted into concentrations by means of a calibration curve, plotted from data from protein solution of known concentrations.

The filtration experiments were carried out on a LSta05 SPS from Sima-Tec (Germany) eqipped with a cross-flow filtration cell having an active area of 80 cm^2. The flow-chart is given in Fig. 2. With this test unit we are able to run filtration experiments in the constant flux mode and in the constant pressure mode.

Surface modified membranes were prepared as follows:

In a first step the membranes samples were dipped for 30 sec in a solution of 1 wt.-% of the macroinitiator in 2-butanone. The coated membranes were placed in a reactor containing a degassed aqueous solution of acrylic acid (c = 3 wt.-%) preheated to 70–90°C. The reaction time was set to 2–4 hours for the preparation of membranes with different graft yields. The thus graft-modified membranes were washed intensively with deionized water and dried for 24 h at 40°C in vacuum. The graft yield (GY) was determined

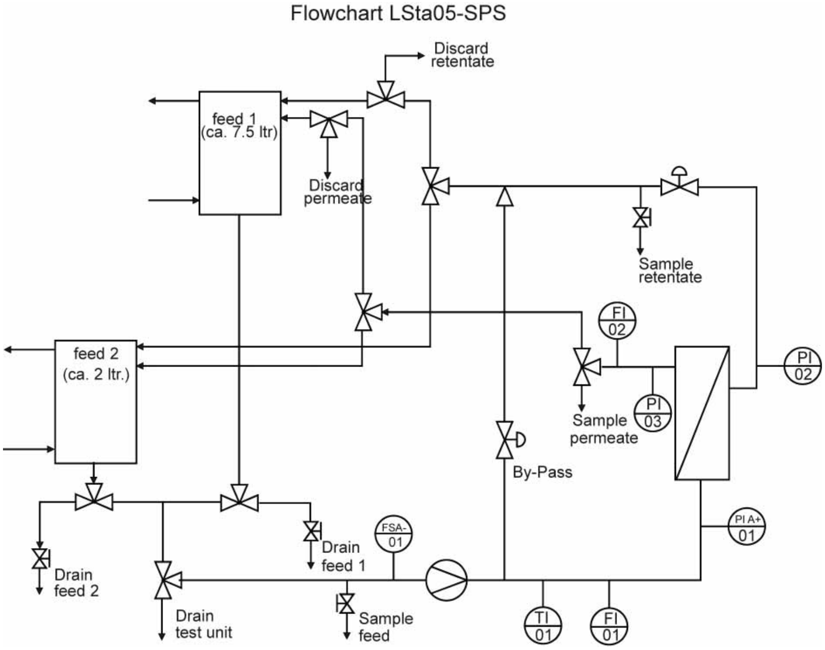

Figure 2. Flowchart of the filtration set-up used in this study.

by the weight difference method (Eq. 3).

$$GY = \frac{W_{\text{mod}} - W_{\text{unmod}}}{W_{\text{unmod}}} \cdot 100\% \tag{3}$$

Filtration experiments with modified as well as unmodified membranes were conducted with pure water, aqueous solution of $NaHCO_3$ (c = 0.1 g/l, pH 7.9) and an aqueous bovine serum albumine (BSA) solution (c = 1 g/l) with 0.1 g/l added $NaHCO_3$ (pH 7.9). The feed flow velocity was set to 10 l/h. A spacer placed at the feed side of the membrane provided a turbulent flow.

RESULTS AND DISCUSSION

The polypropylene membranes were grafted with acrylic acid using the macroinitiator method described in an earlier paper (14). Depending on the reaction conditions (time, temperature) graft yields ranging from ca. 1 up to 4 wt.-% were achieved. The successful grafting was verified by ATR-FTIR spectroscopy (Fig. 3) indicated by the new absorption band at 1714 cm^{-1} in the IR spectrum originating from the carbonyl valence vibration of the grafted poly(acrylic acid).

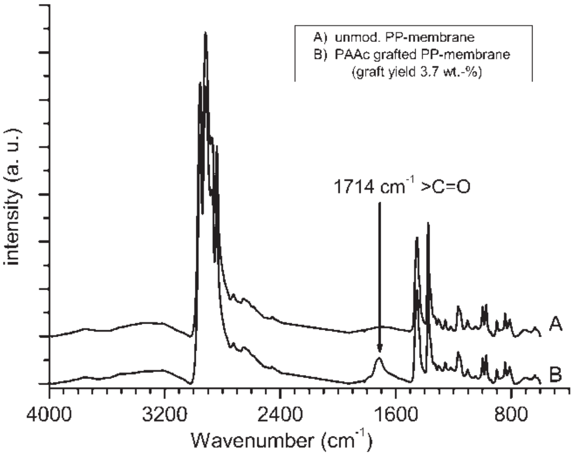

Figure 3. ATR-FTIR spectra of A) unmodified polypropylene membrane and B) a polypropylene membrane graft-modified with 3.7 wt.-% polyacrylic acid (PAAc).

Figure 4 shows the result of a typical flux-stepping experiment for an unmodified PP-membrane conducted with pure water. The TMP remained unchanged after each return from high flux to low flux, indicating that no fouling and structural change of the membrane occurred during the filtration steps at higher fluxes. Plotting the mean fluxes as a function of the transmembrane pressure (TMP) (Fig. 5) a linear flux-pressure relationship was found for pure water and aqueous sodium bicarbonate solution. The permeabilities were 96 l/m^2h·bar and 80 $l/m^2h \cdot$ bar, respectively.

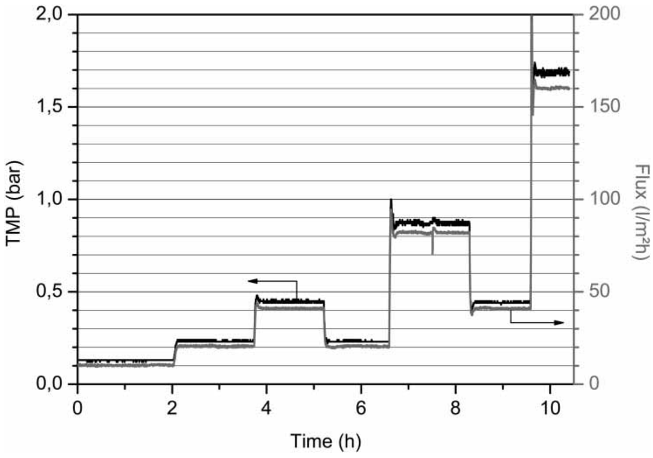

Figure 4. Flux TMP-profiles (black TMP; gray Flux) for the filtration of pure water with an unmodified PP-membrane.

The situation changed when filtrating an aqueous BSA solution at pH 7.9 (Figs. 5 and 6) through the unmodified membrane. At low fluxes/TMPs (up to 20 l/m^{2}h and 0.3 bar) the permeability was approximately the same as for the sodium bicarbonate solution. With increasing flux/TMP the data points deviate from those of the pure solvent filtration experiment. For a given flux a higher TMP was needed than in the solvent filtration experiment, indicating the start of the fouling process. From these results, which are visualized in Fig. 5, a strong form of fouling during the filtration of a BSA solution through an unmodified PP-membrane could be deduced. It should be noted, that the protein retention was in the range from 93% to 98% in the experiments conducted at fluxes up to 40 l/m^{2}h. Only at a flux of 80 l/m^{2}h, the retention was lowered to 60%. A rejection of sodium bicarbonate was not observed.

The filtration properties of graft-modified membranes (PAAc grafted) showed a strong response on pH change as outlined in Fig. 7. The TMP drops immediately (at constant flux) on the change from high pH (7.9) to low pH (3.0), while changing back to high pH it takes a much longer time until the TMP has stabilized. At high pH the carboxylic acid groups of the grafted polyacrylic acid are completely transferred into their salt form thus carrying one negative charge per repeating unit. This leads to an extended chain conformation due to repulsive forces between the equally charged sites. On the other hand at low pH, the carboxylic acid groups are mainly protonated, thus carrying no charges, resulting in a more compact conformation

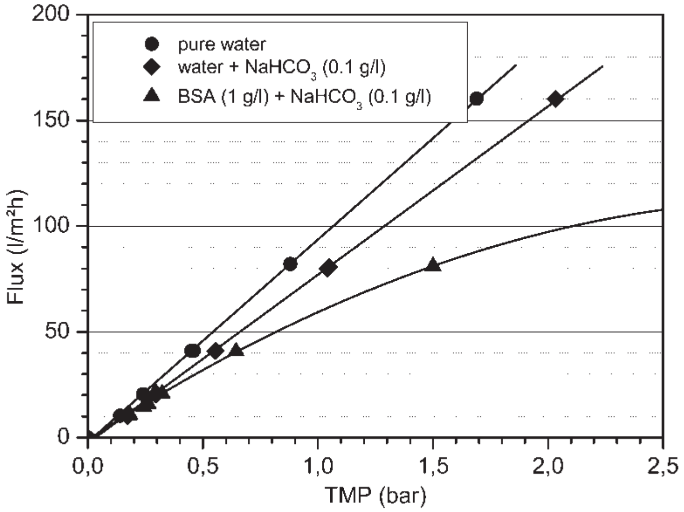

Figure 5. Flux-pressure relationship for pure water, sodium bicarbonate solution (pH 7.9) and a BSA solution at pH 7.9 derived from flux-stepping experiments for an unmodified PP-membrane.

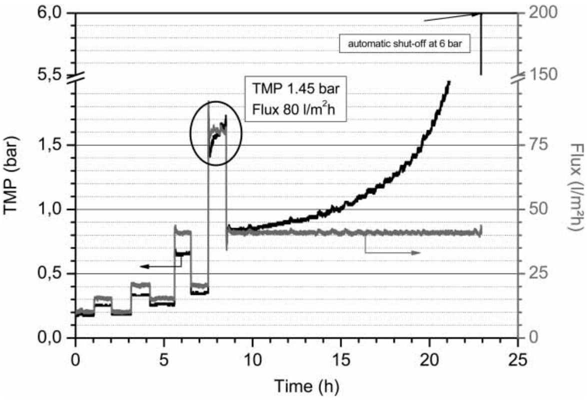

Figure 6. Flux TMP-profiles (black TMP; gray Flux) for the filtration of a BSA solution at pH 7.9 with an unmodified PP-membrane.

of the grafted chains. In the charged form (at high pH) the grafted poly acrylic acid chains are covering a larger area of the supporting membrane thus leading to a higher pore blockage and a lower permeate flux than in the case of the low pH.

The results of the flux-stepping experiments with the graft-modified membranes at pH 7.9 is shown in Fig. 8. Contrary to the findings with the unmodified membrane, for the graft-modified membrane a linear relationship between flux and TMP was found for the filtration of a BSA solution. The permeabilities were 13.5 $l/m^2h \cdot bar$ for pure solvent and 12.9 $l/m^2h \cdot bar$ for the

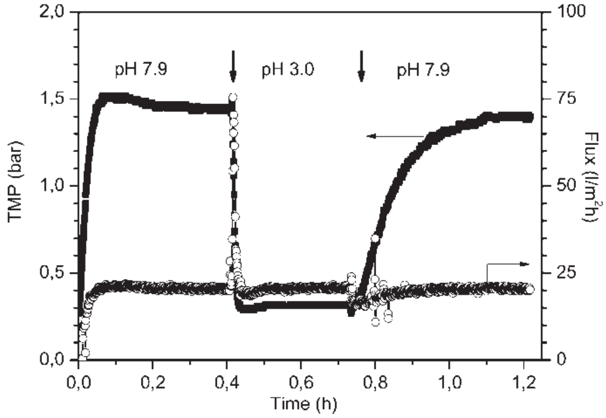

Figure 7. Effect of pH of the feed solution on TMP (solid symbols) needed for a constant flux of 20 l/m^2h (open symbols) through a graft-modified (2.5 wt.-% PAAc) PP-membrane.

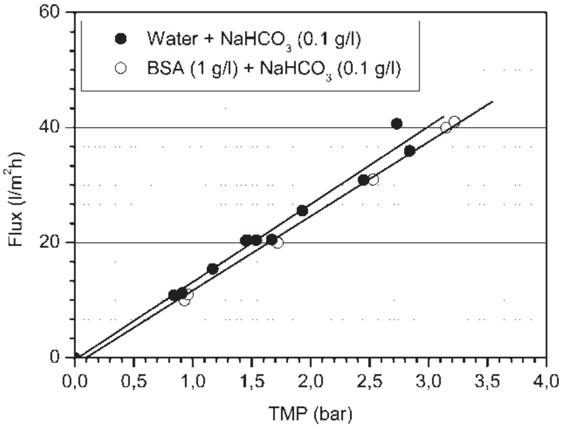

Figure 8. Flux-pressure relationship for a graft-modified membrane (2.5 wt.-% PAAc) using a sodium bicarbonate solution (pH 7.9) and a BSA solution at pH 7.9 as feed derived from flux-stepping experiments.

BSA solution, respectively. The slope of the BSA experiment deviates slightly from that of the pure solvent filtration experiment, which might be an indication for the weak form of critical flux. However, the critical flux defined as the point were the data deviate from linearity was not reached in these experiments, which covered a flux range up to 40 $\mathrm{l/m^2h}$. Although the fouling behavior could be positively influenced by the surface modification, this technique suffers from lower permeability of the such modified membranes. Compared to the unmodified membranes a six-fold higher TMP was necessary to maintain the same permeate flux through the graft modified membranes.

CONCLUSION

In this study PP microfiltration membranes were successfully modified by grafting of poly(acrylic acid) by applying the macroinitiator method. The results lead to the conclusion that on surface modification the course of fouling changed. For the unmodified membrane the strong form of critical flux could be deduced, while the results from the filtration experiments with modified membranes lead to the conclusion that the weak form of critical flux occurs. Furthermore, the determined critical flux for the modified membrane was ca. twice that of the unmodified membrane. This might be a result from both, the introduction of charges onto the membrane surface leading to repulsive electrostatic forces between the feed components and the membrane surface and the reduction of pore size as a result of the graft layer formation as observed earlier by SEM (16).

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