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Concentration Polarization and Fouling during Ultrafiltration of Colloidal Suspensions and Hydrophobic Solutes

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ABSTRACT

Flux reductions experienced during ultrafiltration are due either to concentration polarization or fouling. It is usually difficult to distinguish between these two phenomena, but by using a turbulence-promoting module it is possible to determine the reversibility of a flux reduction, and thus distinguish between concentration polarization and fouling. By using a turbulence-promoting module, it is also possible to distinguish between different cases of fouling. In this paper, fouling caused by the deposition of material at the surface of the membrane is illustrated by results from tests with a silica sol, and fouling due to interactions in the membrane matrix is illustrated by results from ultrafiltration of a low-molecular organic solute.

Key Words. Ultrafiltration; Concentration polarization; Fouling; Silica sol; Fatty acid; Soap

INTRODUCTION

Membrane processes are used in a wide range of separation applications, and the number of such applications is growing. As membrane processes are very complex, it is often difficult to predict the membrane performance in advance. It is not unusual that the capacity of a membrane plant is lower than originally expected. It even happens that the membrane performance is so drastically (and irreversibly) reduced that the membranes have to be replaced.

The flux reductions experienced during ultrafiltration are due to two phenomena: concentration polarization and fouling. Concentration polarization arises as a concentration gradient is established when solute molecules are retained at the surface of the membrane. The causes of fouling vary depending on the nature of the solutes. Two major causes of fouling can, however, be identified. The first is characteristic of colloidal suspensions. In this case the fouling is caused by the deposition of solute molecules at the surface of the membrane where a cake is formed. The second type of fouling appears when low-molecular hydrophobic solutes are treated. In this case the fouling is caused by deposition of solute molecules in the membrane matrix, either by adsorption on the pore walls or swelling of the membrane material.

It is usually very difficult to distinguish between the two flux reducing phenomena, concentration polarization and fouling. However, a flux reduction that is reversible is, as a rule, due to concentration polarization, whereas an irreversible flux reduction is due to fouling. By using a turbulence-promoting module it is possible to determine the reversibility of the flux, and thus distinguish between concentration polarization and fouling (1–3). It is also possible, by using a turbulence-promoting module, to distinguish between the two typical cases of fouling mentioned above.

In this paper it is demonstrated how the flux behavior differs depending on the cause of the flux reduction. Fouling caused by the formation of a cake layer at the membrane surface is exemplified by results from ultrafiltration of a silica sol. Fouling due to solute–membrane interactions in the membrane matrix is illustrated by results from ultrafiltration of a solution containing a fatty acid.

EXPERIMENTAL PROCEDURE

Membranes and Membrane Equipment

Two membranes were included in the investigation: a hydrophobic membrane made of polyethersulfone (PES25) with a nominal cutoff of 25,000, and a hydrophilic membrane made of regenerated cellulose (C30) with a nominal cutoff of 30,000. Both membranes were manufactured by Hoechst Werk Kalle.

The experiments were performed in a module manufactured by ABB Flootek, Sweden, equipped with one membrane above and one below a rotor blade. The diameter of the membrane cell was 257 mm and the distance between the two membranes was 18 mm. The thickness of the rotor blade was 5 mm and the length and width were 247 mm and 60 mm, respectively. The membrane area of each membrane was 0.05 m^2.

Chemicals

A colloidal suspension (silica sol) and two low-molecular hydrophobic solutes, octanoic acid and sodium octanoate, were included in the investigation. The negatively charged colloidal hydrophilic silica, Ludox HS-40 from Du Pont, had an average particle diameter of 12 nm. The density of silica is 2450 kg/m^3 and the molecular weight of a silica particle is 1,300,000 Dalton. The octanoic acid was of synthesis grade and was obtained from Merck. The molecular weight of octanoic acid (caprylic acid, $C_8H_{16}O_2$) is 144. Its solubility in water at 20°C is 4.7 mM (4). The molecular weight of the surfactant sodium octanoate is 166 and the critical micelle concentration at 25°C is 350 mM (5). The sodium octanoate was obtained from Merck. The concentration of different chemicals is given as weight percent in the figures in this paper.

Performance of Experiments

The operating pressure used was 0.1 MPa, apart from one test where the influence of the operating pressure was studied. The temperature was maintained at 25°C and the circulation flow was 0.3 m^3/h. The volume of solution was 15 L. The retentate, as well as the permeate, was recirculated back to the feed tank during all tests. The rotor speed was varied between 0 and 1000 rpm.

All chemicals were first dissolved in deionized water and then gradually added to the feed tank. During the addition of chemicals the water was recirculated in the system at maximum rotary speed, 1000 rpm. After each addition of chemicals the solution was recirculated through the module for 10 minutes in order to ensure stable conditions before measurement of the flux. After changing the rotary speed, 2 minutes were allowed to elapse before commencing measurements of the flux.

The membranes were cleaned with a 0.5 wt% solution of the alkaline cleaning agent Ultrasil 10 from Henkel before and after each series of experiments. First, the equipment was thoroughly rinsed with deionized water. Then the cleaning solution was recirculated at 60°C for 15 minutes and 0.1 MPa. The system was then drained and thoroughly rinsed with new deionized water.

Analysis

The concentration of octanoic acid in retentate and permeate was determined as total organic carbon (TOC) using a Shimadzu TOC5000. However, analysis could only be performed when the feed concentration was below the saturation concentration due to the phase separation between water and octanoic acid at higher concentrations. However, no phase separation in the feed tank was noticed until the highest concentration, i.e., at 0.2% (14 mM). The feed solution was slightly white at this concentration, indicating that an emulsion had formed.

RESULTS

Crozes et al. (6) used backwashing to distinguish between flux reductions due to membrane surface phenomena and those due to adsorption in the membrane. Another, simple way to distinguish between flux reduction phenomena which occur at the surface of the membrane and in the membrane matrix is to vary the rotary speed in the module described above. If the flux decreases as the rotary speed is decreased, then it is accumulation of material in the boundary layer at the membrane which is causing the flux reduction. If the flux is unaffected by the rotary speed, then it is solute–membrane interactions in the interior of the membrane which are responsible for the flux reduction.

Concentration Polarization

The flux is influenced by concentration polarization when the flux decreases as the rotary speed is decreased, and then increases again when the rotary speed is increased. An example of this is shown in Fig. 1.

Deposition of Solutes at the Surface of the Membrane

When process streams in commercial plants are treated, it is often impossible to increase the flux again after a decrease in the rotary speed (2). If the flux does not increase when the rotary speed is increased, as shown in Fig. 2, the flux reduction is due to fouling at the surface of the membrane.

The type of fouling shown in Fig. 2 appears when the interactions between the solute molecules in the boundary layer are so strong that it is impossible to remove the particles in the boundary layer by increasing the shear rate in the module. Colloidal suspensions induce different types of fouling. The most common are associated with changes in pH and ionic strength (3, 7–9), but operating pressure, concentration, and temperature also influence the flux reduction (10, 11). In the experiment shown in Fig.

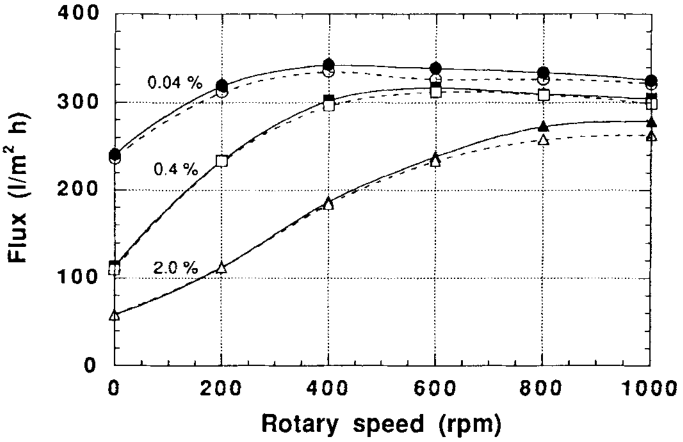

FIG. 1 The influence of rotary speed on the flux of a polyethersulfone membrane during ultrafiltration of a silica sol. The solid symbols denote decreasing rotary speed and the open symbols denote increasing rotary speed. The pH of the silica sol was 9.5, and the concentration of sodium chloride was less than 1 mM.

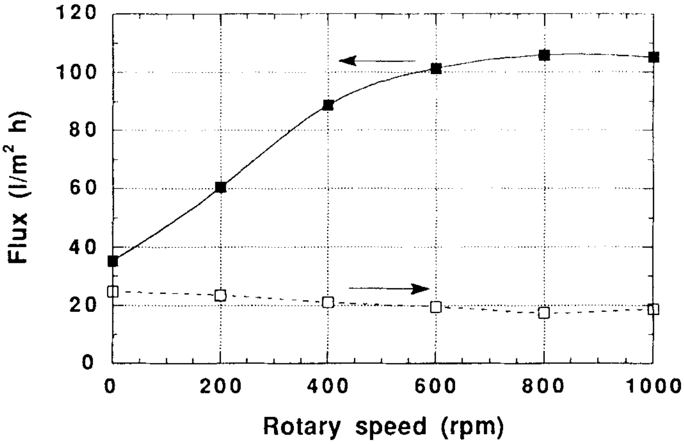

FIG. 2 The influence of rotary speed on the flux of a polyethersulfone membrane during ultrafiltration of a 0.4% silica sol with 1 M sodium chloride added to the solution. The solid symbols denote decreasing rotary speed and the open symbols denote increasing rotary speed.

2, the electrostatic repulsion between the silica particles diminishes and particles aggregate, forming a cake at the surface of the membrane when sodium chloride is added to the silica sol.

Deposition of Solutes in the Membrane Matrix

If the solute molecules are large enough to be retained by the membrane, they may be deposited at the surface of the membrane, as shown in Figs. 1 and 2. If low-molecular solutes, small enough to enter the membrane pores, are treated, they may be deposited in the membrane matrix. If solute molecules are adsorbed on the pore walls, they will restrict the effective pore diameter, and the flux decreases as a consequence of pore blocking.

Hydrophobic interactions probably play an important role when membranes are fouled by organic compounds. Evidence for this is found in the numerous observations showing the marked difference in fouling tendency of hydrophobic and hydrophilic membranes (12–14). Furthermore, hydrophobic solutes, e.g., BSA, are known to be more readily adsorbed onto the surface of the membrane than hydrophilic solutes, e.g., dextran (15). Characteristic of fouling due to solute–membrane interactions in the membrane matrix is the fact that the flux is unaffected by the rotary speed. Figure 3 illustrate the finding that solute–membrane interactions dominate membrane performance when a low-molecular hydrophobic solute is treated.

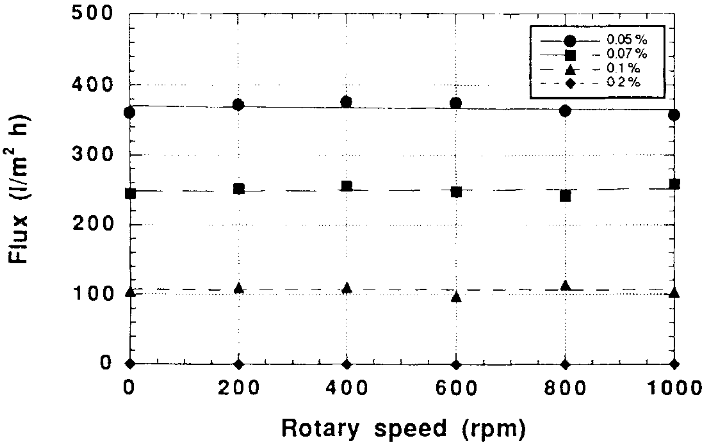

FIG. 3 The influence of rotary speed on the flux of a polyethersulfone membrane during ultrafiltration of octanoic acid.

The octanoic acid molecule, used to obtain the results shown in Fig. 3, should be too small to be retained by the membrane. This was confirmed by analyzing samples of retentate and permeate as TOC. The concentrations in the retentate and permeate were found to be the same.

Reducing the Flux Decline

A wide spectrum of parameters influence the membrane performance during ultrafiltration. The measures that have to be taken to minimize the reduction in the flux are highly dependent on whether it is concentration polarization (16–20) or fouling (7, 21–29) which is causing the flux decline.

When the flux reduction is dominated by concentration polarization, the flux is controlled primarily by the rate at which the retained solutes can be transferred from the membrane wall back into the bulk fluid. Thus, operational variables which aid backtransport from the membrane will increase the flux. The shear rate at the membrane wall is the major depolarizing parameter. The traditional way of increasing the shear rate is by increasing the circulation velocity in the membrane module. However, in traditional modules the pressure increases as the circulation velocity is increased due to frictional losses. The increased pressure results in an increase in the convective transport of solute to the membrane and a steeper concentration gradient at the membrane. The flux therefore levels off as the circulation velocity increases. In the module used in the experiments presented in this paper, the shear rate can be varied without affecting the operating pressure. Increasing the shear rate (by increasing the rotary speed) results only in a decrease in the thickness of the boundary layer.

When the operating pressure is increased, the flux increase is very limited at zero rotary speed, as shown in Fig. 4, although the circulation flow in the module is still quite high. However, as the rotary speed increases, the difference in flux at the different pressure levels becomes very marked.

Both concentration polarization and fouling at the surface of the membrane are boundary layer phenomena. The difference is that during fouling the solute–solute interactions between molecules/particles in the material accumulated at the membrane are so strong that it is impossible to decrease the thickness of the layer of accumulated material by increasing the shear rate. Membrane surface fouling is commonly encountered when colloidal suspensions are ultrafiltered. This type of fouling is minimized by reducing the parameters that affect aggregation, primarily ionic strength (i.e., salt concentration) and pH (3, 23, 25). For example, when treating feed streams containing silica particles or clay, it is important to maintain a high pH in the solution, whereas when treating feed streams

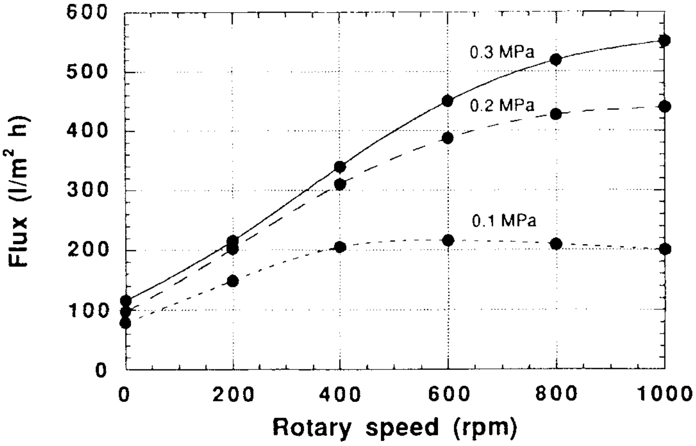

FIG. 4 The influence of rotary speed on the flux of a membrane of regenerated cellulose during ultrafiltration of a 2.0% silica sol at varying operating pressures. The pH was 9.5, and the concentration of sodium chloride was less than 1 mM.

containing metal ions it is important to keep the pH low enough to avoid precipitation of metal complexes, e.g., iron hydroxide and calcium sulfate.

Flux decline due to deposition of solute molecules in the membrane matrix can be reduced by minimizing the solute–membrane interactions. Changing to a membrane of a more hydrophilic material is often successful. A membrane of regenerated cellulose or cellulose acetate can be used instead of one of polysulfone or polyethersulfone, for example. As shown in Fig. 5, the flux of the membrane of regenerated cellulose is not affected at all by the octanoic acid, in contrast to the flux of the hydrophobic polyethersulfone membrane in Fig. 3.

Hydrophilic membranes are, however, less chemically resistant. If the operating conditions do not allow the use of a hydrophilic membrane, the flux decline may be reduced by improving the solubility of the solute. The solubility of fatty acids, for example, is improved by converting the fatty acid into the corresponding salt by increasing the pH of the solution. As shown in Fig. 6, the flux reduction was slight when the salt of octanoic acid, sodium octanoate, was treated.

The solubility of the solute affects the severity of both the fouling at the surface of the membrane and in the membrane matrix. Pretreatment of the feed solution by adjusting the pH, or sedimentation in an aerated tank, is successful when reducing the influence of fouling of iron hydroxide, for example. Converting hydrophobic solutes to soap by increasing

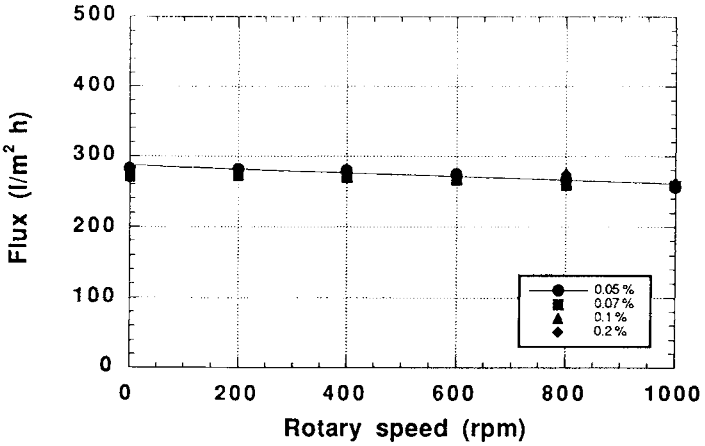

FIG. 5 The influence of rotary speed on the flux of a membrane of regenerated cellulose during ultrafiltration of octanoic acid.

the pH may be successful when treating hydrophobic organic solutes as fatty acids. However, it is important to be aware of the fact that if it is fouling at the surface of the membrane that causes the flux decline, nothing is gained by changing to a more hydrophilic membrane. This is demonstrated in Fig. 7.

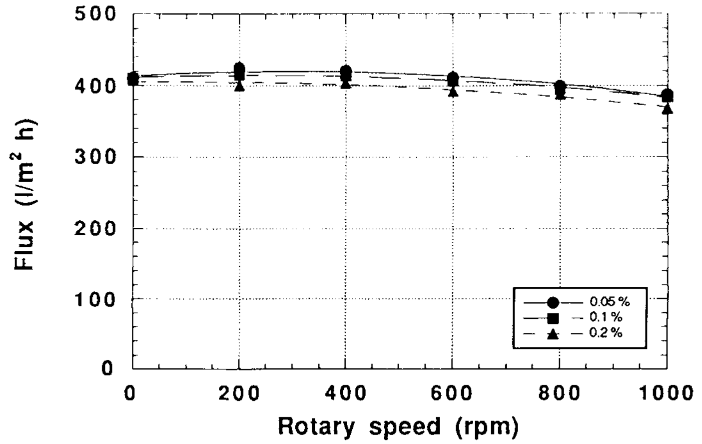

FIG. 6 The influence of rotary speed on the flux of a polyethersulfone membrane during ultrafiltration of sodium octanoate. The solubility of sodium octanoate in water is almost 100 times higher than the solubility of octanoic acid.

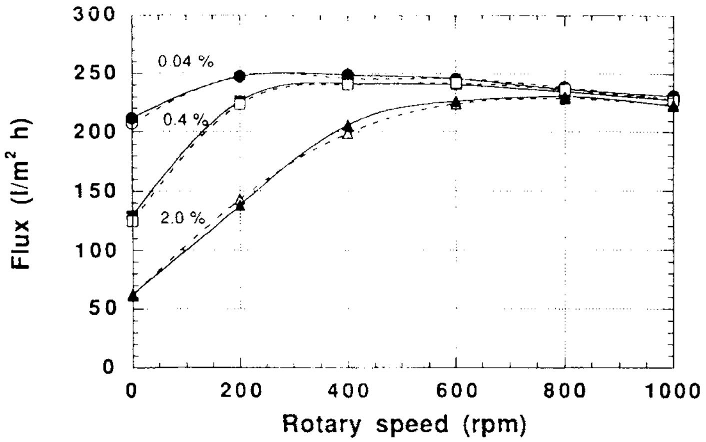

FIG. 7 The influence of rotary speed on the flux of a membrane of regenerated cellulose during ultrafiltration of a silica sol. The solid symbols denote decreasing rotary speed and the open symbols denote increasing rotary speed. The pH of the silica sol was 9.5, and the concentration of sodium chloride was less than 1 mM.

CONCLUSIONS

The development of new membrane process applications is, to a great extent, based on experience from membrane plants already in operation. Many problems encountered in membrane plants can be solved in this way, but our understanding of the phenomena which reduce membrane performance is still inadequate.

In this paper it is shown that it is possible to distinguish between the two flux-reducing phenomena, concentration polarization and fouling. It is also shown how fouling caused by solute–solute interactions at the surface of the membrane and solute–membrane interactions in the membrane matrix may be distinguished. Different ways of reducing the influence of fouling are demonstrated.

The most important property affecting fouling is the solubility of the solute. Parameters that affect the solubility are the concentration (it is important to be aware of the fact that during ultrafiltration the concentration is much higher at the surface of the membrane than in the bulk solution), the temperature, the pH, and the ionic strength of the solution. In this paper it is shown how fouling can arise when the ionic strength of a silica sol is increased, and the importance of the hydrophobic/hydrophilic properties of both the solute and the membrane is demonstrated.

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