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Fouling During Ultrafiltration of a Low Molecular Weight Hydrophobic Solute

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ABSTRACT

The influence of a small hydrophobic solute (octanoic acid) on the flux reduction and the flux recovery of two ultrafiltration membranes was studied in this investigation. The two membranes were made of polyether sulfone and regenerated cellulose, both with a nominal molecular weight cutoff of 20,000 Da. The concentration of the octanoic acid solution was found to have a significant influence on not only the extent of flux reduction during treatment of the octanoic acid solution, but also on the flux recovery when the membrane was rinsed with deionized water. After treatment of the octanoic acid solution, a pure water flux increase of 1.5 times the pure water flux of the new, unused polyether sulfone membrane was observed. Different causes of the increased pure water flux after treatment of the octanoic acid solution are presented, and the serious consequences this apparent positive effect can cause in industrial applications are discussed.

Key Words. Fouling; Ultrafiltration; Adsorption; Low molecular weight solute; Hydrophobic interactions

INTRODUCTION

The severe influence of low molecular weight hydrophobic solutes, such as alcohols and carboxylic acids, on membrane flux when treating various process streams in ultrafiltration plants, is often neglected because of the modest size and the usually low concentration of these substances. The extent of flux reduction depends on the membrane material (1) as well as the membrane cutoff (2); even the flux of membranes with a molecular weight cutoff many times greater than the molecular weight of the solute can be significantly reduced.

In previous investigations (1, 3) a membrane of regenerated cellulose was found to exhibit no flux reduction when treating an octanoic acid (caprylic acid) solution. Furthermore, the pure water flux was almost the same before and after ultrafiltration of the solution. In contrast to the stable flux performance of the cellulose membrane, a membrane of polyether sulfone was found to exhibit a severe flux reduction when treating the same solution, but the pure water flux after cleaning the membrane was higher than it was initially (1). This pure water flux increase is puzzling as the flux recovery, i.e., the ratio between the pure water flux before and after treating a solution, is often used to estimate the fouling susceptibility of a membrane [even though the flux recovery is not a reliable measure of the cleaning efficiency, as pointed out by, for example, Trägårdh (4)]. The increased pure water flux raises the question of whether hydrophobic solutes have a negative effect on ultrafiltration membranes, or if they can be used as cleaning or "wetting" agents. However, the increased pure water flux of the polyether sulfone membrane observed by Jönsson and Jönsson (1) could have been due to interactions between remains of octanoic acid and the cleaning agent, as the membranes were cleaned with an alkaline cleaning agent. Remains of octanoic acid could thus have been converted to the surface-active agent sodium octanoate during the cleaning procedure.

However, in the previous investigation (1) the influence of both sodium octanoate and octanoic acid on the flux and the flux recovery of a PES20 membrane was studied. The pure water flux of a new membrane, after cleaning with the alkaline cleaning agent Ultrasil 10 from Henkel, was first measured. The pure water flux after cleaning was identical with the flux of the uncleaned membrane. Then a 5.6 mM sodium octanoate solution was treated. The flux of the sodium octanoate solution was 85% of the initial pure water flux. The pure water flux after cleaning was the same as the pure water flux of the new, unused membrane. When, finally, an octanoic acid solution was treated, the flux was zero. However, after cleaning the membrane, the pure water flux was 140% of the pure water flux of the new membrane. The hydrophobic compound octanoic acid thus caused a flux increase whereas the pure water flux remained constant after treatment of the surfactant, sodium octanoate.

Surfactants are otherwise known to often have a positive effect on the membrane performance. An increase of the pure water flux after passive adsorption of a surfactant was experienced by Swaminathan et al. (5), for example. Surfactant pretreatment has been used to enhance the flux (6–8). However, in this paper it is shown that a solute which is *not* a surfactant can bring about an increase of the pure water flux. This pure water flux increase is not beneficial, but represents a serious problem, as discussed in this paper.

In this investigation the flux reduction and the flux recovery of a hydrophobic and a hydrophilic ultrafiltration membrane were studied without the use of cleaning agents in order to reveal whether the pure water flux performance was due to the solute or to the cleaning agent. Deionized water only was used to rinse the membranes. The influence of the concentration, the duration of exposure, and the hydrophobic/hydrophilic properties of the membrane were investigated.

MATERIALS AND METHODS

Membranes

Two membranes were used in the investigation; a hydrophobic membrane made of polyether sulfone (PES20) and a hydrophilic membrane made of regenerated cellulose (C20). Both membranes are manufactured by Hoechst AG, Germany. The nominal molecular weight cutoff of both membranes is 20,000 Da.

Chemicals and Analysis

The hydrophobic solute used in the investigation was octanoic acid. The octanoic acid was of *pro analysi* grade and supplied by Merck. The molecular weight of octanoic acid is 144 Da. Its saturation concentration in water at 20°C is 4.7 mM (0.7 g/L) (9). The pH of the octanoic acid solutions used in this investigation was 3.8–4.0 (depending on the concentration). The concentration of octanoic acid was determined as Chemical Oxygen Demand (COD) using Dr Lange LCK 214 cuvettes and a pocket filter photometer.

All water used was deionized and filtered through a 0.2-μm filter before use. The conductivity of the water at 20°C was <7 μS/cm.

Experimental Procedure

The experiments were performed in a crossflow module equipped with a circular, flat membrane with an area of 19.6×10^{-4} m^2. The permeate flow was continuously measured with a PhaseSep flowmeter. Pressure, temperature, and permeate flow were continuously recorded in a computer. The operating conditions were the same in all experiments. The transmembrane pressure was 100 kPa, the temperature was maintained at 25°C, and the circulation flow was 0.1 m^3/h, which corresponds to an average flow velocity across the membrane of approximately 1.5 m/s. A stirrer in the feed tank was used to ensure that the solute was evenly distributed in the feed solution. Both the retentate and the permeate were recirculated back to the feed tank.

The total volume of liquid in the system was 4 liters. The rinsing procedure was performed at the same operating conditions as during the treatment of the acid, i.e., at 100 kPa and 0.1 m^3/h. The temperature of the deionized water was 26–27°C. When rinsing the system, the liquid in the system was withdrawn to drain until the feed tank was nearly empty. The total volume of liquid remaining in the system was then approximately 0.5 liters. Five liters of deionized water were added to the feed tank, recirculated in the system for approximately 3 minutes, and withdrawn to drain. In this way an efficient removal of the old solution from the system was obtained. When the feed tank was almost empty, 5 more liters of water were added. The addition of fresh deionized water was carried out five times. When rinsing out the octanoic acid solution, the pure water flux reached its optimum after the third addition. Two further rinsing cycles were run in order to ensure that all solute had been rinsed out of the system.

New, unused pieces of membrane were used in all tests. Before being mounted in the equipment, the membrane was thoroughly rinsed with deionized water. When mounted in the module, the membrane was rinsed with five times 5 liters of deionized water, according to the description above. Two types of experiments were performed; short-term and long-term. The pure water flux of the PES20 and the C20 membranes was stable from the very beginning. The membranes were therefore conditioned for only a short time at the beginning of the experiments: 30 minutes in the short-term experiments and 2 hours in the long-term experiments. The octanoic acid was added dropwise to the feed tank.

Short-Term Experiments

The pure water flux was measured for 30 minutes before the octanoic acid was added to the feed tank. After 1 hour the system was rinsed with deionized water, but just prior to this, samples were withdrawn from the retentate and the permeate. The pure water flux was measured during a period of 2 hours, after which the acid was once again added to the feed tank. This procedure was then repeated a third time.

Long-Term Experiments

The pure water flux was measured for 2 hours before the octanoic acid was added to the feed tank. After 22 hours the system was rinsed with deionized water and the acid was once again added to the feed tank after 2 hours' filtration of deionized water. This procedure was repeated four times, whereafter the pure water flux was finally measured for 70 hours. During the treatment of the solution, samples were withdrawn from the retentate and the permeate every hour during the first 6 hours and, finally, after 22 hours, immediately before rinsing.

RESULTS AND DISCUSSION

Short-Term Exposure

A significant flux reduction during treatment of an octanoic acid solution, and the succeeding increase in the pure water flux when the solution is rinsed out of the system, is characteristic of the polyether sulfone membrane PES20. This typical behavior of the PES20 membrane is demonstrated in Fig. 1. In this experiment the initial pure water flux of the new membrane was approximately 70 L/m^2·h, and the pure water flux after treatment of the octanoic acid solution was 105 L/m^2·h.

When repeatedly exposed to an octanoic acid solution, the flux reduction of the PES20 membrane became increasingly severe with time, as shown in Fig. 2, whereas the flux recovery was approximately constant.

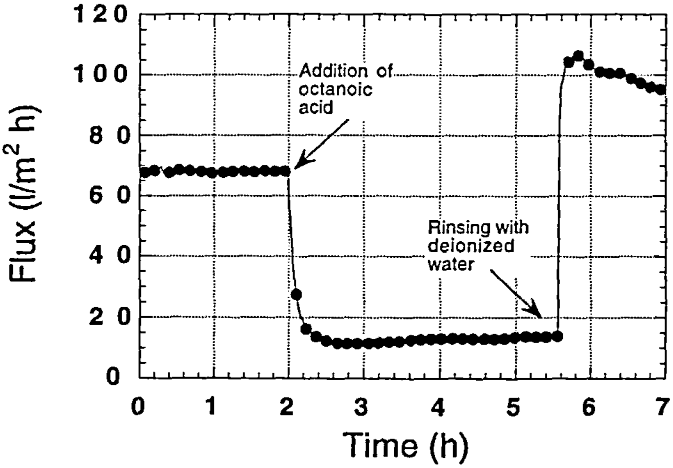

FIG. 1 Flux of the polyether sulfone membrane, PES20, before, during, and after ultrafiltration of a 4.1 mM octanoic acid solution. The permeate concentration at the end of the experiment, i.e., immediately before rinsing with water, was 1.3 mM.

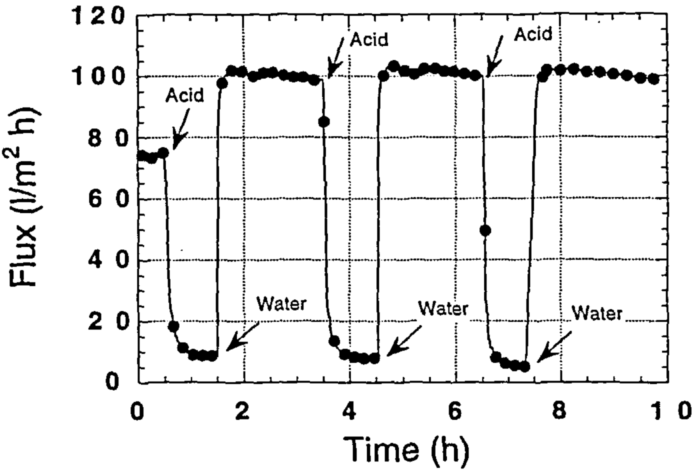

FIG. 2 Flux of the polyether sulfone membrane, PES20, during repeated treatment of a 4.2 mM octanoic acid solution. The arrows indicate when octanoic acid was added and when the membrane was rinsed with deionized water. The permeate concentration at the end of the three tests with octanoic acid was 1.5, 1.5, and 1.2 mM.

Flux Performance of the Hydrophilic Membrane

In contrast to the polyether sulfone membrane, no flux reduction nor change in the pure water flux of the hydrophilic membrane made of regenerated cellulose was observed when treating an octanoic acid solution, as shown in Fig. 3. This is in agreement with earlier investigations of the behavior of hydrophilic membranes (1, 3).

Influence of Concentration

The concentration of the octanoic acid solution has been found to have a marked influence on the flux reduction (1–3, 10), but the influence of the concentration on the flux recovery has not, as far as we know, been studied previously. A 1.6 mM octanoic acid solution was therefore treated three times with 2 hours' filtration of deionized water between each treatment of the solution. A flux reduction was observed even at this low concentration of octanoic acid, but no influence on the pure water flux was recorded, as can be seen in Fig. 4.

In the ensuing experiment the octanoic acid concentration was increased somewhat with each addition. As expected, the flux reduction became more pronounced as the octanoic acid concentration was in-

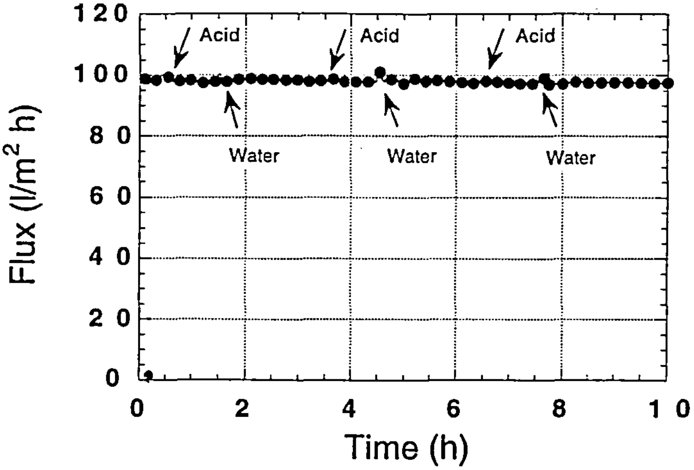

FIG. 3 Flux of the regenerated cellulose membrane, C20, during repeated treatment of a 4.1 mM octanoic acid solution. The arrows indicate when octanoic acid was added and when the membrane was rinsed with deionized water. The permeate concentration at the end of the three tests with octanoic acid was 3.4, 3.6, and 3.6 mM.

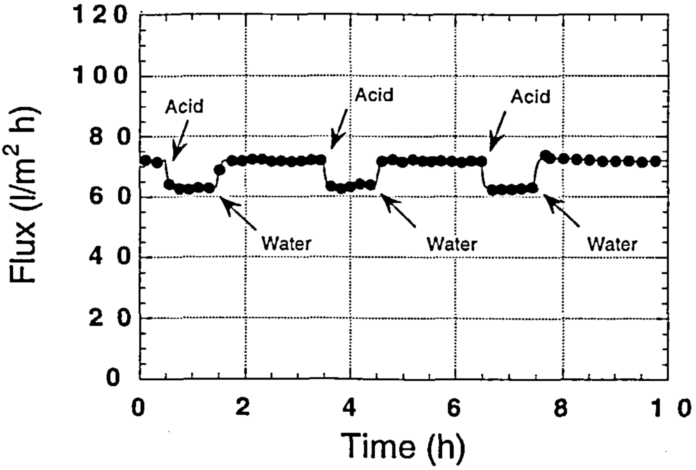

FIG. 4 Flux of the polyether sulfone membrane, PES20, during repeated treatment of a 1.6 mM octanoic acid solution. The arrows indicate when octanoic acid was added and when the membrane was rinsed with deionized water. The permeate concentration at the end of the three tests with octanoic acid was 1.5 mM.

creased. However, an increase in the flux recovery was registered at the same time, as shown in Fig. 5.

Retention

Octanoic acid molecules would be expected to pass more or less freely through a 20,000 Da cutoff membrane. However, the retention was surprisingly high. The retention of octanoic acid in the experiment shown in Fig. 2 was approximately 65%. The high retention of octanoic acid is, however, only an illusion as the permeate concentration increases and the retentate concentration decreases with time. Constant retention is first attained after several hours, as illustrated by the experiment shown in Fig. 6. In this experiment the retention was 40% after 1 hour, but only 2% at the end of the experiment, i.e., after 22 hours' filtration.

Long-Term Exposure

In the short-term experiment shown in Fig. 2, the flux recovery of the PES20 membrane was approximately the same each time the octanoic acid solution was rinsed out of the system. However, the membrane was exposed to octanoic acid for periods of only 1 hour in this experiment.

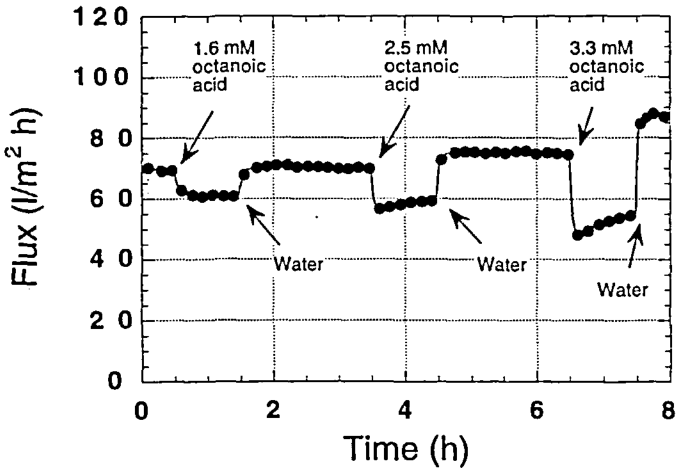

FIG. 5 Flux of the polyether sulfone membrane, PES20, during treatment of an octanoic acid solution of increasing concentration. The arrows indicate when octanoic acid was added and when the membrane was rinsed with deionized water. The permeate concentration at the end of each octanoic acid filtration stage was 1.4, 2.1, and 2.6 mM..

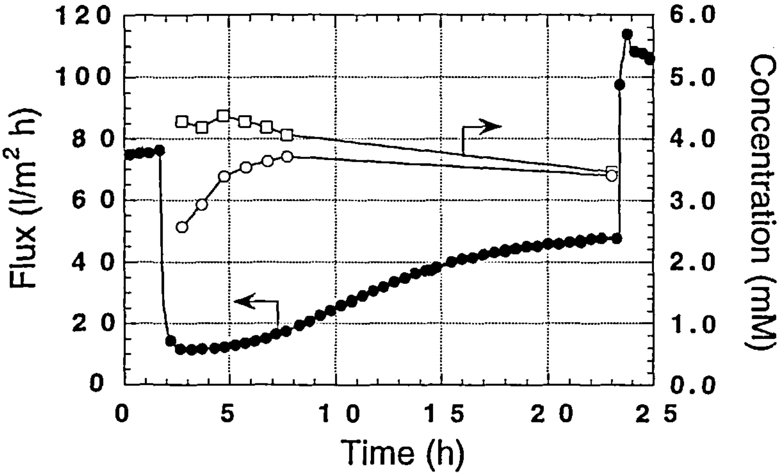

FIG. 6 The flux, and the retentate and permeate concentrations during treatment of a 4.2 mM octanoic acid solution. The black dots denote the flux of the PES20 membrane, and the open rectangles and circles the retentate and the permeate concentration, respectively.

In a separate experiment the long-term effect of octanoic acid on the pure water flux was studied by repeated treatment of an octanoic acid solution for 22 hours, followed by filtration of deionized water for 2 hours and then treatment of octanoic acid for another 22 hours. The octanoic acid treatment was repeated four times. During this long-term experiment the octanoic acid flux, as well as the pure water flux, was found to be lower each time, as shown in Fig. 7.

When treating the octanoic acid solution, a certain flux increase with time was noted, as shown in Fig. 6. The flux after 22 hours was significantly higher than during the first few hours of filtration, possibly as a consequence of the decrease in the concentration due to the octanoic acid being adsorbed in the membrane and on the solid surfaces in the system. Each time the membrane had been exposed to octanoic acid, the increase in flux during the filtration of the octanoic acid was less and less marked, and at the same time the pure water flux recovery was reduced. The difference between the membrane performance the first time the membrane was exposed to octanoic acid and the fifth time is clearly demonstrated by comparing Fig. 6 (the first addition) and Fig. 8 (the fifth addition).

The pure water flux was reduced after repeated long-term treatment of an octanoic acid solution, as shown in Fig. 7. A lower flux recovery was

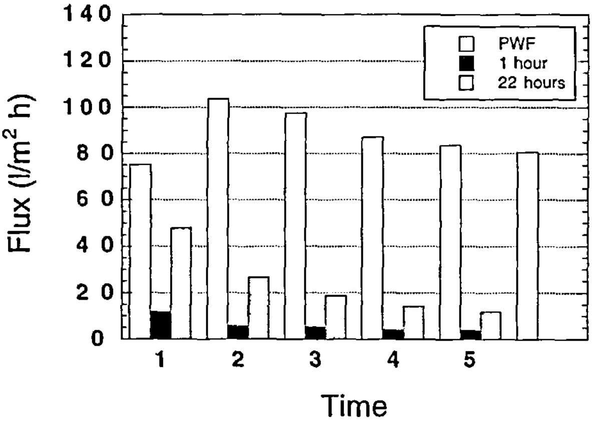

FIG. 7 The pure water flux (PWF) and the flux after 1 and 22 hours' treatment of a 4.2 mM octanoic acid solution. The pure water flux was measured 2 hours after the octanoic acid solution from the preceding experiment had been rinsed out of the system. The addition of octanoic acid was repeated four times. The same PES20 membrane was used throughout the test.

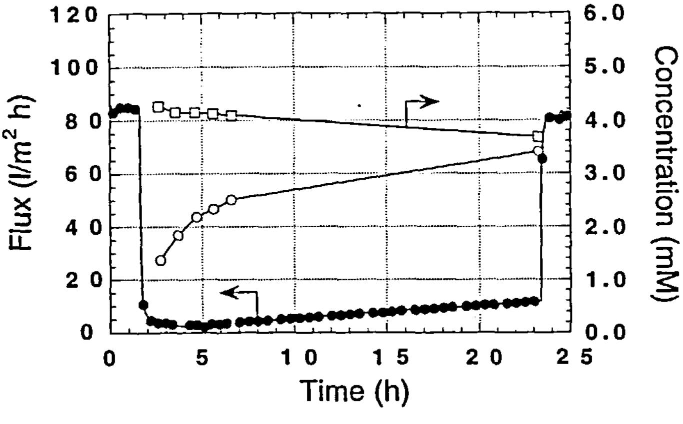

FIG. 8 Flux of the polyether sulfone membrane, PES20, during repeated treatment of a 4.2 mM octanoic acid solution. Octanoic acid was added, and 22 hours later rinsed out with deionized water. The figure shows the flux performance at the fifth addition. The black dots denote the flux, and the open rectangles and circles the retentate and the permeate concentration, respectively. The retention of octanoic acid was 68 and 7% after 1 and 22 hours, respectively.

also observed when octanoic acid was treated continuously for 70 hours. After rinsing, the pure water flux was 75 L/m^2·h (see Fig. 9), which is approximately the same as for the unused membrane. It can also be seen in Fig. 9 that the flux increase when treating the octanoic acid solution ceased after approximately 60 hours.

An Attempt to Explain the High Flux Recovery

The flux reduction of polyether sulfone membranes observed when treating octanoic acid solutions is presumably due to adsorption and capillary condensation in the membrane pores, as proposed by Jönsson et al. (10). The ensuing high pure water flux may be due to adsorption of octanoic acid molecules on the membrane pore walls (rendering the surface hydrophilic), a chemical reaction between the polymeric material of the membrane and the octanoic acid molecules, solubilization of octanoic acid in the membrane polymeric matrix, or to contraction of the membrane matrix due to octanoic acid molecules remaining in the small membrane pores.

If octanoic acid molecules are adsorbed onto the pore walls, the carboxylate group of the molecule can render the membrane material more hydrophilic in character. However, it is unlikely that octanoic acid molecules remain adsorbed on the membrane pore wall when the solution is rinsed away by water. Indeed, ellipsometry measurements of the adsorption/

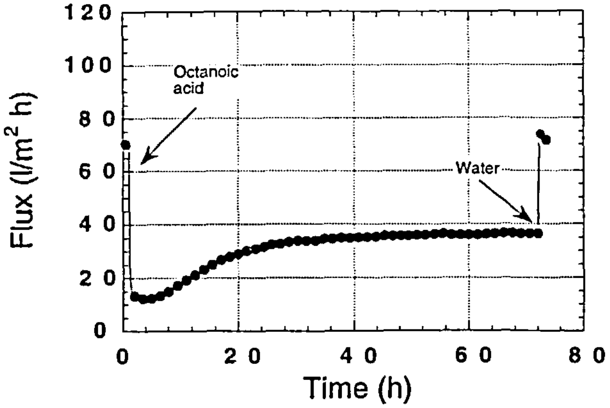

FIG. 9 Flux of the polyether sulfone membrane, PES20, during treatment of an octanoic acid solution with an initial concentration of 4.2 mM. The retentate and permeate concentrations after 70 hours' filtration were identical, 2.8 mM.

desorption behavior of octanoic acid on a flat, hydrophobic surface demonstrated that the adsorption, as well as the desorption, process is completed in less than 5 minutes (10). Neither is a chemical reaction between the membrane material and the octanoic acid likely, since octanoic acid is quite a stable compound.

Solubilization of octanoic acid in the membrane matrix, with an accompanying swelling of the matrix, can explain the gradual pure water flux decline each time the membrane was exposed to octanoic acid (see Fig. 7), but does not explain why the pure water flux after treatment of octanoic acid is higher than before. However, accumulation of acid in small pores and an accompanying contraction of these pores can explain the high flux recovery after the octanoic acid treatment. This affect can be explained as follows. Due to the attractive interaction between the octanoic acid and the polymeric material of the membrane, the energy gain of octanoic acid settling in small pores is higher than in large pores. When the matrix is incompressible, this causes a distribution of the solute to smaller pores in favor of the larger pores (capillary condensation). If the matrix is slightly compressible, this interaction will give rise to a force on the membrane matrix tending to reduce the volume of the pore. This force is more important for small pores than for large ones, giving rise to a contraction of small pores and a corresponding enlargement of large pores. An enlargement of the large pores results in a higher permeability of the membrane, even though some of the small pores are still blocked by octanoic acid molecules. The flux enhancement is, of course, more marked the more blocked pores are "dead-end" pores through which no fluid flows anyway.

The pure water flux of new, unused PES20 membrane samples was very stable, and the same whether the membrane was cleaned with the alkaline cleaning agent Ultrasil 10 (Henkel) or not. The pure water flux decline with time after the treatment of octanoic acid was in definite contrast to the pure water flux performance before the membrane was exposed to octanoic acid. After filtration of octanoic acid the pure water flux decreased with time, as shown in Fig. 10. At the same time a slight increase in the concentration was registered. This concentration increase partly explains the "pure water" flux decline. It is true that rinsing the membrane with deionizied water caused a small increase in flux, as shown in Fig. 10, but the flux after rinsing (when pure water once again filled the system) was still much lower than initially, and the flux continued to decrease with time.

The decline in pure water flux with time can be explained by the contraction theory. If octanoic acid remains in some pores, the flux decline with time can be due to a slow, diffusive release of octanoic acid from these pores. When octanoic acid molecules leave the pores, this results in the

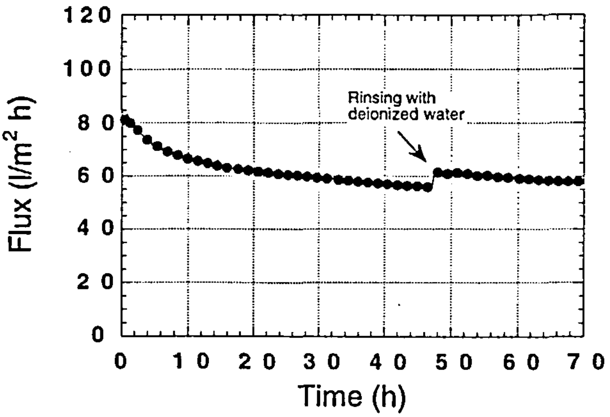

FIG. 10 The pure water flux after the final treatment of octanoic acid in the test summarized in Fig. 7. The concentration at time zero was 0.1 mM in the retentate and 0.15 in the permeate; 48 hours later, just before rinsing, the concentration in both the retentate and the permeate was 0.5 mM.

membrane structure resuming its original shape, and hence, the pure water flux decreases. However, this hypothesis fails to explain why the flux recovery deteriorates when the membrane is repeatedly exposed to octanoic acid. This phenomenon is probably due either to swelling of the membrane due to increasing solubilization of octanoic acid in the membrane or to accumulation of adsorbed, low-rate desorbing impurities present in the octanoic acid.

Serious Long-Term Effects on the Membrane Performance

As demonstrated in this investigation and in Ref. 1, an ultrafiltration membrane may still be contaminated by the remains of a solute, even though the pure water flux has been restored by rinsing/cleaning the membrane. This is a serious problem, especially in pharmaceutical applications, as it makes it difficult to validate the sanitary status of the membrane after the cleaning process.

In other applications where the sanitary regulations are not so stringent, solute remains present a problem as there will be a flux reduction during the succeeding treatment, not due to constituents in the treated solution, but because of remains of hydrophobic solute in the membrane. This flux reduction will become more and more serious with time as material accumulates in the membrane. As indicated by the results in Ref. 1, this long-term contamination occurs even when the membrane is cleaned with a commercial cleaning agent.

CONCLUSIONS

Low molecular weight hydrophobic solutes affect hydrophobic ultrafiltration membranes in two significant ways. First, a severe flux reduction is observed. This flux reduction is due to pore restriction by adsorption and/or capillary condensation in the membrane matrix. Second, the pure water flux is higher afterward. The pure water flux increase is probably due to contraction of the membrane matrix by solute remaining in the small membrane pores, which causes the larger pores to widen. Both the solute concentration and the exposure time affect flux reduction during treatment as well as the pure water flux afterward.

ACKNOWLEDGMENTS

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