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Publication Date
1994-09-01

COLLOIDAL FOULING OF REVERSE OSMOSIS MEMBRANES

By

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TECHNICAL COMPLETION REPORT
Project Number UCAL-WRC-W-793
September 1994

University of California, Water Resources Center

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ABSTRACT

The general objective of this project was to better understand the role of chemical factors in colloidal fouling of reverse osmosis membranes. The results of this research are of paramount importance for efficient operation of RO installations used in water reclamation and reuse and in potable water treatment.

Fouling experiments of thin film composite and cellulose acetate reverse osmosis membranes by aluminum oxide colloids are described. Membrane fouling was investigated at various solution chemistries under fixed hydrodynamic conditions. Results show that the fouling rate increases with an increase in the ionic strength of the solution. Fouling was significant at high ionic strengths, including in the presence of background dissolved organic matter, resulting in a gradual decrease in product water flux and salt rejection. Under the chemical conditions tested, colloidal fouling was found to be reversible, thus indicating that pore blockage is not an important mechanism in colloidal fouling of reverse osmosis membranes.

A qualitative model for the role of chemical-colloidal interactions in colloidal fouling of reverse osmosis membranes is proposed. Fouling is controlled by particle–membrane and particle–retained particle interactions, which, in turn, are determined by solution chemistry, chemical properties of colloids and membranes, and the magnitude of permeation drag.

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PROBLEM STATEMENT AND OBJECTIVES

Population expansion and intermittent water shortages in California and other regions in the United States have stimulated a resurgence of interest in desalination for water supply augmentation. Several reverse osmosis (RO) plants for processing brackish water, wastewater, sea water, or groundwater are currently in place (Buros 1989, Mariñas 1991, Smith 1992). Membrane technology has also proved to be effective for reclamation and reuse of agricultural drainage waters (Smith 1992, Mariñas and Selleck 1992). This technology has great potential in other environmental applications, including the removal of metals from liquid wastes (Walker et al. 1990) and treatment of drinking water supplies containing arsenic and other undesired dissolved species (Clifford et al. 1986).

It has long been recognized that membrane fouling is a major problem in efficient operation of RO plants (e.g., Potts et al. 1981, AWWA Membrane Technology Research Committee 1992). Fouling refers to the attachment or adsorption of substances (foulants) onto the membrane surface and/or within the membrane pores, which results in a decline in product water flux. Fouling of RO membranes places a large economic restriction on membrane plant operation. Hence, a fundamental understanding of the factors controlling the fouling of RO membranes is of paramount practical importance.

RO membrane foulants are usually classified into four major categories (Potts et al. 1981). These are (i) sparingly soluble salts, (ii) dissolved organic substances, (iii) colloidal and particulate matter, and (iv) biological growth. Among these foulants, colloidal particles are considered to be an important cause of membrane fouling (Brunelle 1980, Potts et al. 1981). Colloids are ubiquitous in all process waters and may include clays, iron oxide, colloidal silica, large organic macromolecules, organic colloids and suspended matter, and calcium carbonate precipitates (Stumm 1992).

Unlike the vast literature on fouling of ultrafiltration (UF) and microfiltration (MF) membranes, published research on the fouling of RO membranes is rather limited. One should bear in mind that fouling mechanisms of ultrafiltration and microfiltration membranes are not directly applicable to RO because of the great differences in membrane pore sizes and permeation rates. For instance, pore blockage is an important

mechanism in the fouling of MF and UF membranes by colloids and macromolecules (Fane and Fell 1987, Wiesner et al. 1989, Lahoussine-Turcaud et al. 1990), but its role in RO membrane fouling is probably insignificant. Previous works on RO membrane fouling have focused primarily on precipitate fouling (e.g., Jackson and Landolt 1973, Gilron and Hasson 1987) and fouling by biological growth (e.g., Ridgway et al. 1984, 1985). However, the mechanisms of precipitate and biological fouling of RO membranes are quite different than those involved in colloidal fouling.

Only a few experimental studies on colloidal or particulate fouling of RO membranes are available in the literature. Winfield (1979a, 1979b) has investigated the fouling of cellulose acetate RO membranes by secondary wastewater effluents and has concluded that dissolved organic materials play a much more significant role in membrane fouling than large suspended particles. The findings of Winfield, however, are not conclusive due to the great variability in the chemical properties of colloids and dissolved organic materials in secondary wastewater effluents. In a later study by Cohen and Probstein (1986), the fouling rate of cellulose acetate RO membranes by colloidal ferric hydroxide was reported. Fouling was related to the foulant layer growth and a linear dependence between permeate flux and foulant layer thickness was found for the initial stages of fouling. The solution chemistry in their study, however, was limited to deionized water so that the role of chemical-colloidal interactions in membrane fouling could not be investigated.

At this writing, the mechanisms of colloidal fouling of RO membranes are poorly understood. The general objective of the research reported here was to better understand the role of chemical-colloidal interactions in colloidal fouling of RO membranes. More specifically, in this report we (i) present the results of colloidal fouling experiments with model colloids and solution chemistries using a laboratory RO test unit, (ii) identify the chemical-colloidal factors which control the rate of colloidal fouling, and (iii) postulate a qualitative model for colloidal fouling.

MATERIALS AND METHODS

Reverse Osmosis Membranes

Two types of commercial RO membranes, cellulose acetate and thin film composite, were used in this research. Each of these membranes was supplied by Hydranautics (San Diego, California) and Desalination Systems (Escondido, California). The cellulose acetate and thin film composite membranes from Desalination Systems and the thin film composite membrane from Hydranautics were supplied as dry, flat sheets and were stored at room temperature. The cellulose acetate membrane from Hydranautics was supplied as wet, flat sheet and was stored in a 0.5% formaldehyde solution. The thin film composite and cellulose acetate membranes from Hydranautics are identified by the manufacturer as CAP2 and CAB2, respectively, while those from Desalination Systems are identified as Desal 3 and CE, receptively. Other relevant characteristics of these membranes can be found elsewhere (Petersen 1993, Elimelech et al. 1994).

Aluminum Oxide Colloids

Commercial aluminum oxide colloids ("Aluminum Oxide C"), which consist primarily of δ-Al_2O_3, were used as model colloids in the fouling experiments (Degussa Corp., Akron, Ohio). The aluminum oxide is supplied as a powder and has a BET surface area in the range of 80 to 130 m^2/g, an isoelectric point between 8 to 9, and a density of 2.9 g/cm^3 (Kummert and Stumm 1980, Stone 1989, Degussa Technical Bulletin 1990). Suspensions were prepared by adding a known amount of aluminum oxide to deionized water followed by intense mixing and an ultrasonication for 30 minutes. The manufacturer reports that the aluminum oxide consists of primary particles with an average size of 20 nm. However, dynamic light scattering measurements (Nicomp Model 370, Particle Sizing Systems, Santa Barbara, California) of a stable particle suspension (in deionized water) resulted in a diameter of about 120 nm. Rigorous ultrasonication and addition of surfactant or various detergents to the aluminum oxide suspension revealed that the smallest mean diameter measured was close to 100 nm. Observations by TEM show that the particles are indeed aggregates which are made of primary particles of about 20 nm (Degussa

Technical Bulletin 1990). These primary particles are probably bonded together irreversibly to form the observed aggregates.

Solution Chemistries

The NaCl and CaCl$_2$ salts used were analytical reagent grade (Fisher Scientific, Pittsburgh, Pennsylvania). All solutions and suspensions were prepared with deionized water of conductivity less than 1 μmhos/cm (Nano Pure II, Barnstead, Dubuque, Iowa). When necessary, pH adjustments were done by adding small amounts of HCl or NaOH. Commercial humic acid (Aldrich Chemical Company, Milwaukee, Wisconsin) was used in some of the fouling experiments. The humic acid stock solution was prepared by dissolving a known amount of the granular humic material in deionized water and adjusting the pH to about 11. The solution was agitated for 24 hours, and the pH was adjusted to 8 after this mixing time. Following this step, the solution was filtered through coarse glass filter and then through a 0.2 μm Millipore filter. The filtration rate through the 0.2 μm filter was extremely slow because of surface clogging, and filters were replaced frequently to allow a reasonable amount of dissolved humic materials to be collected. The TOC of the resulting stock solution was 1355 mg/L. The stock solution was stored in a refrigerator at 4°C.

Electrokinetic Properties of Colloids and Membranes

Electrophoretic mobility of the aluminum oxide colloids under various chemical conditions was measured by microelectrophoresis (Lazer Zee Model 501, Pen Kem Inc., Bedford Hills, New York). The instrument is equipped with a laser beam for illumination of the particles, a TV monitor for viewing the particles, and a rotating prism. With the rotating prism, the average mobility of many particles is determined simultaneously at each measurement. This technique is imperative for measuring the electrophoretic mobility of very small particles as those used in this research.

Zeta potentials of the RO membranes were determined by a novel streaming potential analyzer (BI-EKA, Brookhaven Instruments Corp., Holtsville, New York). The streaming potential as well as the streaming current are measured simultaneously by the instrument. The zeta potential for each solution chemistry was calculated from the corresponding measured streaming potential using the Helmholtz-Smoluchowski

equation (Hunter 1981). A detailed description of the instrument and these measurements is given elsewhere (Elimelech et al. 1994).

Colloid Stability

The colloidal stability of the aluminum oxide particles was determined by coagulation experiments in 20 mL glass vials. A suspension of 100 mg/L particles was filled into the vials, and the solution chemistry of each vial was adjusted by adding the appropriate chemicals from stock solutions using a micropipete. The vials were shaken gently and immediately placed in a dynamic light scattering spectrophotometer (Nicomp Model 370, Particle Sizing Systems, Santa Barbara, California) for monitoring the particle size evolution with time. The degree of coagulation was assessed by the relative change of the particle size after 1 minute of coagulation (i.e., the particle size after 1 minute divided by the initial particle size). Attempts to accurately measure the stability ratio (or collision efficiency) by dynamic light scattering were unsuccessful, most likely due to the polydispersity of the suspension and the irregular structure of the particles.

Reverse Osmosis Test Unit

A plate and frame, closed-loop (recirculation) laboratory RO unit was employed in the fouling tests (Fig. 1). In this system, the colloidal particles are suspended in a 20 liter, continuously mixed feeding tank. The temperature in the tank is held constant during the fouling experiment by passing tap water through a stainless steel coil submerged in the feeding tank. The suspension is fed to the RO membrane by a positive displacement pump (Milton-Roy Model R221, Ivyland, Pennsylvania) capable of providing hydraulic pressures up to 1000 psi. From the pump, the suspension splits into two parallel streams, feeding into duplicate membrane test cells. The rectangular cells contain membranes with dimensions of 2.5 by 6.4 cm. Permeate is removed from the top of each membrane test cell, while the brine exits from the side of each cell. The brine is collected and fed into a back-pressure regulator set at a desired pressure. The brine in the recirculation system is returned to the continuously mixed feeding tank after passing through the regulator.

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Temperature-Controlled
Reservoir

Bladder
Accumulator

Suspension   Milton-Roy Pump

Permeate

Back-Pressure
Regulator

Permeate

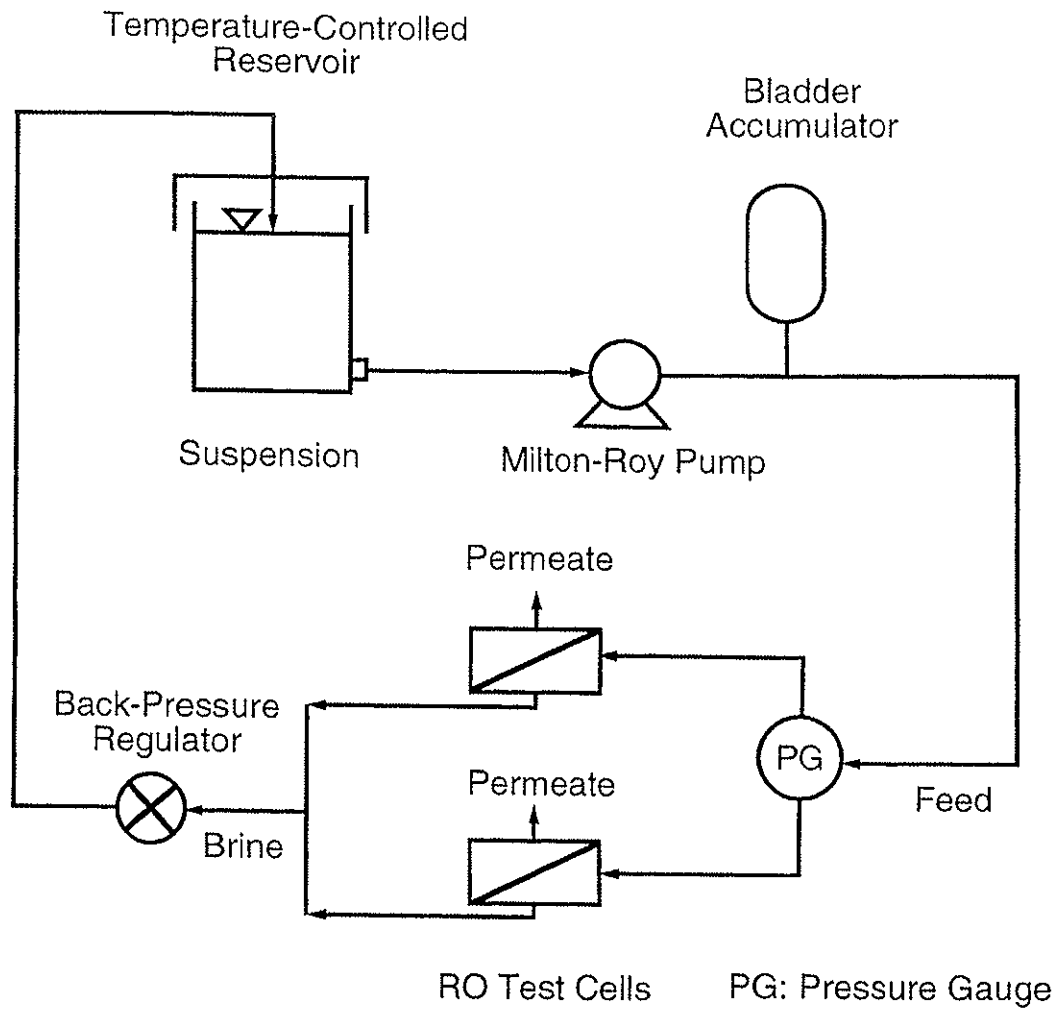Brine

Feed

RO Test Cells   PG: Pressure Gauge

FIGURE 1. Schematic Description of the Laboratory Reverse Osmosis Unit.

Fouling Experiments

In a typical RO fouling test, a particle-free solution of a desired chemistry was circulated through the membrane unit at fixed cross flow velocity and transmembrane pressure. The average fluid velocity over the membrane under the hydraulic conditions employed in the tests was 5.2 cm/s, resulting in a Reynolds number close to 300. After 14 hours of equilibration at this mode, a concentrated stock suspension of particles was added to the feeding tank to establish a desired particle concentration. This was considered the initial time of the fouling experiment. The measured product water flux just before adding the particles was the reference flux, and all subsequent measured fluxes were referred to this flux (*i.e.*, the relative flux is the actual flux at any time divided by the reference flux).

Samples to determine the permeate water flux and salt rejection were taken at various time intervals. Product water flux was measured volumetrically and salt (NaCl) rejection was determined from the measured feed and permeate conductivities (YSI 32, Yellow Springs Instrument Co., Yellow Springs, Ohio). In addition, samples from the feeding tank were taken once or twice a day to measure the turbidity and the particle size of the suspension by dynamic light scattering.

In all experiments, the transmembrane pressure (*i.e.*, the applied pressure minus the bulk osmotic pressure) was maintained at 400 psi, so that the role of solution chemistry on the extent of colloidal fouling can be investigated without considering pressure effects. The pH of the feed suspension during the fouling experiments ranged from 5.6 to 6.0 and the average temperature was about 22°C. Under the above operating conditions, the average water flux after 14 hours of equilibration was about 1.2×10^{-5} and 0.7×10^{-5} m/s, for the thin film composite and the cellulose acetate membranes, respectively.

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DISCUSSION OF RESULTS AND THEIR SIGNIFICANCE

Electrokinetic Properties of Colloids and Membranes

The electrophoretic mobility of the aluminum oxide colloids as a function of solution pH and concentration of dissolved humic substances (expressed as mg/L TOC) is presented in Fig. 2. As shown, the isoelectric point of the aluminum oxide colloids in the absence of humic substances is approximately 8.5, which is consistent with previous studies using these colloids (Kummert and Stumm 1980, Stone 1990, Stumm 1992). As the concentration of humic substances increases, the isoelectric point shifts to a lower pH. With 0.6 mg/L TOC in solution, the isoelectric point is about 3.5; the particles are negatively charged at pH values above this point.

The marked influence of humic substances on the electrophoretic mobility of the colloids indicates that humic substances strongly adsorb onto the surface of the aluminum oxide colloids. Humic substances are comprised of macromolecules with ionogenic functional groups; carboxyl is among the most abundant oxygen-containing functional groups (Liang and Morgan 1990, Morel and Hering 1993). These anionic macromolecules may adsorb onto the aluminum oxide colloids through one or more of the following mechanisms (Stumm 1992): (i) electrostatic attraction between negatively charged functional groups of the humic macromolecules and positively charged sites of the aluminum oxide, (ii) specific chemical interaction between humic carboxyl functional groups and OH-groups on the aluminum oxide, and (iii) hydrophobic interactions between the particles and non-polar segments of the humic macromolecules. Regardless of the mechanism of adsorption, the electrokinetic charge of the particles becomes more negative due to the negatively charged functional groups of the humic macromolecules adjacent to the Stern layer.

Typical zeta potential curves of the RO membranes used in this research at various solution chemistries were presented elsewhere (Elimelech et al., 1994). It was found that the cellulose acetate membranes are negatively charged over the entire pH range investigated (3 to 11), whereas the thin film composite membranes are negatively charged above pH of 3.4 and positively charged below this pH. It was also reported that the zeta potential of the membranes becomes more negative in the presence of humic substances. Hence, at the pH range of 5.6 to 6.0, used in all the
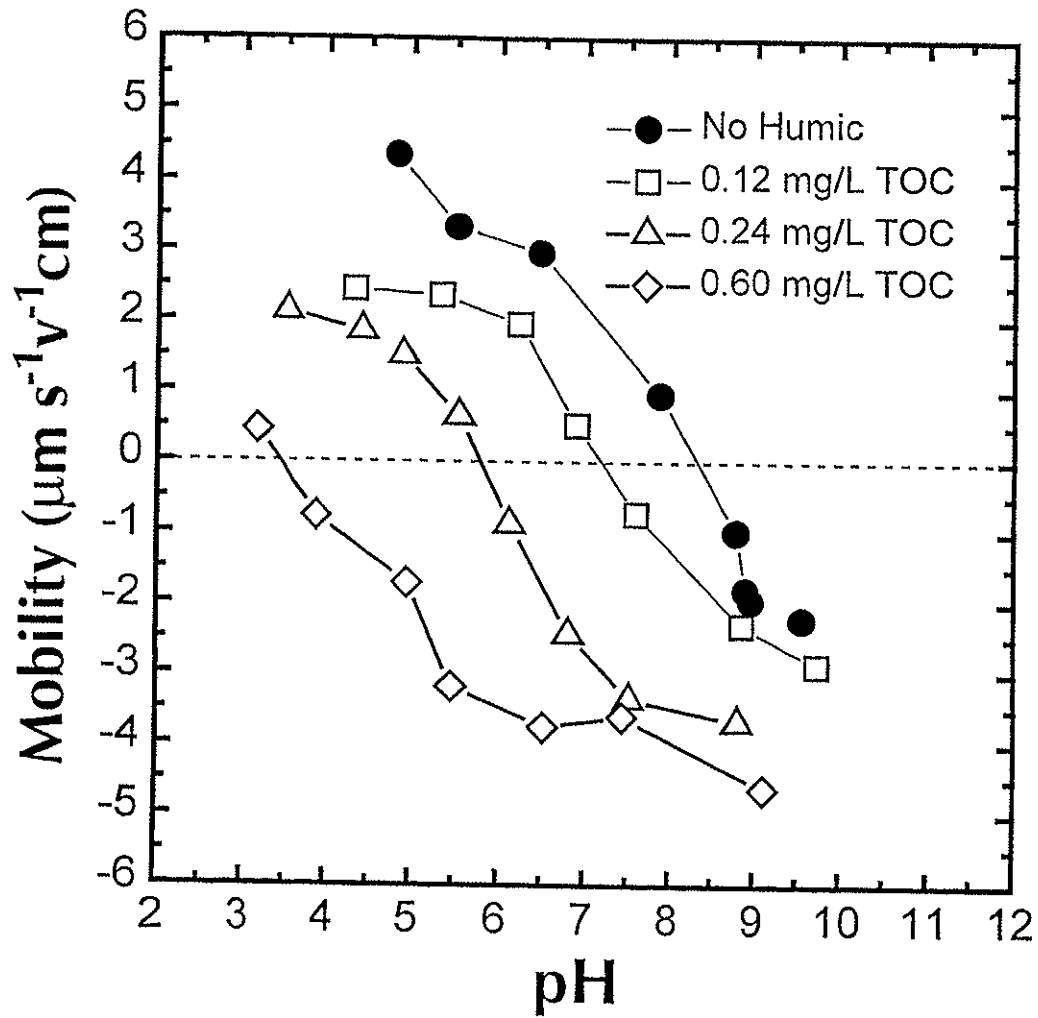
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FIGURE 2. Electrophoretic Mobility of the Aluminum Oxide Colloids as a function of pH for Different Concentrations of Humic Substances (Particle Concentration=100 mg/L; NaCl Concentration=10^{-3} M).
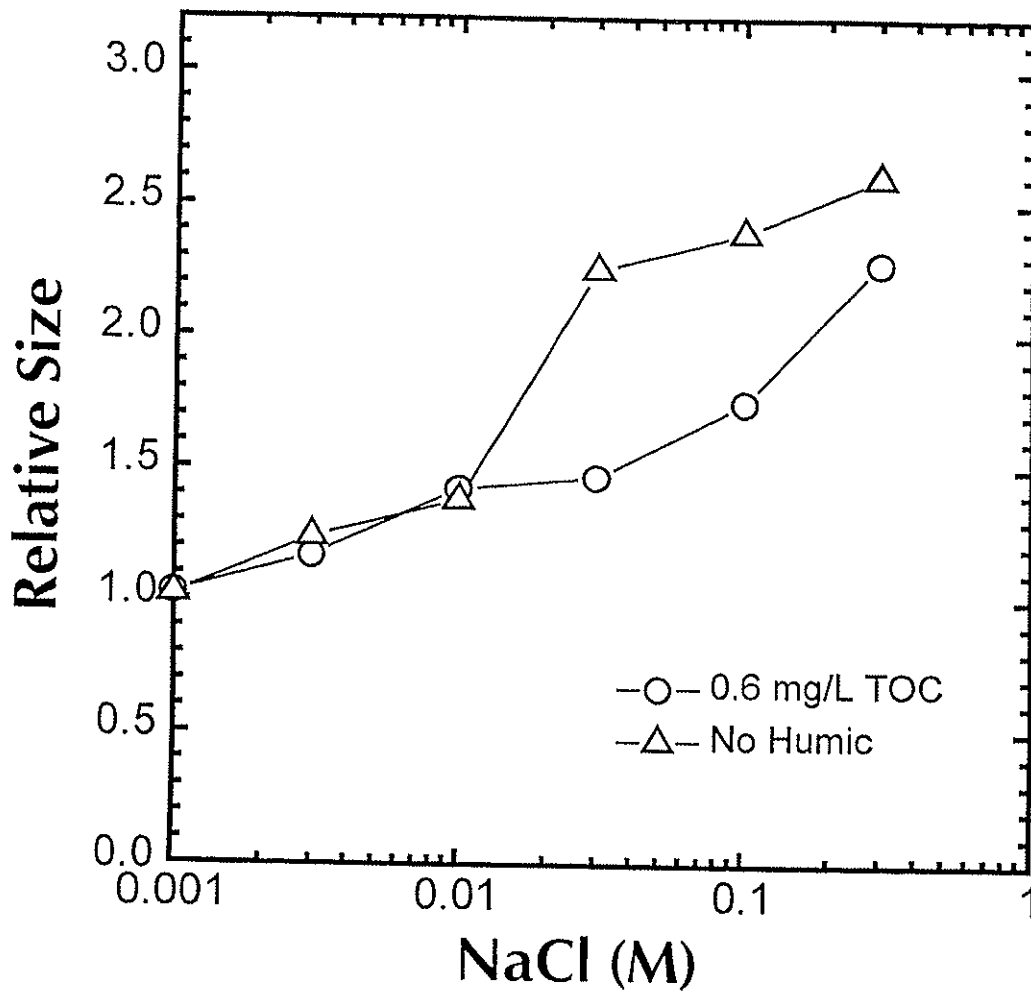
FIGURE 3. Relative Size of the Aluminum Oxide Colloids as a Function of Molar NaCl Concentration After 1 Minute of Coagulation (pH=5.6 to 6.0).

Tiller 1993). Tiller and O'Melia (1993) have shown that, under similar conditions, steric stabilization of humic-coated hematite colloids is not possible, even at high ionic strength where the range of double layer forces is very small. They attributed their results to the flat conformation of the humic macromolecules which do not extend sufficiently into the solution to cause steric stabilization. Hence, the observed coagulation behavior of the aluminum oxide in the presence of humic substances can be explained qualitatively by classical double layer theories. The humic-coated particles are stable at low ionic strengths because of the long range and large magnitude of interparticle double layer repulsion, while they are unstable at high ionic strength due to compression of their electric double layers.

The colloidal stability of the aluminum oxide colloids under various solution chemistries is very important for understanding the fouling behavior of the RO membranes. When colloids are unstable, they deposit onto previously retained particles resulting in a thick fouling layer. Detailed discussion of this important aspect is given later in the report.

Effect of Ionic Strength on Colloidal Fouling

Accelerated fouling tests, demonstrating the effect of ionic strength on membrane fouling, are presented in this section. Accelerated fouling tests were carried out at high particle concentrations (100 mg/L) so that fouling may be observed within reasonable time scales (i.e., within 100 hours of operation). Other experiments, presented in subsequent sections, were carried out at lower particle concentrations (10 mg/L), which may be more typical of actual fouling conditions.

Representative fouling results with thin film composite membranes are shown in Fig. 4. These tests were conducted at three NaCl concentrations: 0.001, 0.01, and 0.1 M (58.4, 584.5, 5845.0 ppm, respectively). The results are presented in terms of the relative water flux as a function of time. The relative flux is the flux at any time during the fouling test divided by the initial water flux through the membrane, just before adding the particles at the end of the membrane equilibration time. The corresponding base line curves for each ionic strength are also included in this figure. The base-line data are for the relative flux in test runs with a particle-free solution.
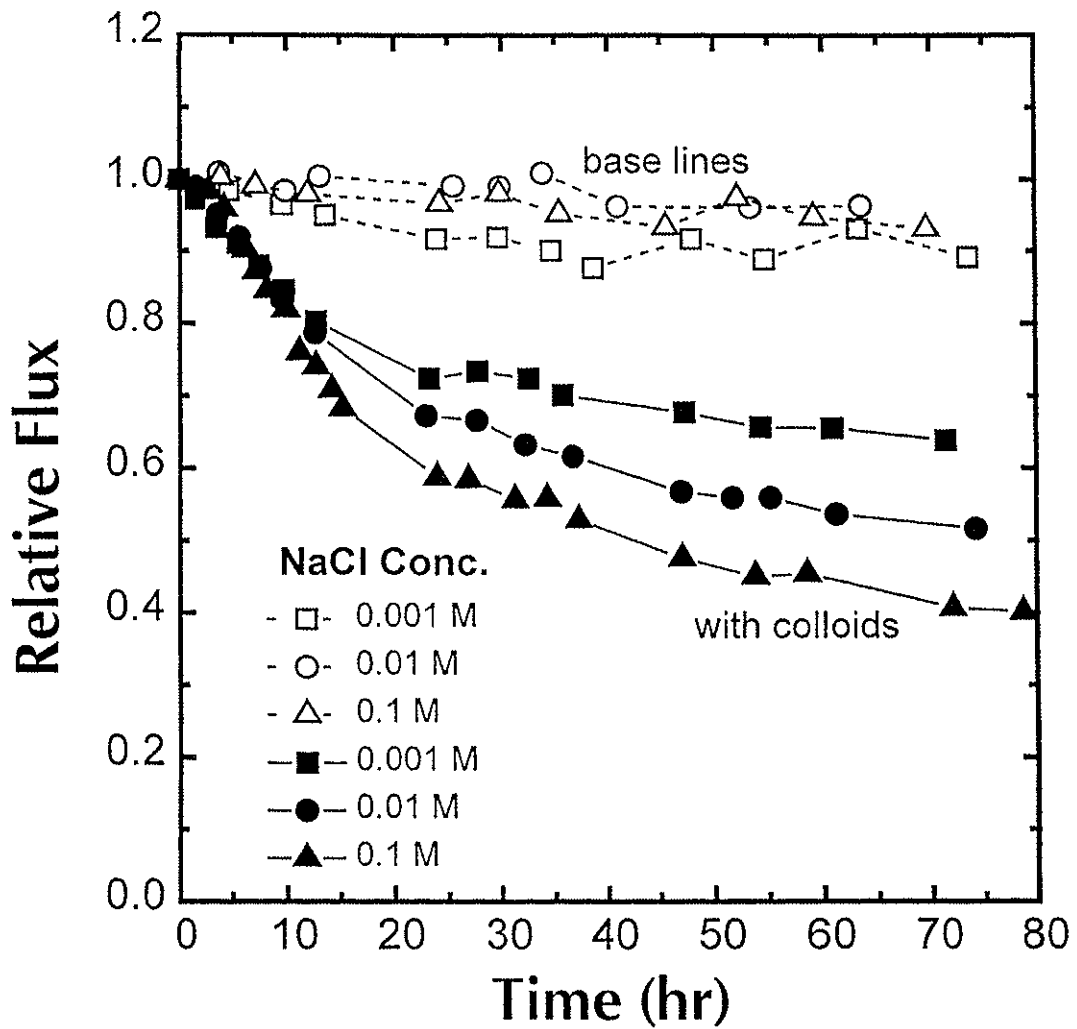
FIGURE 4. Relative Flux as a Function of Time for Three Different Solution Ionic Strengths (Particle Concentration=100 mg/L; pH=5.6 to 6.0; Membrane=Thin Film Composite from Desalination Systems).

The difference between the water flux with particles and the base line represents the net contribution of colloidal particles to membrane fouling.

The base line curves show that water flux decline is obtained even in the absence of colloidal particles in solution. The decrease in permeate water flux in the base line experiments may be attributed to membrane compaction, concentration polarization effects, and certain fouling which is inherent of closed-loop membrane systems (Cohen and Probstein 1986, Mariñas and Selleck 1992, DiGiano et al. 1994). In the presence of aluminum oxide colloids, the rate of membrane fouling and the extent of fouling are more pronounced at higher ionic strengths. Colloidal fouling is very severe at high ionic strength. For example, it is shown that the water flux drops by 60% after 80 hours of operation when the solution ionic strength is 0.1 M.

To explain the fouling behavior observed in Fig. 4, it is imperative to understand the interaction of colloids with the membrane. At the solution pH investigated (5.6 to 6.0), the particles are positively charged (see Fig. 2) while the membranes are negatively charged. At the initial fouling stage, the interaction of particles with membrane surfaces is favorable because particles and membranes are oppositely charged. As the membrane is being covered with aluminum oxide colloids, particles start to interact with previously retained particles rather than with bare membrane surface. At low ionic strength, there exists a strong double layer repulsion between retained particles and newly approaching particles, while at high ionic strength this double layer repulsion is significantly reduced. The extent of fouling layer growth will therefore be dependent on the overall interaction between suspended particles and retained particles on the membrane. In addition to the double layer repulsion, a permeation drag force, perpendicular to the membrane surface, acts continuously in an opposite direction to the double layer repulsion force. The permeation drag, which is proportional to the permeation velocity, can be significant and overcome the double layer repulsive force, thus resulting in particle deposition and formation of a thick fouling layer. The observed fouling curves indicate that even in the presence of strong double layer repulsion (i.e., at 0.001 M NaCl, as implied from the colloidal stability curve shown in Fig. 3), particles deposit onto the membrane to a certain degree because of the transverse transport by permeation drag. At high ionic

strength (0.1 M), double layer repulsion is eliminated and transport by preemption drag results in a thick fouling layer and a significant reduction in water flux.

Representative fouling tests for the cellulose acetate membranes, similar to those discussed above, are shown in Fig. 5. The average base-line curve for the three ionic strengths is also presented at that figure. It is observed that colloidal fouling is significant only at high ionic strength (0.1 M). At the lower ionic strengths investigated, the positively charged aluminum oxide colloids deposit onto the membrane to form a monolayer of particles. The surface coverage by the particle deposit layer is probably small due to the lateral double layer force between retained particles (Song and Elimelech 1993, Adamczyk et al. 1994), so that the impact of the sparse deposit layer on water flux is small. Furthermore, because the permeation velocity through the cellulose acetate membrane is about half of that of the thin film composite, the permeation drag in this case may be smaller than the double layer repulsion force and, as a result, particles cannot deposit onto previously retained particles. On the other hand, at 0.1 M NaCl, double layer repulsive forces are significantly reduced and particles deposit favorably onto previously retained particles, forming a thick fouling layer. This thick fouling layer significantly increases the resistance to water flow, thus reducing the water flux through the membrane.

Figure 6 illustrates the effect of particle concentration on the rate of colloidal fouling of thin film composite membranes at high ionic strength. As expected, under favorable particle–particle interactions, the overall rate of particle deposition onto the membrane increases as the bulk particle concentration increases. Consequently, the thickness of the fouling layer increases and the permeation water flux decreases at a higher rate.

The results shown in Figs. 4 and 5 suggest that an interplay between double layer repulsion and permeation drag may be important in colloidal fouling of RO membranes. It was also shown that particle–membrane and particle–retained particle interactions are key factors controlling the extent of colloidal fouling. These important aspects and additional discussion on the mechanisms of colloidal fouling are given in more details later in this report.

An interesting observation in the fouling experiments discussed above (and those described later in this report) is that membrane salt rejection decreases over time

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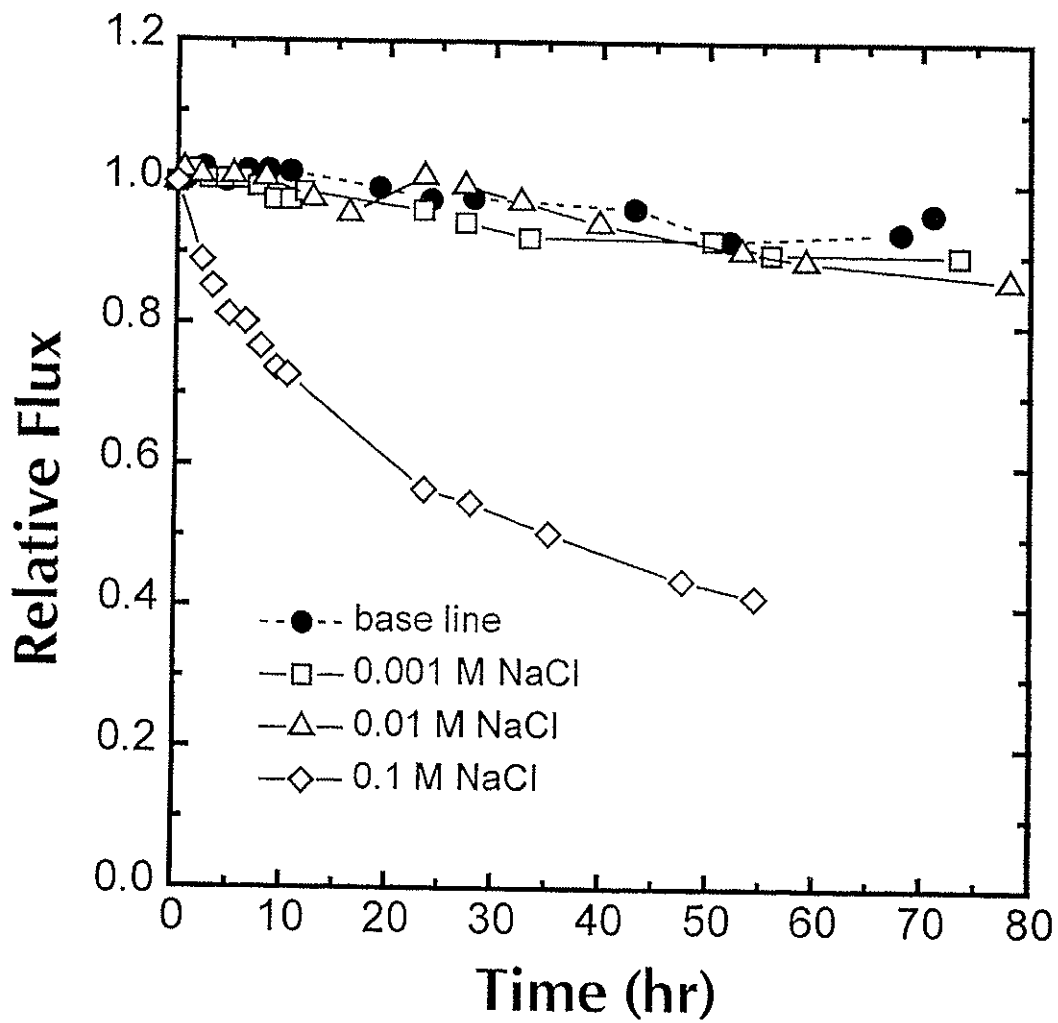
FIGURE 5. Relative Flux as a Function of Time for Three Different Solution Ionic Strengths (Particle Concentration=100 mg/L; pH=5.6 to 6.0; Membrane=Cellulose Acetate from Hydranautics).
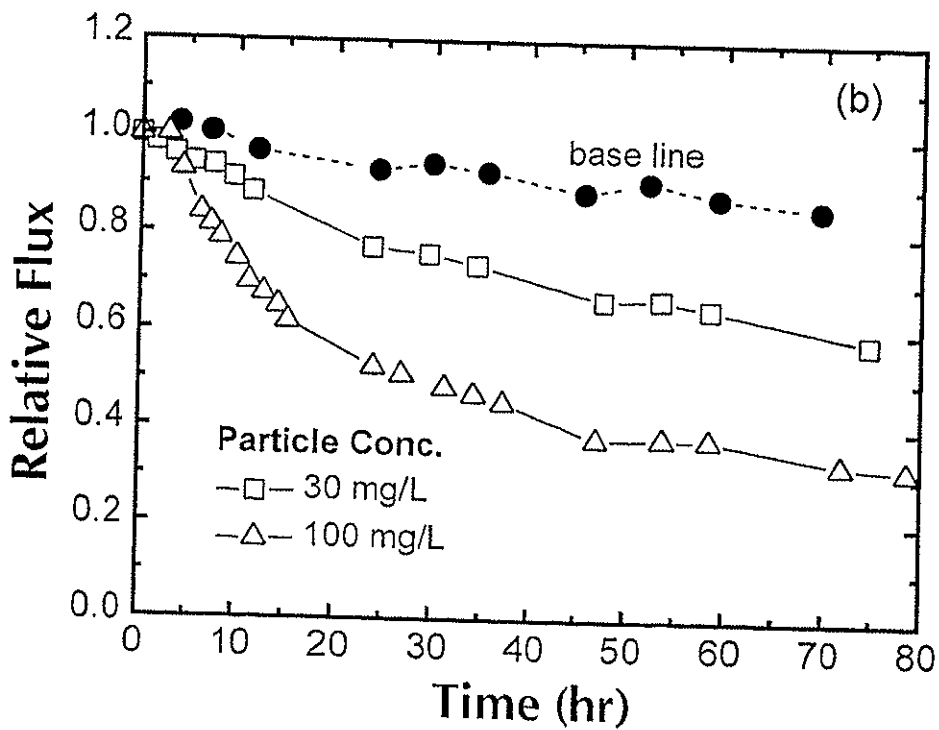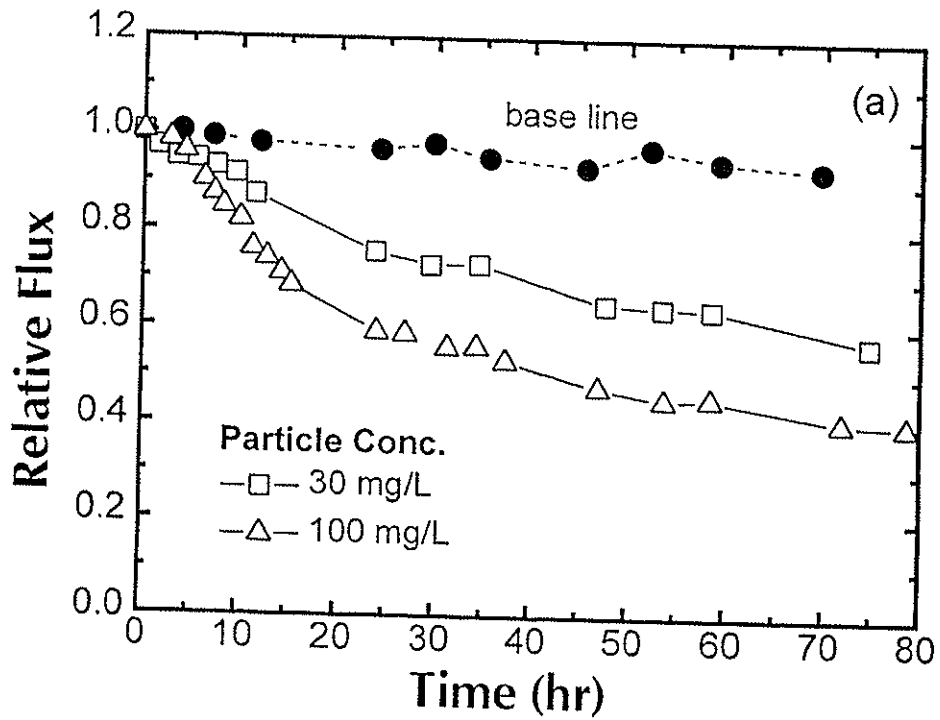
FIGURE 6. Relative Flux as a Function of Time for Two Different Particle Concentrations: (a) Thin Film Composite Membrane from Desalination Systems; (b) Thin Film Composite Membrane from Hydranautics (All Experiments Conducted with 0.1 M NaCl and pH between 5.6 to 6.0).

in the presence of colloidal fouling. This phenomenon was much more pronounced with the cellulose acetate membranes compared to the thin film composite membranes. The decrease in salt rejection (or increase in salt passage) may be attributed to several factors. The first is related to the poor mixing within the fouling layer which enhances concentration polarization and thus increases the passage of salt through the membrane. Such an effect was also observed in cellulose acetate membranes which were subject to biological fouling (Ridgway 1984, 1985). The second reason may be attributed to the reduced permeate water fluxes as fouling occurs, the so-called "dilution effect". As the permeate water flux decreases, the salt concentration in the permeate increases thus resulting in lower salt rejection. We are currently investigating systematically the effect of colloidal fouling on salt passage through RO membranes and will present the results in future publications.

Effect of Humic Substances

Humic substances are the predominant fraction of dissolved natural organic matter (Stumm 1992, Morel and Hering 1993). The effect of humic substances on colloidal fouling should be investigated because most feed waters for RO contain measurable levels of dissolved organic matter. Representative results for the effect of humic substances on colloidal fouling of thin film composite membranes are shown in Fig. 7. These experiments were conducted with three particle concentrations at 0.1 M NaCl and 0.6 mg/L TOC. Also shown in this figure is the base line curve for each membrane; that is, the relative water flux versus time for a solution containing the NaCl and humic substances as used in the fouling tests but without colloidal particles.

The results show that fouling under the above conditions is quite significant. As expected, fouling is more pronounced at higher particle concentrations. It is further shown that, in the absence of colloidal particles (i.e., base line data), the water flux through the membrane does not change with time, thus indicating that the humic substances at the concentration used do not induce membrane fouling. In fact, the base line curves in the presence of humic substances and NaCl show a much more stable water flux than the case with NaCl alone (see data in Fig. 7 compared to those of Figs. 4 and 6).
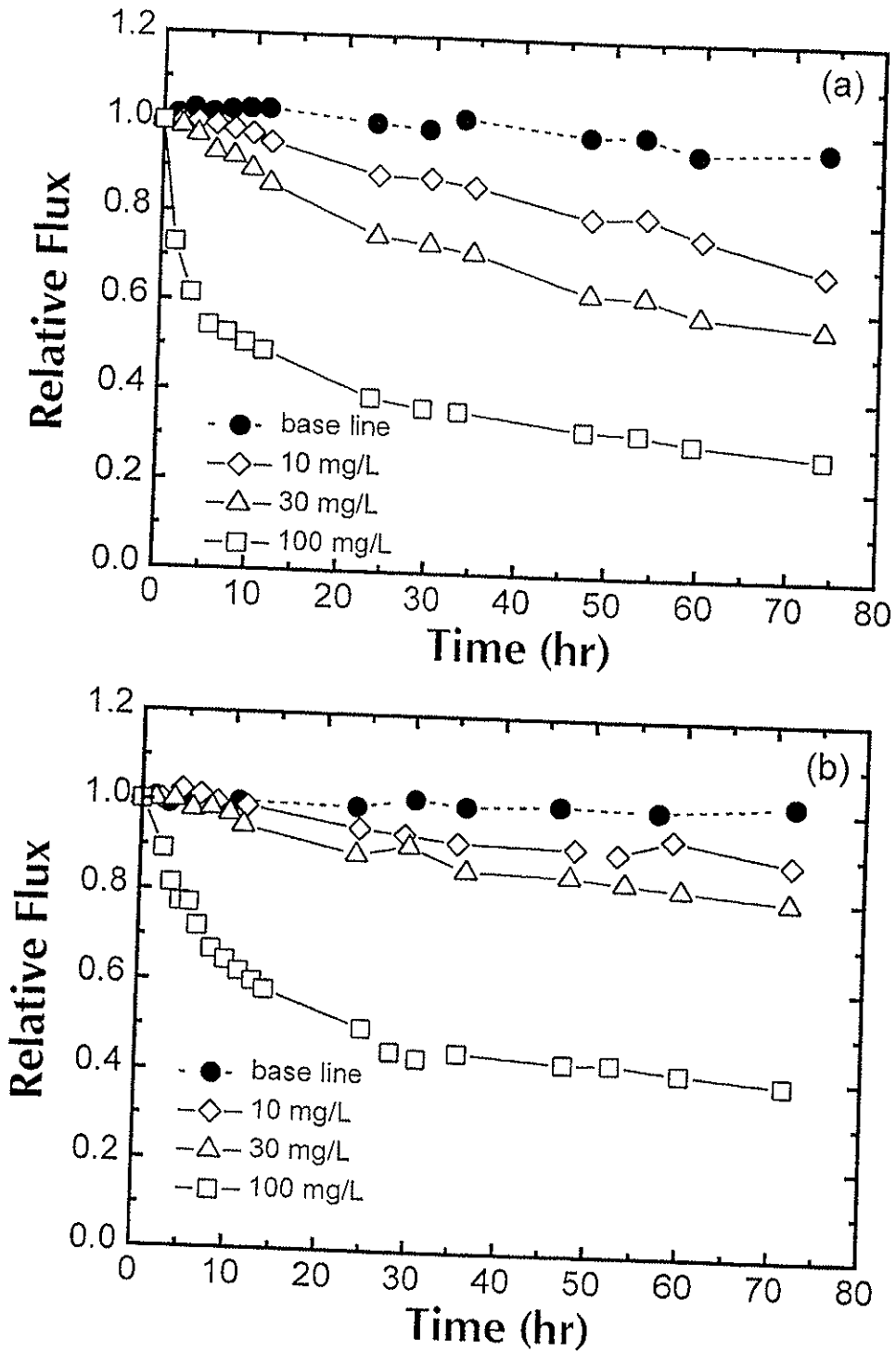
FIGURE 7. Relative Flux as a Function of Time for Three Different Particle Concentrations in the Presence of Humic Substances: (a) Thin Film Composite Membrane from Hydranautics; (b) Cellulose Acetate Membrane from Desalination Systems (All Experiments Conducted with 0.1 M NaCl, 0.6 mg/L TOC, and pH between 5.6 to 6.0).

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To explain the results shown in Fig. 7, we need to refer back to our previous discussion on the electrokinetic properties of particles and membranes and the colloidal stability of the aluminum oxide. Under the chemical conditions employed in the experiments described in Fig. 7, both the membranes and colloidal particles are negatively charged. At 0.1 M NaCl, the electric double layer repulsion between particles and the membrane surface is significantly reduced due to compression of the diffuse double layers of particles and membranes. As a result, particles which are transported to the membrane surface by permeation drag deposit favorably onto the membrane surface. Furthermore, because of the low stability of colloids in a 0.1 M NaCl solution (see Fig. 3), particles also deposit favorably onto previously retained particles. The thick fouling layer formed under these conditions increases the hydraulic resistance, and subsequently, reduces the permeate water flux.

As discussed previously in this report, steric stabilization is not likely to occur when humic substances adsorb onto aluminum oxide at pH below its isoelectric point. Therefore, particle deposition and subsequent fouling of the membranes at high ionic strength under the above conditions cannot be prevented. It is worthwhile to mention that the ionic strength adjacent to the membrane surface is higher than that in the bulk solution due to concentration polarization. Hence, the attachment efficiency of colloids to previously retained particles would be even greater than that expected from the colloidal stability experiments at 0.1 M NaCl. Moreover, the inherent permeation drag acting in opposite direction to the double layer repulsion, further increases the attachment efficiency of suspended particles to the outer surface of the porous fouling layer beyond that predicted from the colloidal stability data.

Finally, it should be indicated that aggregation of particles in the bulk suspension, before transport and attachment to the membrane, complicates the analysis of the experimental results. This aggregation problem is inherent of closed-loop laboratory RO units operating at chemical conditions where particles in suspension are unstable. Samples taken from the feed suspension showed that the particle size measured immediately after sampling increased much less than that under similar chemical conditions in the static coagulation experiments. This is most likely because of aggregate breakage induced by the mixing in the feeding tank and because of the hydrodynamic shear created as the suspension flows through the narrow stainless still

tubes and the various accessories of the closed-loop RO system. The use of a flow-through RO unit (instead of a closed-loop unit) in such controlled fouling experiments is prohibitive because of the excessive quantities of deionized water and chemicals needed for each fouling test.

Reversibility of Colloidal Fouling

To better understand the mechanisms of colloidal fouling, experiments were conducted to test the reversibility of colloidal fouling. In reversibility experiments, a fouling test similar to those described earlier was conducted for 100 hours. After 100 hours, the operation of the RO unit was stopped for a short period of time during which the membranes were gently removed from the cells and rinsed thoroughly by deionized water with a squeeze bottle. After rinsing the membranes and the cells, the membranes were placed back in the cells and operation was resumed for additional 100 hours of fouling.

Results of typical reversibility experiments for a thin film composite membrane and a cellulose acetate membrane are shown in Figs. 8(a) and 8(b), respectively. These experiments were conducted with 10 mg/L aluminum oxide colloids and high ionic strength (0.1 M NaCl) where fouling is significant. The results for both membranes show that flushing with deionized water is sufficient to remove the fouling layer and restore the water flux to a level comparable to that with no particles in solution. The flux of the thin film composite membrane is not restored to its initial value, but the corresponding base line data show that the flux after cleaning is about what expected for operation with a particle-free 0.1 M NaCl solution for a period of 100 hours. The water flux of the cellulose acetate membrane, on the other hand, is completely restored after cleaning with deionized water. After cleaning, the fouling behavior is similar to that observed in the first 100 hours of operation as evident from the shape of the relative flux curves.

The data shown in Fig. 8 indicate that fouling by aluminum oxide colloids under the above chemical conditions is reversible. The results also strongly suggest that aluminum oxide particles do not bind to the membrane surface or block pores in the membrane (the so-called "pore blockage") as usually the case with UF and MF membranes. Fouling is caused by the increased resistance to water flow due to the
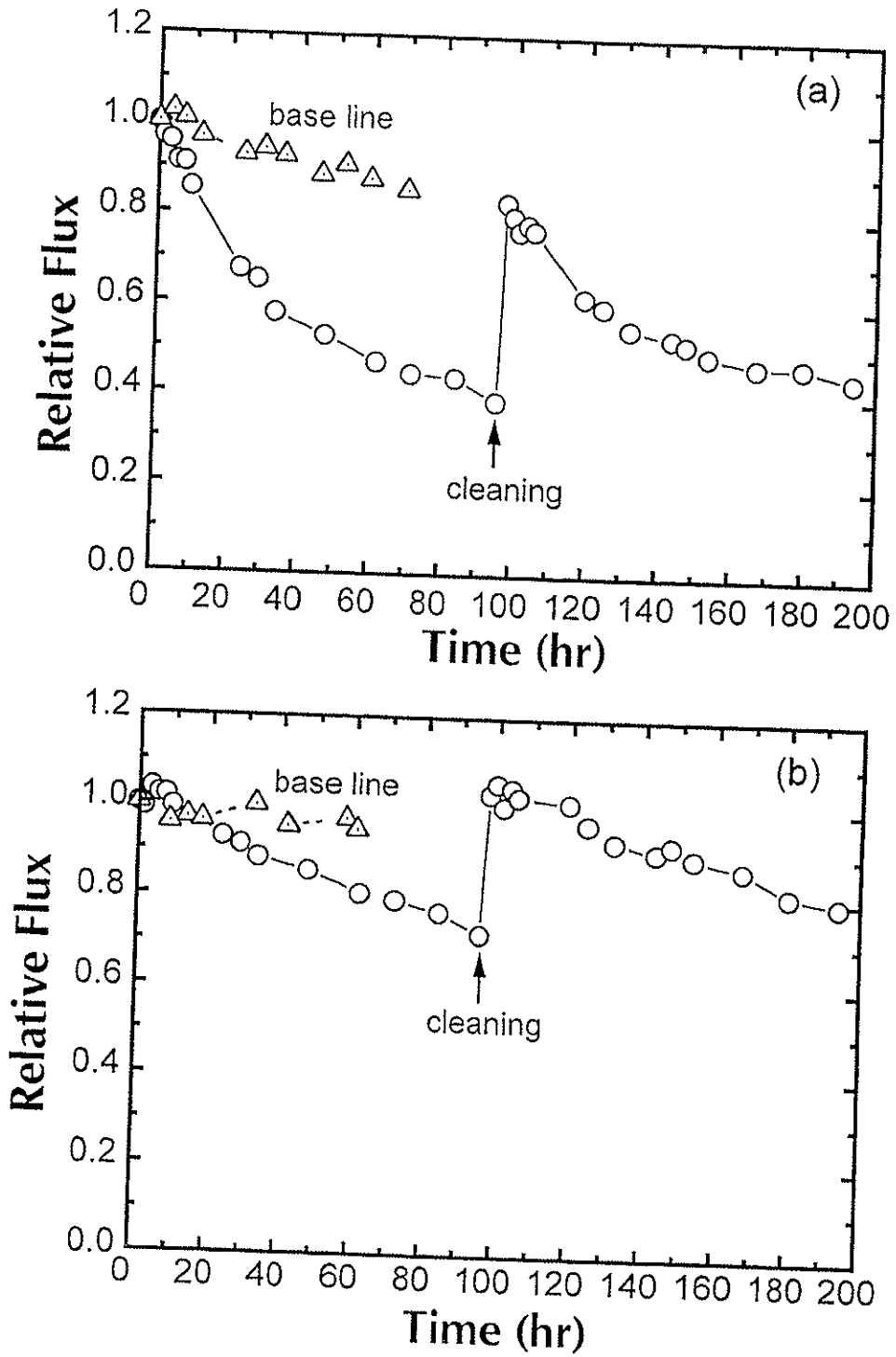
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FIGURE 8. Relative Flux as a Function of Time Before and After Cleaning: (a) Thin Film Composite Membrane from Hydranautics; (b) Cellulose Acetate Membrane from Desalination Systems (All Experiments Conducted with 10 mg/L particles, 0.1 M NaCl, and pH between 5.6 to 6.0).

thick fouling layer. The thick fouling layer of aluminum oxide was clearly visible as the membrane was removed for cleaning and it was seen that flushing removes the fouling layer from the membrane surface.

Reversibility of fouling was also examined for fouling tests in the presence of humic substances (0.6 mg/L TOC) and 0.1 M NaCl in solution. A comparison of such reversibility curves, for fouling of a thin film composite membrane in the presence and absence of humic substances is shown in Fig. 9. It is evident that fouling is reversible also for the case when humic substances are present in solution. As shown earlier (base lines of Fig. 7), the humic substances alone do not induce membrane fouling. In the presence of humic substances and colloidal particles, particles deposit favorably onto the membrane surface at high ionic strength, albeit at a slower rate than the case with NaCl alone. As with the previous results (Fig. 8), particles do not bind to the membrane surface or block pores in the membranes.

Additional reversibility experiments (not shown here) were conducted in the presence of $CaCl_2$ and with humic substances plus $CaCl_2$. Under both chemical conditions, the fouling behavior was similar to that observed in Figs. 8 and 9. None of these cases resulted in irreversible fouling of the membranes by aluminum oxide colloids.

Particle Transport and Deposition Mechanisms onto Semi-permeable Membranes

Prior to postulating a general qualitative model for colloidal fouling, it is essential to understand the mechanisms by which particles are transported from the bulk and deposit onto the membrane surface in cross-flow membrane filtration. Song and Elimelech (1994) have formulated rigorously the complete convective diffusion equation for laminar cross flow over a permeable surface with the inclusion of all relevant particle transport mechanisms. These transport mechanisms include transverse transport due to permeation drag and inertial lift, and transport due to gravitational, van der Waals, and double layer forces. Their analysis showed that the average particle deposition rate onto a permeable membrane surface is determined by an interplay between several transport and interaction mechanisms, among which permeation drag, double layer repulsion, and inertial lift are most important. It was
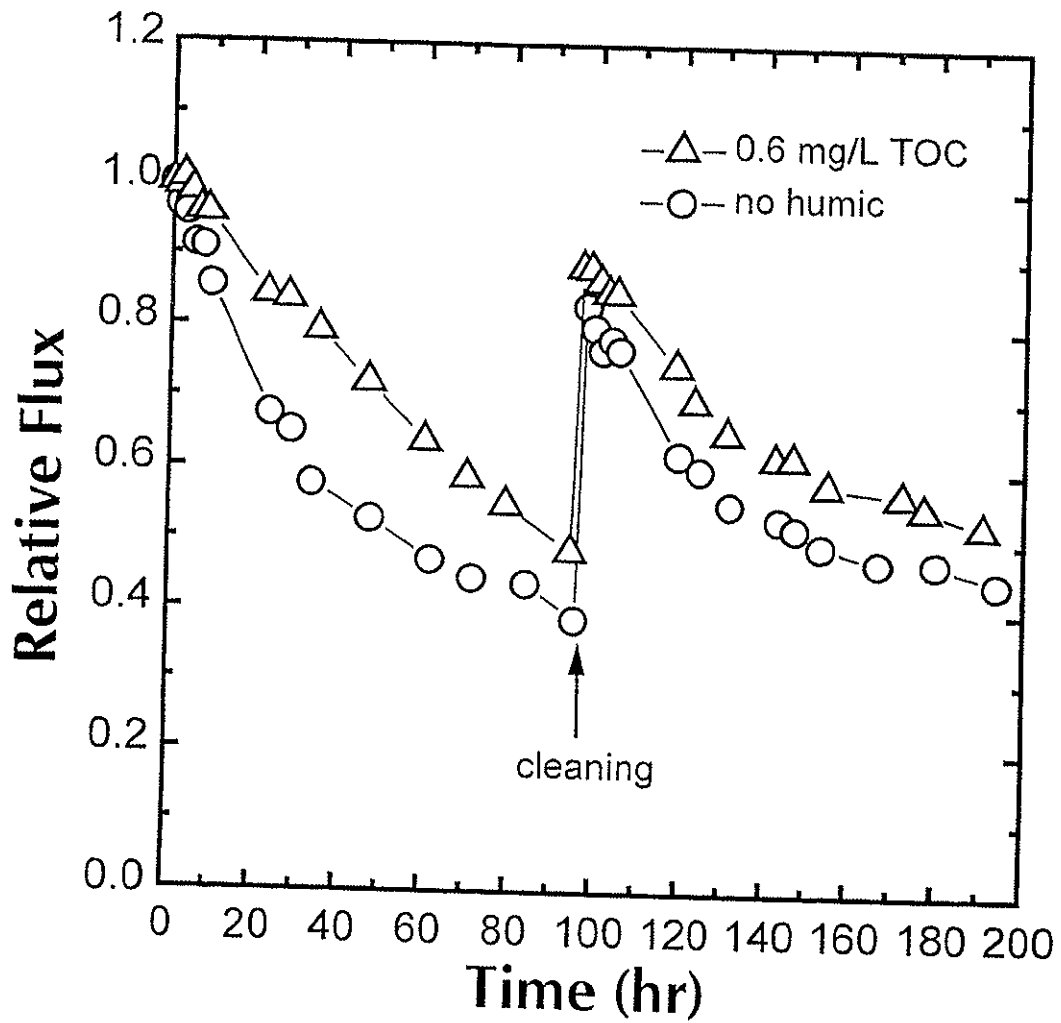
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FIGURE 9. Relative Flux as a Function of Time Before and After Cleaning, with and without Humic Substances (Membrane=Thin Film Composite from Hydranautics; Particle Concentration=10 mg/L, TOC=0.6 mg/L; NaCl Concentration=0.1 M, and pH=5.6 to 6.0).

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also found that deposition of Brownian particles onto semi-permeable membrane surfaces can be significant. This has direct implications for membrane fouling, because Brownian particles which deposit onto the membrane exert higher resistance to water flow than large non-Brownian particles.

Inertial lift is an important mechanism by which large, non-Brownian particles are transported away from the membrane surface (Altena and Belfort 1984, Belfort 1989, Chellam and Wiesner 1992). As a result, this mechanism does not influence the transport and deposition of the submicron aluminum oxide colloids used in this research. The transport mechanisms which mostly apply to our system are the permeation drag force which acts perpendicular to the membrane surface and double layer repulsion which acts in opposite direction to the permeation drag. The theoretical investigation of Song and Elimelech (1994) has shown that at very small permeation drags (i.e., for small permeation fluxes), double layer repulsion may significantly hinder the rate of particle deposition onto the membrane surface. However, as the permeation flux through the membrane increases, permeation drag may overcome double layer repulsion and thus result in particle deposition even at strong double layer repulsions between the particles and membrane. When the permeation drag is large enough, as in the case of UF membranes, permeation drag completely dominate the rate of particle deposition and double layer repulsion does not play any role in particle deposition. It is most interesting to note that the transition from double layer repulsion dominated deposition regime to permeation drag controlled deposition regime occurs at permeation velocities that fall in the range of those employed in RO membranes. Cellulose acetate membranes usually display smaller permeation fluxes than thin film composite membranes (at a comparable applied pressure). Therefore, we should expect that the interplay between double layer repulsion and permeation drag will have a direct effect on colloidal fouling of RO membranes as discussed below.

Colloidal Fouling Mechanisms

Based on the results presented in this report, analysis of transport and deposition mechanisms in cross flow membrane filtration (e.g., Chellam and Wiesner 1992, Song and Elimelech, 1994), and the vast literature on particle deposition onto non-permeable surfaces (e.g., Elimelech 1994ab, Song and Elimelech 1993), we propose the following

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qualitative mechanistic model for colloidal fouling of RO membranes. The fouling behavior of RO membranes in our model is related to solution chemistry, stability of the colloids, electrokinetic charge of particles and membranes, and permeation drag. Four different fouling scenarios, based on the ionic strength and electrokinetic charge of colloids and membranes, are discussed. These cases are for (1) moderate to high ionic strength, particles and membranes are oppositely charged; (2) moderate to high ionic strength, particles and membranes are similarly charged; (3) low ionic strength, particles and membranes are oppositely charged; and (4) low ionic strength, particles and membranes are similarly charged.

(1) Moderate to high ionic strength, particles and membranes are oppositely charged. In this case, the initial deposition of particles onto the oppositely charged membrane surface is favorable. At high ionic strength, there is no lateral repulsion between deposited particles so that their density on the membrane surface is relatively high (Privman et al. 1991, Song and Elimelech 1993, Adamczyk et al. 1994). Since the particles are unstable at high ionic strength, the deposition of suspended particles onto previously retained particles is also favorable. This deposition behavior results in a thick fouling layer, the thickness of which is highly dependent on the hydrodynamic conditions (note that the hydrodynamic conditions were kept unchanged in this research). A schematic representation of this case is shown in Fig. 10. The total resistance to water flow, R_T, is the sum of the clean membrane resistance, R_m, and the fouling layer resistance, R_f. It is hypothesized that, under these conditions, there will be a significant water flux decline and an observable increase in salt passage.

The behavior discussed above is representative of our fouling experiments with aluminum oxide colloids at salt concentrations greater than 0.01 M NaCl (Figs. 4-6). Scanning electron micrographs of a cellulose acetate membrane before and after a fouling test at high ionic strength (0.1 M NaCl) are shown in Fig. 11. These micrographs demonstrate that, as expected, a thick fouling layer of deposited particles is formed on the membrane surface. It should be noted that the fouling behavior described here may also be suitable to RO systems operating at a moderate ionic strength, because an elevated salt concentration at the membrane surface is formed due
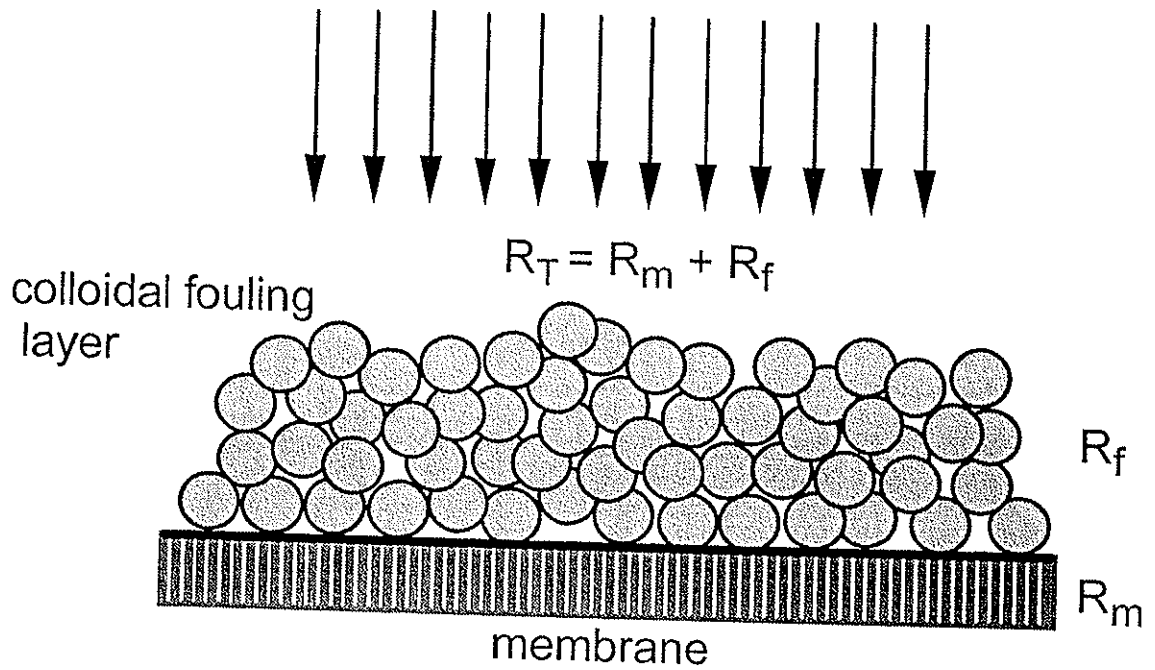
18

FIGURE 10. Schematic Description of a Colloid Fouled Membrane at High Ionic Strength (R_T=Total Resistance; R_m=Membrane Resistance; R_f=Fouling Layer Resistance).
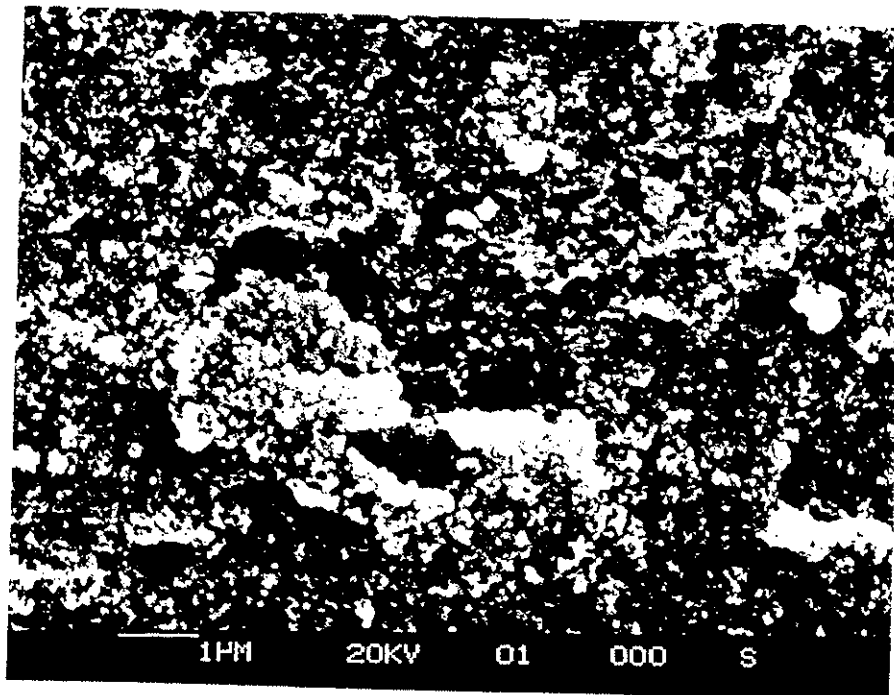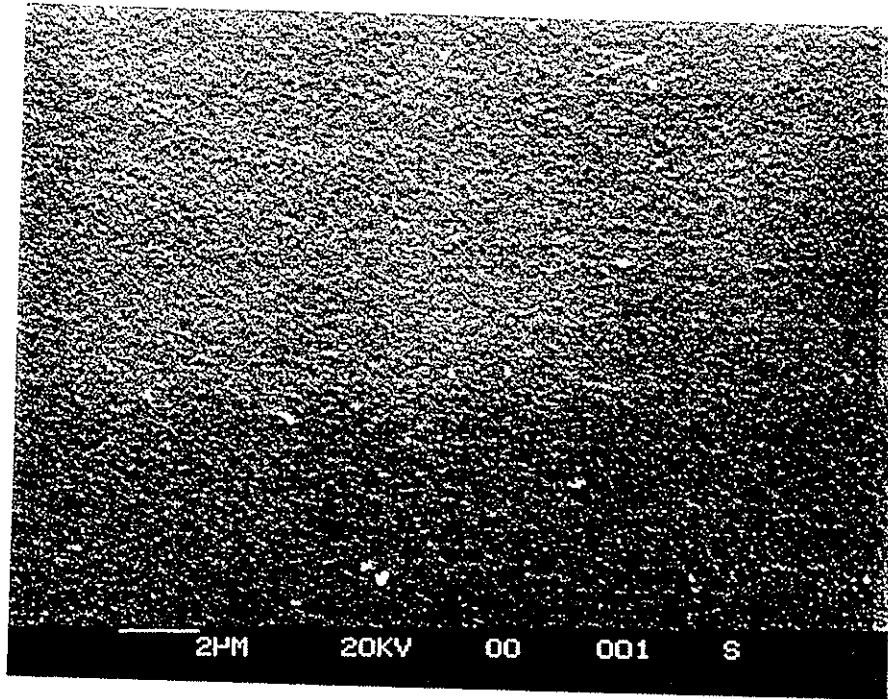
FIGURE 11. Scanning Electron Micrographs of a Cellulose Acetate membrane from Hydranautics: Top - Before Fouling Experiment; Bottom - After Fouling with 100 mg/L Aluminum Oxide Particles at 0.1 M NaCl.

to concentration polarization. In addition, large permeation drags can overcome small double layer repulsion which develops at moderate ionic strengths.

(2) Moderate to high ionic strength, particles and membranes are similarly charged. In this case, the repulsive double layer forces between particles and the membrane surface and between suspended and retained particles are small. As a result, particles deposit favorably onto the membrane surface and form a thick fouling layer as in the previous case. It is hypothesized that, in this case, there will be a significant water flux decline and an observable increase in salt passage. This situation applies to our fouling experiments in the presence of humic substances and high ionic strength, where the particles and membranes are similarly charged (Figs. 7 and 9). It also applies to most RO desalination units processing brackish or sea water, because particles in aquatic environments are usually negatively charged (e.g., O'Melia 1980, Tipping and Higgins 1982, Stumm 1992), and all available commercial RO membranes are negatively charged at the pH range of operation (Elimelech et al. 1994).

(3) Low ionic strength, particles and membranes are oppositely charged. In this case, the initial deposition of particles onto the oppositely charged membrane surface is favorable. Because of the low ionic strength, a strong lateral double layer repulsion exists between retained particles, and the initial density of surface coverage is not too high (Adamczyk et al. 1994). Under these conditions, there also exists a strong double layer repulsion between retained particles and approaching suspended particles. It is postulated that in this case the extent of colloidal fouling will depend on the interplay between double layer repulsion and permeation drag. For RO membranes operating at high permeation rates, permeation drag may overcome double layer repulsion between approaching and retained particles, resulting in the formation of a fouling layer on the membrane surface. Consequently, the permeation flux and salt rejection will be reduced as discussed before. On the other hand, when operating at small permeation rates, double layer repulsion may overcome the opposing permeation drag and fouling will be minimized.

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(4) Low ionic strength, particles and membranes are similarly charged. In this case, a strong double layer repulsion exists between particles and membrane surface. The extent of particle deposition, and subsequently membrane fouling, is dependent on the interplay between double layer repulsion and permeation drag. When operating at small permeation rates, particle deposition may be prevented by the strong double layer repulsion and no fouling will occur. On the other hand, at high permeation rates, as encountered in most operations of thin film composite RO and nanofiltration (NF) membranes, particles may deposit onto the membrane surface and onto previously retained particles because of the strong permeation drag. In this case, fouling can be significant for waters containing measurable levels of suspended colloidal particles.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results reported here, the following conclusions are made:

1. Colloidal fouling of RO membranes results in reduced permeate water flux and salt rejection. The decrease in permeation rate is attributed to the greater resistance to water flow as colloids deposit onto the membrane and form a fouling layer. Increased salt passage (or reduced salt rejection) may be attributed to the poor mixing within the fouling layer which results in enhanced concentration polarization at the membrane surface.

2. The rate of colloidal fouling increases as the solution ionic strength and particle concentration in suspension increase. The increase in fouling rate in this case is attributed to the higher rate of particle deposition onto the membrane surface.

3. To better understand colloidal fouling of RO membranes, one should consider particle–membrane and particle–retained particle interactions. These interactions are controlled by solution chemistry, chemical characteristics of colloids and membranes, and permeation drag force. At high ionic strength, the magnitude and range of double layer repulsion is small, and the rate of deposition of Brownian colloids onto the membrane surface is controlled by permeation drag. At low ionic strength, on the other hand, double layer repulsion may be significant and the rate of particle deposition will be determined by the interplay between permeation drag and double layer repulsion.

4. Permeation drag plays an important role in particle deposition onto membrane surfaces and may ultimately control the rate of colloidal fouling. Because of the inherent permeation drag, significant fouling can be observed even under chemical conditions where a strong double layer repulsion between particles and the membrane surface exists.

5. Under the chemical conditions investigated, fouling of RO membranes by aluminum oxide colloids appear to be reversible. Fouling is attributed to deposition of particles at the membrane surface and no pore blockage mechanism can be invoked.

6. Colloidal fouling can be minimized by reducing the membrane permeation rate or by other hydrodynamic (physical) means. Under usual RO operating conditions, fouling by feed waters with high levels of colloids may not be eliminated by chemical means (e.g., by increasing the stability of colloids) because of permeation drag.

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