SIMULATION OF REVERSE OSMOSIS PROCESSES CONCENTRATING INDUSTRIAL WASTES

(key words: reverse osmosis, membrane, electroplating wastewater, process simulation)

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ABSTRACT

The process parameters of a reverse osmosis system concentrating industrial wastewater in a closed-loop operation have been studied. The model describes system solute concentration as a function of operating time and can be used to predict separation efficiency and permeate flux. The model uses seven parameters that are obtained from membrane and solution data. Simulation of a simple salt system was compared to the experimental data of an inorganic chemical effluent composed of typical plating metals. The results indicate variance from predicted mass transfer and overall membrane performance. The model is useful in predicting performance when membrane fouling is not a major problem.

INTRODUCTION

Separation and concentration techniques are key processes in industrial effluent treatment. Membrane processes have advanced in industrial applications over traditional separation processes like distillation, evaporation, extraction, etc. The membrane processes of reverse osmosis (RO), ultrafiltration...
(UF), microfiltration (MF), and pervaporation (PV) are being viewed strongly by the industrial community due to their ability to purify a process fluid of its solute(s) and recover the solute(s) in a concentrated form [1]. Industrial wastewater treatment applications have been found in the agricultural, biochemical, chemical, electrochemical, food, pharmaceutical, petrochemical, and pulp and paper industries.

This paper discusses the use of a closed-loop reverse osmosis process for concentrating industrial effluents. Comprehensive reviews of membrane process applications to the various industries for wastewater treatment are available [2,3]. The electrochemical industry has been used here as one example. Process utilization of reverse osmosis for pollution abatement and resource recovery in the electrochemical industry is presented.

Separation methods employing reverse osmosis have become practical in the electroplating industry because of the inherent disadvantages of end-of-the-pipe treatment - that is, loss of valuable plating chemicals, cost of treatment chemicals, and cost of toxic sludge disposal - recycle and recovery [4-6]. Although other techniques are under development, reverse osmosis is one of the processes accepted for rinse water recovery. Recovery of 90 to 95% of the water from plating operations has been achieved, together with separation of most metal species in these treatment and reuse systems [7,8]. Case studies on electroplating commercial operations using reverse osmosis membrane technology have shown that it is an effective and economical approach to the wastewater problem [6,9].

McNulty et al [10] evaluated a hollow fiber unit for treatment of rinse water from a Watts-type nickel electroplating bath. Dissolved solids, including nickel, were rejected satisfactorily, and the conductivity of the treated water was, as expected, very low. Nickel can be recovered efficiently from the rinse waters of these plating baths; cellulose acetate membranes reject nickel at levels of 99% [11]. Tin-nickel plating wastes have also been renovated successfully and reused [12]. Schrantz [13] has described how copper-laden wastewater is recycled through a closed-loop reverse osmosis system at an electroplating plant. Weekly copper consumption was reduced by one-third. Copper cyanide rinse waters were also treated by reverse osmosis at two major plating companies, however, membrane life was a significant problem [14].
Several different membrane materials were used successfully by McNulty and Hoover [15] to treat electroplating rinse water with high oxidizing power and extreme pH levels. A membrane cast of poly(ether/amide) on polysulfone was found to be superior to other membranes for separation of concentrated copper and zinc cyanide and chromic acid wastes at plating bath concentrations up to 25%. Cellulose acetate membranes failed because of operation outside their pH range of 2.5 to 7.0.

Slater et al [16] have used thin film composite membranes composed of polyamide on polysulfone to separate a cadmium laden waste stream. Cadmium levels were reduced from 165 to 0.003 mg/l under optimal processing conditions. Concentrations of other metals (copper, zinc, nickel) and overall conductivity were rejected in excess of 98%. Cadmium can be effectively concentrated in batch operation while generating high quality water for reuse. The thin film composite membranes were effective in operating at a broad range of processing conditions such as acidic and basic pH levels and pressures up to 900 psi. Studies with the actual plant waste stream indicate that prefiltration before reverse osmosis is necessary to eliminate the problem of membrane fouling.

Removal of toxic inorganic substances present in electrochemical industry wastewaters was summarized by Kosarek [17]. RO is capable of removing the toxic metals, i.e., antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc, that along with cyanide can threaten drinking water supplies. All of these species were rejected in excess of 90% (ionic removal). In addition to wastewater renovation, these expensive metals can be concentrated and reclaimed to reduce overall operating costs.

**THEORY**

Mass transfer through a reverse osmosis membrane can occur by several mechanisms in which various models have been proposed [9,18-21]. This paper utilizes the solution-diffusion models to represent water and solute transport through the membrane. In this model species goes into solution with the membrane and diffuses through the membrane at a rate corresponding to the
applied transmembrane pressure, $\Delta P$, and the individual concentration gradient, $\Delta C_i$, across the membrane.

The water flux, $J_w$, is directly related to the transmembrane or hydraulic pressure driving force, $\Delta P$, minus the difference in osmotic pressure, $\Delta \pi$, on both sides of the membrane:

$$J_w = A_w(\Delta P - \Delta \pi)$$  \hspace{1cm} (1)

The flux and pressure gradients are related by the water permeability coefficient, $A_w$.

The solute flux, $J_s$, is related to the concentration gradient on both sides of the membrane, $\Delta C_s$, by a solute permeability coefficient, $B_s$:

$$J_s = (B_s)(\Delta C_s)$$  \hspace{1cm} (2)

The concentration gradient is denoted as feed solute concentration in the boundary layer at the membrane, $C_{fm}$, minus permeate solute concentration, $C_p$:

$$\Delta C_s = C_{fm} - C_p$$  \hspace{1cm} (3)

For simplicity the boundary layer concentration can be set equal to the bulk stream concentration although a more accurate equation based on feed stream conditions may be employed [18-21].

Solute rejection, $R$, can be measured as a relationship between feed and permeate solute concentrations:

$$R = \frac{C_f - C_p}{C_f}$$  \hspace{1cm} (4)

It can be demonstrated from the solute and water flux equation that rejection is a function of pressure and concentration gradients. Water flux is dependent on pressure; therefore, an increase in pressure will increase water flux at constant solute flux, i.e., decrease permeate solute concentration and increase percent solute rejection. This can be shown by combining the flux equations and relating them to solute rejection. The final form of this relationship is:

$$R = \left[ 1 + \frac{(B_s)(C_{wp})}{A_w(\Delta P - \Delta \pi)} \right]^{-1}$$  \hspace{1cm} (5)

In this relationship $C_{wp}$ is the concentration of the water in the permeate.
Various configurations of membranes can be used for operation in industry. The simple case of single-pass operation is shown in Figure 1. In this configuration a constant feed rate and composition are utilized. Retentate (concentrate) and permeate streams are removed separately from the membrane module. The flow rate of the feed (f), retentate (r) and permeate (p) is represented by Q. The solute concentrations in those streams are C_f, C_r and C_p, respectively. In the absence of any effects of fouling or membrane compaction, all process parameters, e.g., permeate concentration and flux, remain the same with time.

An overall system material balance for steady-state operation yields:

$$Q_f = Q_r + Q_p$$  \hspace{1cm} (6)

A mass or component balance on the solute yields:

$$(C_f)(Q_f) = (C_r)(Q_r) + (C_p)(Q_p)$$  \hspace{1cm} (7)

Single-pass system recovery or conversion, Y, is the ratio of permeate flow rate per feed rate to the membrane:

$$Y = \frac{Q_p}{Q_f}$$  \hspace{1cm} (8)

Large scale commercial units are designed on a modular basis. To increase feed capacity, modules can be combined in the parallel arrangement. This
arrangement allows for the accommodation of high feed rates and for the option of varying feed rates to produce constant production of permeate. To increase single-pass recovery a series of modules is normally employed. A combination of the above two configurations yields a tapered or cascade arrangement (Figure 2). This is the processing mode commonly employed in large-scale commercial installations.

A continuous closed-loop or recycle configuration returns a fraction of the retentate stream to the feed stream (Figure 3). A system arranged in a closed-loop configuration with an initial feed volume can be used to simulate higher recoveries using one or several membrane modules. Overall, or final, system recovery, $X$, in this closed-loop operating mode is defined as the volume
FIG. 3. Closed-loop or recycle membrane system.

of product produced per initial feed volume over a given time interval:

\[ X = \frac{V_f}{V_{fo}} \]  \hspace{1cm} (9)

Modeling of systems operating in this mode are strenuous due to the many variables that exist. A thorough development is presented by Slater et al [22], and a mathematical derivation will be limited here since it is not the primary focus of this paper. Material balances are made around the membrane and feed tank express the change in performance characteristics the system. Differential equations are written in terms of operating time. A relationship between the system material balances and mass-transfer models is made. The solute and water flux equations can be expanded by a relationship between osmotic pressure and solute concentration. The resulting equation can be represented by the following:

\[ \frac{dC_f}{dt} = \left( C_{fo}, V_{fo}, S, \Delta P, A_w, B_s, \frac{\pi}{C} \right) \]  \hspace{1cm} (10)

The initial system and operating parameters that must be known for this equation to be solved are as follows: initial solute concentration of the feed, \( C_{fo} \); initial feed volume, \( V_{fo} \); membrane surface area, \( S \); transmembrane pressure, \( \Delta P \); water permeability coefficient, \( A_w \); solute permeability coefficient, \( B_s \); and the osmotic pressure to solute concentration ratio, \( \pi/C \), [23].
The actual equation is a nonlinear differential equation that can be solved numerically. The solution establishes feed tank solute concentration as a function of processing time. Once $C_t$ is calculated at any time, the permeate concentration, rejection and flux can be obtained from the solution-diffusion models. Final system recovery is calculated from the amount of permeate produced per original feed volume.

**EXPERIMENTAL PROCEDURE**

The closed-loop configuration (Figure 3) is the basis for the work described in this paper. The retentate stream is recycled to the feed tank in this process. An initial feed volume is utilized. As time of operation progresses, the feed solute concentration increases due to the returning retentate stream. The volume of feed decreases in proportion to the production rate of the membrane. As feed volume diminishes and concentration increases, the system will operate as if it were running in sequential increments of increasing concentration in a simple single-pass operation. This type of system allows operation at high feed flow rates. It also allows the use of a small-scale system to obtain high final system recoveries that are usually only obtainable with large-scale commercial units. At some point the system must be stopped because the solute concentration in the feed can exceed its solubility limit and precipitate out or foul the membrane. High solute concentrations can also cause problems with concentration polarization even with high feed velocities.

The experimentally modeled system was composed of a 4" diameter - 40" long, spiral wound cellulose acetate membrane in a high-pressure module, both manufactured by Fluid Systems-UOP. A high pressure, low-volume pump was used to feed the membrane module from a $7.57 \times 10^5$ cm$^3$ (200 gal maximum capacity) tank. The temperature was maintained at 25 °C, and the pH was kept at 5.0 for all studies. The system was flushed between runs with an enzymatic detergent to clean the membranes. Since the initial modeling studies were done on a salt water system, membrane compaction, and not fouling, would be the reason for any flux decline. Fouling was evident in the industrial wastewater study.
TABLE 1
Experimental Parameters for Reverse Osmosis Study #1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_0 ) (initial)</td>
<td>( 1.00 \times 10^3 ) g/cm(^3)</td>
</tr>
<tr>
<td>( V_0 ) (initial)</td>
<td>( 3.785 \times 10^5 ) cm(^3)</td>
</tr>
<tr>
<td>( S )</td>
<td>( 6.50 \times 10^4 ) cm(^2) (one membrane module)</td>
</tr>
<tr>
<td>( \Delta P )</td>
<td>27.2 atm</td>
</tr>
<tr>
<td>( Q_f )</td>
<td>328.6 cm(^3)/sec</td>
</tr>
<tr>
<td>( Y )</td>
<td>10.0%</td>
</tr>
<tr>
<td>( \pi/C )</td>
<td>( 775.5 ) atm/(g/cm(^3))</td>
</tr>
<tr>
<td>( C_p ) (initial)*</td>
<td>( 8.00 \times 10^5 ) g/cm(^3)</td>
</tr>
<tr>
<td>( A_w ) *</td>
<td>( 1.96 \times 10^4 ) g/cm(^2)-atm-sec</td>
</tr>
<tr>
<td>( B_i ) *</td>
<td>( 2.10 \times 10^{-5} ) cm/sec</td>
</tr>
</tbody>
</table>

* These parameters were obtained from initial experimental studies at the above process conditions.

Simple analytical assays for total dissolved solids (TDS) were used to measure solute concentrations in the feed, permeate and retentate. Conductivity measurements were performed to confirm the trends. Total organic carbon (TOC) assays were used to determine the organic concentration. All assays were done in accordance with Standard Methods for the Examination of Water and Wastewater [24].

RESULTS AND DISCUSSION

An initial study was conducted to examine the changes in process parameters for the system operating in a closed-loop configuration. A NaCl aqueous feed solution was utilized since; (1) it yields to modeling well, (2) chances of fouling are low, and (3) existing data is available. The following test conditions used in Study #1 are shown in Table 1.
Process time and final system recovery are depicted in Figure 4 for the test case. This is an important relationship in closed-loop operation design. From this simulation it is seen that the final volumetric system recovery is linear until approximately 75% and increases exponentially thereafter. For a system with an initial feed volume of $3.785 \times 10^5$ cm$^3$ (100 gal), it would take 16,200 sec (4.5 hr) to recover $3.71 \times 10^5$ cm$^3$ (98 gal), i.e., 98% final system recovery. This would yield a retentate of $19.55 \times 10^3$ g/cm$^3$ (19,500 mg/l) which is almost a 20-fold increase in the initial concentration of the feed (Figure 5). At high concentrations, concentration polarization would become a problem as would fouling when processing high strength industrial wastewaters [25]. Therefore, estimation of actual processing performance at lower recoveries or concentration increases is more accurate.

This model also shows how the permeate flux decreases with system recovery or time (Figure 6). The flux was initially $5.20 \times 10^4$ g/cm$^2$-sec and remained within 10% of its original value up to 80% final system recovery where its value was $4.68 \times 10^4$ g/cm$^2$-sec. The flux decreased rapidly at this

FIG. 4. Process time vs. final system recovery for simulation Study #1.
SIMULATION OF REVERSE OSMOSIS

FIG. 5. Feed and permeate solute concentrations vs. final system recovery for simulation Study #1.

FIG. 6. Permeate flux vs. final system recovery for simulation Study #1.
FIG. 7. Feed solute concentration vs. final system recovery for initial feed concentrations of 0.5, 1.0, 2.0, 5.0, and 10.0 x 10^{-3} g/cm^3 (Study #2).

point because of the large increase in osmotic pressure of the feed. At 98% final system recovery, the flux was 2.61 x 10^{-4} g/cm^2-sec, which was 50% less than it was before the system started concentrating. At this time in the system operation the osmotic pressure of the feed was 15.2 atm.

Study #2 simulates the effects of increase in initial feed concentration on performance of this membrane process. Various initial feed concentrations were studied in this simulation utilizing the same process conditions of Study #1. Figures 7 and 8 show the effects of increasing the feed concentration from 0.50 to 10.00 x 10^{-3} g/cm^3 on system concentration and flux profiles.

As the initial feed concentration increased, initial permeate flux dropped due to the effects of the high solute osmotic pressure. The flux decreased more sharply for the more concentrated feed due to the effects of the high solute
osmotic pressure on the production rate. Concentrating a feed with an initial solute concentration of 10.0 x 10^{-3} g/cm^3 would be more difficult, for the effects of increasing feed osmotic pressure would become more pronounced at lower final system recoveries. An analysis of the system parameters indicated that at a feed concentration of approximately 35 x 10^{-3} g/cm^3, production would cease due to the osmotic pressure of the feed exceeding the applied transmembrane pressure.

An industrial wastewater, characterized by high inorganic salts and dissolved metals, similar to the electrochemical industry, was concentrated in Study #3. Filtration was used as the pretreatment technique prior to reverse osmosis. The concentration of the industrial effluent fed to the membrane system was diluted to the same TDS concentration used in Study #1, 1.00 x 10^{-3} g/cm^3. The pH of the wastewater was adjusted to 5.0 in the pretreatment step.
A diverse mixture of common salts and metals comprised the TDS concentration, the major components were sodium, potassium, copper, nickel and chromium. The organic composition, measured by TOC assay, was $7.50 \times 10^{-3}$ g/cm$^3$. Process trends were compared to Study #1. All processing parameters were the same as in the initial study.

Two major problems were evident upon concentrating this effluent: rejection was lower and the flux declined more rapidly than was expected. Flux versus system recovery is shown in Figure 9 compared to the salt (NaCl) simulation. The initial flux, at 0% final system recovery, was $5.05 \times 10^{-4}$ g/cm$^2$-sec. At 50% final system recovery, flux was 13% less; and at 80% final recovery, flux was 44% less than the salt model predicts. Several reasons exist for this behavior. The osmotic pressure to solute concentration ratio is higher causing a lower initial flux, and fouling is evident at high system recoveries.
Rejection of the industrial constituents was less than that of Study #1. Figure 10 shows the comparison of permeate concentrations in both studies. The industrial wastewater had a lower original rejection due to its higher solute permeability, and, hence, its solute permeability coefficient was higher than that of the salt in Study #1. Due to the fouling that occurred, the permeate concentration was also higher as rejection dropped. At 50% final system recovery the permeate stream concentration was $2.2 \times 10^4 \text{ g/cm}^3$; the salt simulation model on the other hand, predicts a $0.78 \times 10^4 \text{ g/cm}^3$ concentration. At 85% final system recovery deviation from the simple salt case is greater, with the actual permeate concentration being $14.1 \times 10^4 \text{ g/cm}^3$.

At moderate processing times or final system recoveries the salt model is useful in showing processing trends that should be expected. The inorganic wastewater can be more accurately modeled by employing its actual osmotic pressure to solute concentration ratio and solute permeability coefficient. When these factors are employed, initial values agree and simulation profiles more accurately trace the experimental data.
The model does not account for the mass-transfer inhibiting effects of concentration polarization and fouling present in concentrating high-strength industrial wastewaters. This causes deviations from the model at long operating times or recoveries. Evaluation of membrane material from an earlier industrial wastewater study showed that metals present in the waste were on the surface of a fouled membrane. Although many researchers have modeled experimental data on fouling phenomena, prior prediction of its effects on the process trends without extensive work with that particular wastewater are difficult. The contribution of membrane degradation to the flux decline was considered small since the organic content of the waste was relatively low and the pH was initially adjusted to 5.0 and was maintained within operating range for the duration of the processing study.

CONCLUSIONS

The process parameters of a small reverse osmosis system concentrating various feeds in a closed-loop concentration mode can be adequately modeled. This process uses an initial feed volume which is concentrated while permeate is produced. The model describing system performance presents feed concentration as a function of operating time and is dependent on the initial feed concentration, volume, membrane size, transmembrane pressure, mass-transfer and osmotic pressure coefficients. The model is derived by combining mass-transfer relationships for solute and water flux and component material balances. Various process parameters can be examined using this system-specific model. The effect of initial feed concentration on permeate flux was studied, along with concentration vs. recovery profiles of the feed and permeate.

Simulation of a simple salt system can be utilized to predict industrial wastewater processing trends and deviation due to non-ideal mass-transfer. Two deviations from model behavior were evident in concentrating the inorganic wastewater: solute rejection and water flux were lower than the model predicted. The initial deviations were due to the actual osmotic pressure to solute concentration ratio and the solute permeability coefficient of the inorganic wastewater being slightly higher than the simple salt. The presence of
concentration polarization and fouling in treating the industrial effluent were the major factors attributing to deviations from the simulation model.

**NOTATION**

\[ A_w \] = \text{water permeability coefficient (g/cm}^2\text{-atm-sec)}

\[ B_s \] = \text{solute permeability coefficient (cm/sec)}

\[ C_c \] = \text{concentrate solute concentration (g/cm}^3\text{)}

\[ C_f \] = \text{feed solute concentration (g/cm}^3\text{)}

\[ C_{bn} \] = \text{feed solute concentration in the boundary layer at the membrane (g/cm}^3\text{)}

\[ C_i \] = \text{individual solute concentration (g/cm}^3\text{)}

\[ C_p \] = \text{permeate solute concentration (g/cm}^3\text{)}

\[ C_s \] = \text{solute concentration (g/cm}^3\text{)}

\[ C_{wp} \] = \text{concentration of water in the permeate (g/cm}^3\text{)}

\[ J_s \] = \text{solute flux (g/cm}^2\text{-sec)}

\[ J_w \] = \text{permeate flux (g/cm}^2\text{-sec)}

\[ \Delta P \] = \text{transmembrane pressure (atm)}

\[ Q_c \] = \text{concentrate flow rate (cm}^3\text{/sec)}

\[ Q_f \] = \text{feed flow rate (cm}^3\text{/sec)}

\[ Q_p \] = \text{permeate flow rate (cm}^3\text{/sec)}

\[ R \] = \text{solute rejection}

\[ S_s \] = \text{surface area of the membrane (cm}^2\text{)}

\[ V_{fo} \] = \text{initial feed volume (cm}^3\text{)}

\[ V_p \] = \text{volume of permeate produced (cm}^3\text{)}

\[ X \] = \text{final system recovery}

\[ Y \] = \text{single-pass recovery or conversion}

\[ \Delta \pi \] = \text{osmotic pressure difference between feed and permeate (atm)}

**REFERENCES**


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Descriptors: wastewater treatment; industrial effluents; electroplating; reverse osmosis; membranes; simulation

Metal recovery from wastewater using membranes

This paper outlines the requirements for metal recovery from wastewater, with particular reference to electroplating. The technical features of three alternative membrane processes are described. Nanofiltration is shown to separate ionic species on the basis of coulombic interactions or hydrated ion size, which leads to either a "charge" pattern or a "hydration" pattern of rejection. These rejection patterns provide ion selectivity. Ultrafiltration (UF), coupled with ion-complexing polymers or ion exchange resin, also provides
Surface Finishing Pollution Prevention Citation Database

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Abstract: The membrane separation technologies of microfiltration, ultrafiltration, reverse osmosis and electrolysis all possess characteristics which make them attractive for industrial pollution control applications. A review of the basics of these technologies will aid in understanding how they can be applied to pollution control.

Metal Finishing Information:
Industrial Sector:

Metal Finishing Process
Unit Operation

Other Metal Finishing Process:
Other Unit Operation:
Pollution Prevention/Waste Management Method:

Media Assessed: Air Water Solids Energy

Technology Data:
Performance Notes:
Description Of Application:
Operational Performance:
Maintenance Requirements:
Pollution Prevention Information:

Performance Values:

Volume or Flow:

Toxics Investigated Units Initial Conditions Final Conditions Removal Rate

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