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Selective Coagulant Recovery from Water Treatment Plant Residuals Using Donnan Membrane Process

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Fouling of membrane surfaces by particulate matter and large organic molecules is relatively common for pressure-driven membrane processes, namely, reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF). Donnan membrane process (DMP) or Donnan Dialysis is driven by electrochemical potential gradient across a semipermeable ion exchange membrane. Theoretically, DMP is not susceptible to fouling by fine particulates and/or large organic molecules. According to information available in the open literature, however, DMP has not been tried to treat slurry or sludge with relatively high concentration of suspended solids or large organic molecules. This study presents the salient results of an extensive investigation pertaining to selective alum recovery from water treatment residuals (WTR) using DMP. Water treatment plants use alum, $Al_2(SO_4)_3 \cdot 14H_2O$, as a coagulant, alum being finally converted and discharged as insoluble aluminum hydroxide along with natural organic matters (NOM), suspended solids, and other trace impurities. One commercial cation exchange membrane, namely Nafion 117 from DuPont Chemical Co., was used in the study for treating WTR obtained from two different water treatment plants in Pennsylvania. A series of laboratory tests confirmed that over 70% of alum is easily recoverable, and recovered alum is essentially free of particulate matter, NOM, and other trace metals. Most importantly, after repeated usage in the presence of high concentration of NOM and suspended solids, there was no noticeable decline in aluminum flux through the membrane, i.e., membrane surface fouling was practically absent. The DMP process involves coupled transport of Al^{3+} and H^+ across the cation exchange membrane, and intramembrane transport was the rate-limiting step. Experimentally determined aluminum–hydrogen interdiffusion coefficient ($\bar{D}_{Al-H}$) values within the membrane were quite high ($\sim 10^{-6}$ cm^2/s) under representative conditions, thus confirming high alum recovery rate. DMP was also found equally effective in recovering Fe(III) based coagulants from WTR.

Introduction

During the last two decades, pressure driven membrane processes, namely reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF), have found increased applications in water utilities and chemical industries. Unlike RO, NF,

and UF, Donnan membrane process or Donnan Dialysis is driven by the electrochemical potential gradient across the ion exchange membrane. Theoretically, Donnan membrane process (DMP) is not susceptible to fouling because particulate matter or large organic molecules do not concentrate on the membrane surface, as commonly observed with pressure driven membrane processes. DMP has been used in the past in hydrometallurgical operations (*1*, *2*), for concentration of ionic contaminants (*3*, *4*) and for separation of acids from salts (*5*, *6*). Although information on several applications of DMP is available in the open literature, no work is reported on use of DMP to treat a sludge or slurry with high concentration of suspended solids or large organic molecules. It was conceived that a single-step Donnan membrane process could selectively recover alum, a widely used coagulant, from water treatment plant sludge or water treatment plant residuals (WTR).

There are over 1000 drinking water treatment plants in the United States which use alum, $Al_2(SO_4)_3 \cdot 14H_2O$, as a coagulant for efficient removal of particulate solids and colloids from surface water supply. More than 2 million tons of WTR are generated from these utilities every day (*7*, *8*). Alum is finally converted during the coagulation process into insoluble aluminum hydroxide, a major component (50–75%) of the solids in WTR, along with suspended inorganic particles, natural organic matters (NOM), and trace amounts of heavy metal precipitates (*9*). Due to regulatory changes in the recent past, WTR now have to be disposed of into landfills or through land application (*9*, *10*). In addition, the toxicity of free and complexed aluminum species toward various aquatic life and benthic organisms has been the focus of several studies (*11*, *12*). Some researchers have linked aluminum's contributory influence to occurrence of Alzheimer's disease (*13*). In this regard, the prospect of alum recovery from WTR and its reuse are worthy of scientific investigation.

Several efforts were made in the past to recover alum from WTR. Acid digestion process is the most commonly tried process at laboratory, pilot-scale, and plant level (*14*–*16*). In this process, WTR are sufficiently acidified with sulfuric acid, dissolving insoluble aluminum hydroxide in the form of alum up to aluminum concentration levels of 360–3700 mg/L. However, the process is nonselective; with the dissolution of aluminum hydroxide, NOM like humates and fulvates get dissolved too, and the resulting Dissolved Organic Carbon (DOC) concentration ranges from 326 to 1800 mg/L (*17*). This recovered alum, if reused as a coagulant, may impart a high trihalomethane formation potential (THMFP) during chlorination stage of water treatment. The trihalomethanes are suspected carcinogens, regulated by the U.S. EPA (*18*–*20*). As an alternative to acid digestion process, the amphoteric nature of aluminum oxide also permits alum recovery from the WTR under alkaline conditions. However, the alkali digestion process suffers from the same limitation as the acid digestion process i.e., NOM concentration is very high in the recovered solution. Figure 1 shows both DOC and aluminum concentrations of the Allentown Water Treatment Plant (AWTP) in WTR at different pH levels. It must be noted that DOC tends to increase with dissolved Al(III) under both acidic and alkaline conditions, confirming a nonselective nature of these processes. Ultrafiltration (*21*) application is associated with problems of fouling. The Two-step Composite Membrane Process (TCMP) (*22*), though selective, does not concentrate aluminum to high concentrations. In addition, composite exchangers are not available commercially in large quantities. Liquid Ion Exchange (*23*) process does not

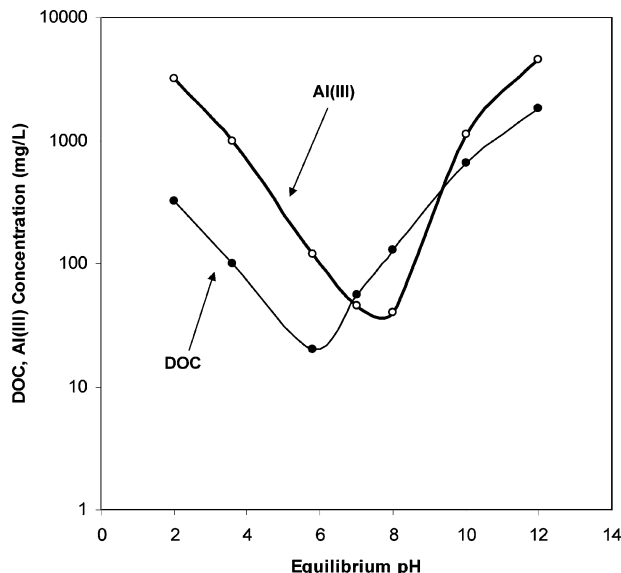* Corresponding author phone: (610)758-3534; fax: (610)758-6405; e-mail: arup.sengupta@Lehigh.edu.

FIGURE 1. Variation of Dissolved Organic Carbon (DOC) and aluminum concentration with pH for Water Treatment Residuals (WTR) from Allentown Water Treatment Plant (AWTP).

concentrate aluminum to a high level, and there is always some solvent carryover that requires further treatment.

Donnan membrane process, as presented later, is uniquely capable of recovering alum from WTR in a single-step process using sulfuric acid and cation-exchange membrane. The primary objective of this study is to present experimental evidences pertaining to selective alum recovery from WTR and its relative purity and reusability. Specific findings with regard to membrane surface fouling caused by NOM and particulate matter, aluminum transport flux and determination of aluminum−hydrogen interdiffusion coefficient values, and rejection of NOM and anions by cation-exchange membranes used in the study are also presented. The sludges from two large water treatment plants were used in the study.

Donnan Membrane Process: Governing Equilibrium

Let us consider aluminum sulfate and sulfuric acid solutions in a Donnan membrane cell divided into two chambers by a cation-exchange membrane that allows only cations to migrate from one side to the other but rejects any passage of anions according to Donnan's co-ion exclusion principle (24). At equilibrium, the electrochemical potential of aluminum ion, Al^{3+}, $(\bar{\mu})$ in the electrolyte solution on the left-hand side (LHS) of the membrane will be the same as that in the electrolyte solution on the right-hand side (RHS) i.e.,

$$\bar{\mu}_{Al}^{L} = \bar{\mu}_{Al}^{R} \qquad (1)$$

or

$$\mu_{Al}^{\circ} + RT\ln a_{Al}^{L} + zF\phi^{L} = \mu_{Al}^{\circ} + RT\ln a_{Al}^{R} + zF\phi^{R} \qquad (2)$$

where superscripts "o", "L", and "R" refer to standard state, LHS, and RHS and $\bar{\mu}$, μ, a, F, and ϕ denote electrochemical potential, chemical potential, activity, Faraday Constant and electrical potential, respectively. The "z" refers to the charge of the diffusing ion, which is 3 for trivalent aluminum ion Al^{3+}. Equation 2 gives the following equality for aluminum ions on two sides of the membrane:

$$\frac{F(\phi^{L} - \phi^{R})}{RT} = \ln\left(\frac{a_{Al}^{R}}{a_{Al}^{L}}\right)^{1/3} \qquad (3)$$

In a similar way, it can be shown for hydrogen ions that

$$\frac{F(\phi^{L} - \phi^{R})}{RT} = \ln\left(\frac{a_{H}^{R}}{a_{H}^{L}}\right) \qquad (4)$$

Assuming nonideality effects are about the same on both sides of the membrane, activities can be replaced by molar concentrations. Equations 3 and 4 then yield the following:

$$\left(\frac{C_{Al}^{R}}{C_{Al}^{L}}\right) = \left(\frac{C_{H}^{R}}{C_{H}^{L}}\right)^{3} \qquad (5)$$

If the ratio C_{H}^{R}/C_{H}^{L} is 10, it means C_{Al}^{R} is 1000 times greater than C_{Al}^{L}. Thus, by maintaining high hydrogen ion concentration on the right-hand side of the membrane, aluminum ions can be driven from the LHS to the RHS even against a positive concentration gradient i.e., from a lower concentration region to a higher concentration one. Figure 2 depicts the conceptualized selective alum recovery from WTR, highlighting the following: (i) aluminum hydroxide precipitates can be dissolved and then concentrated in the right-hand side; (ii) negatively charged NOM, sulfate, and chloride cannot permeate through the membrane; and (iii) the transmembrane pressure does not influence the aluminum transfer flux.

Materials and Methods

Feed and Recovery Solutions. The feed consisted of WTR collected from the Allentown Water Treatment Plant (Allentown, PA) and the Baxter Plant (Philadelphia, PA). The former uses alum as a coagulant, and the latter applies ferric chloride in the coagulation process. Total suspended solids content of the WTR obtained from the Allentown Water Treatment Plant (AWTP) varied between 2% and 4% mass/volume. In some experiments, synthetic feed solutions were prepared using aluminum sulfate (Fisher Scientific) and ferric chloride (Sigma Chemicals). The recovery side solution consisted of 10% (2 N) sulfuric acid purchased from E M Science. To investigate the effect of turbidity on solute flux and membrane fouling, fine (<200 mesh size) inert glass powder (Potters Industries, Product number: 6000) was used as the source of turbidity.

Donnan Membrane Cell. The Donnan membrane cell was made of Plexiglas, partitioned into two chambers, as shown in Figure 3, with dimensions $L = 30$ cm, $W = 7$ cm, and $H = 40$ cm. Fixed volumes of feed (WTR) and recovery (acid) solutions were used for every run; the ratio of WTR volume to acid volume could be adjusted independently in the test cell. Solutions in both chambers were agitated using instrument quality compressed air at 1 psig. Sufficient turbulence was achieved in the chambers of the Donnan cell with 1 psig air pressure, and intramembrane ion transport was the rate-limiting step under the experimental conditions.

The Exchange Membrane. The cation exchange membrane used for experiments was homogeneous Nafion 117 from Dupont, U.S.A. Information on homogeneous membranes can be found elsewhere (25); pertinent details are provided in Table 1. The exchange capacity data was determined in the laboratory following standard experimental protocols (26, 27).

Experimental Procedure and Analytical Techniques. The feed was allowed to exchange aluminum ions with hydrogen ions from the recovery solution for a period of 10−72 h, depending on the objective of each experiment. Samples were collected at regular intervals from both feed and the recovery side. Aluminum was analyzed using UV−vis spectrophotometer. This analysis involved the Eriochrome Cyanine R Method described in Standard Methods (28). Alu-
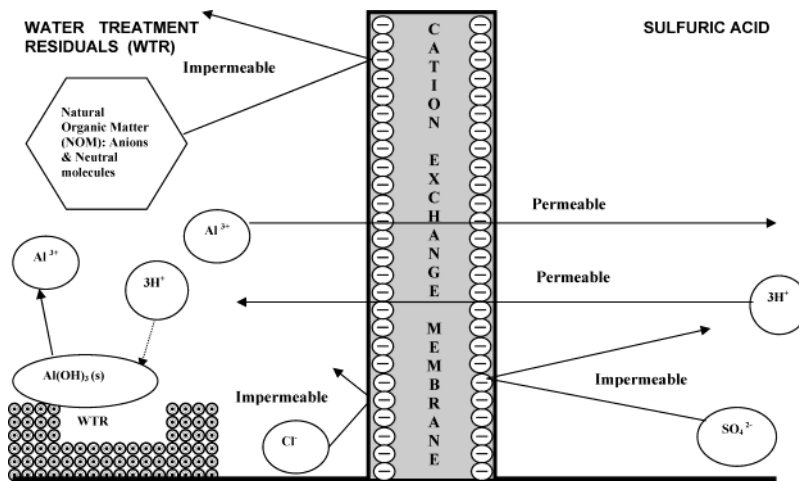
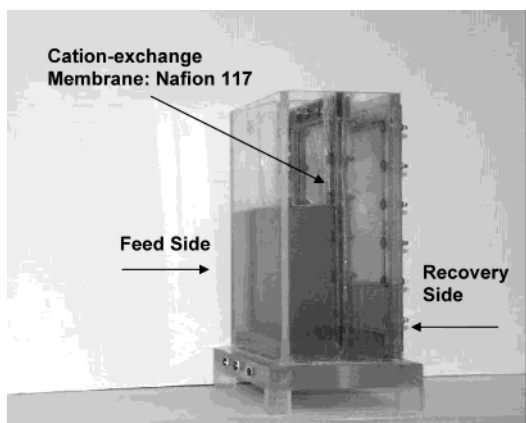**FIGURE 2. A schematic of Donnan membrane process illustrating selective alum recovery from WTR.**

FIGURE 3. Laboratory setup for a variable volume Donnan Membrane Cell.

TABLE 1. Properties of Nafion 117 Membrane

	Nafion 117
type	homogeneous[a]
ionic form as shipped	H^+ [a]
exchange capacity (dry basis)	1693.9 eq/m^3
membrane thickness (dry basis)	0.187 mm[a]
reinforcement	no[a]

[a] Information obtained from www.dupont.com.

minum concentration in the recovered alum was nearly 2 orders of magnitude greater than dissolved iron and any possible interference from iron was avoided through addition of ascorbic acid as prescribed in Standard Methods (28). Other metals such as iron, copper, magnesium, arsenic, and zinc were analyzed with an Atomic Absorption Spectrometer (Perkin-Elmer: Model AA100 and Perkin Elmer: Model SIMAA 6000). The DOC was measured using a TOC Analyzer (Dohrman: Model DC-190), and sulfate ions were analyzed for Donnan exclusion using a Dionex Ion Chromatograph (Model 4500i).

Results

Alum Recovery from Water Treatment Residuals (WTR). In the Donnan membrane cell, the feed side of the membrane contained 6.0 L of the decanted and slightly acidified WTR collected from the AWTP, while the recovery side contained 1.5 L of 10% sulfuric acid solution. At the start, pH of the WTR side was between 3 and 3.5. With the progress of the run, aluminum ions from the WTR side moved to the recovery

side through the cation exchange membrane, while an equivalent amount of hydrogen ions permeated to the WTR side, thus further reducing the pH. Under the experimental conditions of the Donnan run, free aluminum ions, Al^{3+}, was the predominant aluminum species. Figure 4 shows the results of the process for a period of 24 h; the percentage aluminum recovery and the concentration of aluminum in the two chambers were plotted against time. It can be seen that over 70% recovery (72%) was attained in 24 h. The noteworthy observation is that the recovered aluminum concentration was 6650 mg/L as Al, and it was significantly greater than the total aluminum concentration (2400 mg/L) present in the parent sludge. Figure 5 provides detailed composition of the recovered alum from the Donnan membrane process. Besides Al(III) and Fe(III), other contaminants are present only in trace concentrations. It is noteworthy that the recovered alum did not contain any suspended solids, while NOM expressed as DOC was consistently less than 5 mg/L. The ratio of individual contaminants to aluminum in the recovered alum was comparable and in some cases lower than in the commercial alum currently being used in AWTP.

Donnan Exclusion and Fouling. One of the primary attributes of the Donnan membrane process is its ability to exclude anions, NOM, and particulate matter while recovering aluminum from the WTR without being fouled. Figure 6A,B shows the Dissolved Organic Carbon (DOC) and sulfate (SO_4^{2-}) concentrations in the feed side and recovery side of Donnan membrane cell for a run that lasted 72 h. DOC is a measure of NOM in the aqueous phase, and these figures show that both DOC and sulfate remained nearly constant on both sides. DOC concentration in the recovered alum was consistently less than 5 mg/L, while the same in the feed side was over 150 mg/L. Likewise, sulfate concentration was close to 2000 mequiv/L on the recovered solution side and about 200 mequiv/L on the feed side during the course of the experiment which implied that the cation exchange membrane disallowed permeation of NOM and sulfate from one side to the other, validating the premise of the Donnan co-ion exclusion.

Specific experiments were carried out to confirm possible fouling of membranes caused by NOM and particulate matter. During the course of this study, the same Nafion membrane was used repeatedly. The color of the membrane surface turned dark, but no noticeable impairment of aluminum flux was observed even after prolonged usage. Figure 7 shows the results of two successive runs with a membrane already used in the laboratory for nearly 3 months. The same feed obtained from AWTP was used for both runs. Figure 7 demonstrates that the rate of increase in aluminum con-
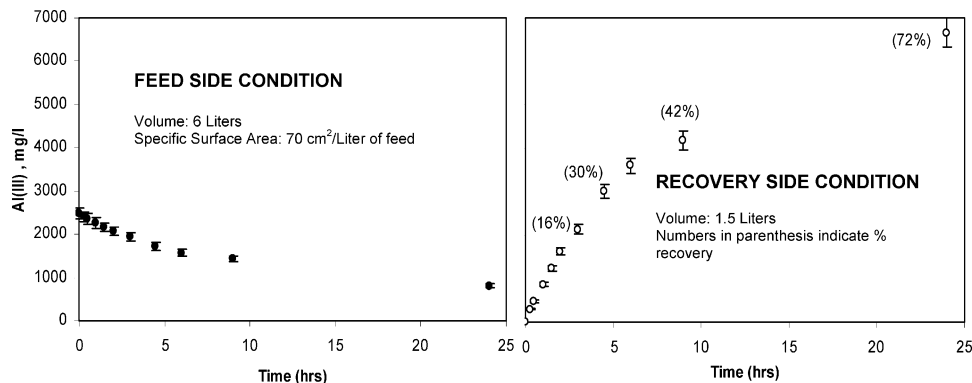
FIGURE 4. Aluminum recovery from AWTP residuals during Donnan membrane process: (a) decrease in Al concentration in feed and (b) percentage recovery and increase in Al concentration in recovery solution.
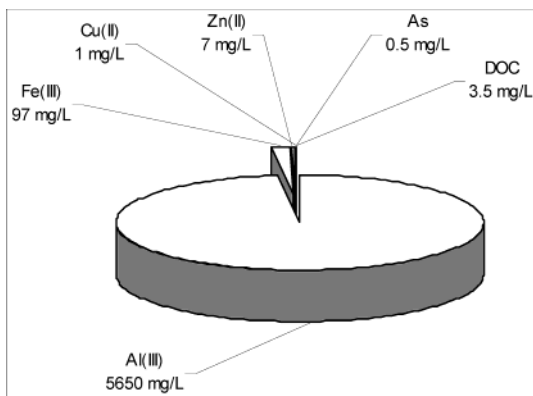

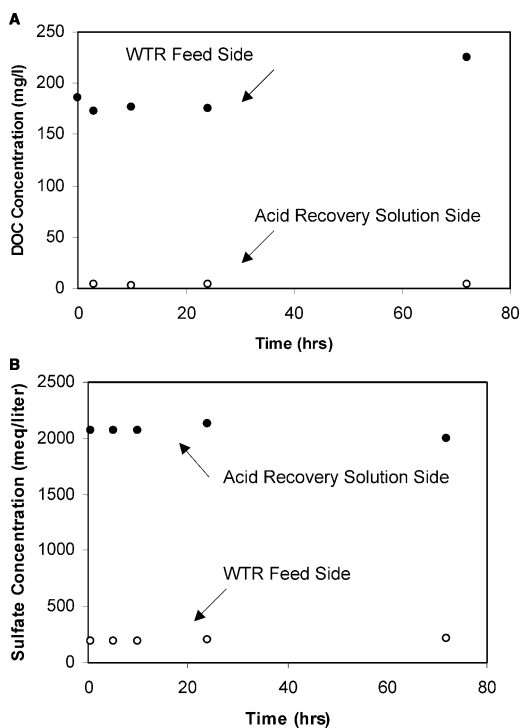**FIGURE 5.** Composition of alum recovered from AWTP using Donnan membrane process.

FIGURE 6. A. Dissolved organic carbon (DOC) concentration in feed and recovery solution during an experimental run using AWTP residuals. B. Sulfate concentration in feed and recovery solution during the same run.

FIGURE 7. Aluminum recovery in two consecutive runs with WTR obtained from AWTP.
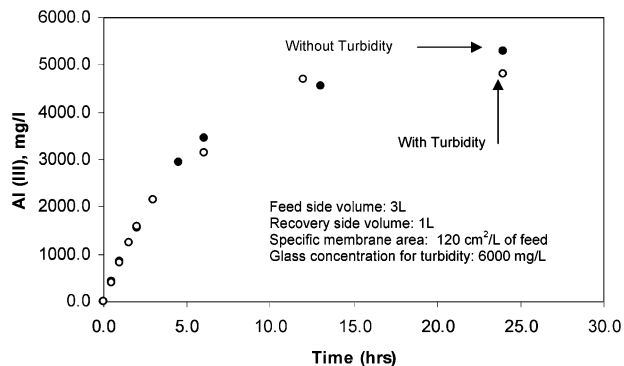
FIGURE 8. Influence of turbidity on removal efficiency.

To investigate the effect of turbidity independently, two parallel Donnan recovery runs were carried out. During the first run, the synthetic alum feed solution was free of any turbidity, while for the second run, 6000 mg/L turbidity was introduced into the feed compartment as fine glass powders with sizes in the vicinity of one micron. All other conditions were exactly the same for the two runs. High turbidity in the feed side did not impair the rate of alum recovery, as evidenced from the experimental results in Figure 8.

Fe(III) Recovery. Ferric salts (chloride or sulfate) are also used as coagulants in water treatment plants (*29*), and the resulting ferric hydroxide precipitates constitute a major portion of the clarifier sludge or WTR. In principle, the Donnan membrane process is capable of selectively recovering Fe(III) coagulants from these WTR as well. To validate the same, the WTR from the Baxter plant (Philadelphia, PA), which utilized $FeCl_3$ as coagulant, was used in several test runs. Figure 9 shows percentage Fe(III) recovery and the concentration of Fe(III) in the feed and recovery side with time. Nearly 75% recovery is attained in 24 h. The resulting

centration with time in the recovery side was slightly lower during the second run, but the overall alum recovery essentially remained the same after 9 h of operation.
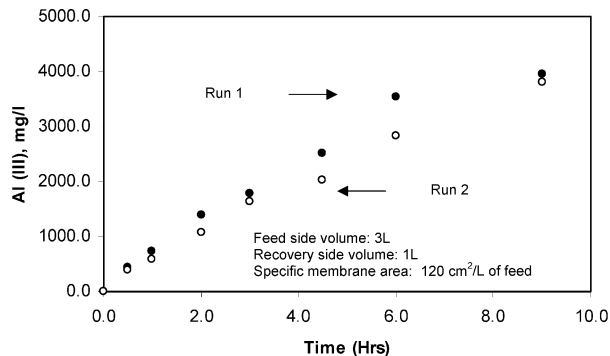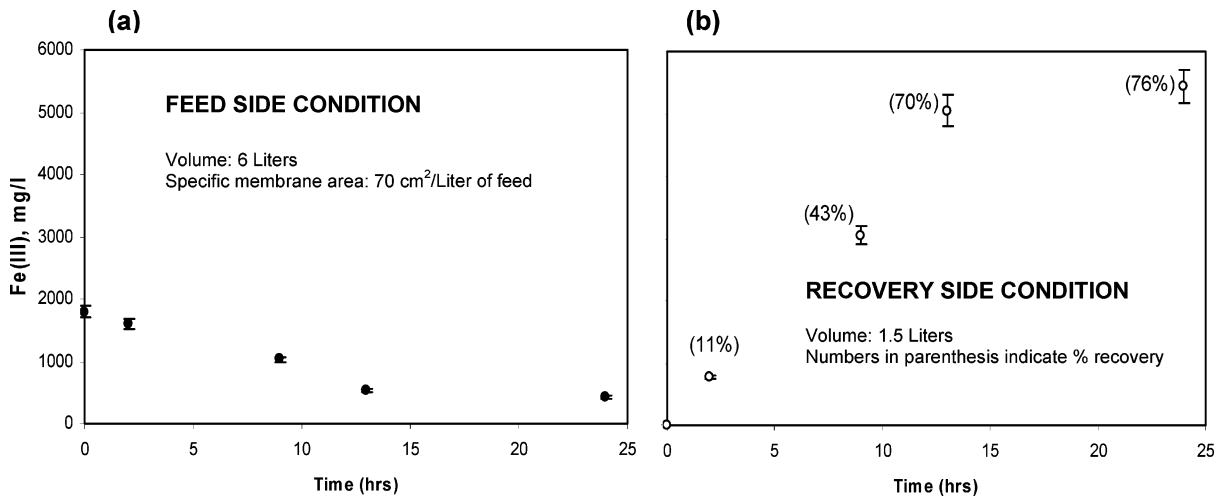
FIGURE 9. Ferric(III) recovery from ferric chloride based WTR from Baxter Water Treatment Plant during Donnan membrane process: (a) decrease in Fe concentration in feed and (b) percentage recovery and increase in Fe concentration in recovery solution.

Fe(III) is essentially free of NOM, particulate matter, and other impurities.

Figure 10A,B shows the visual comparison of recovered coagulants, both alum and ferric sulfate, between traditional acid digestion process and the Donnan membrane process. Higher transparency of the coagulants from AWTP and Baxter Plant, recovered by Donnan membrane process, is readily noticeable due to the absence of turbidity and NOM. Two separate runs were carried out using synthetic solutions of aluminum sulfate and ferric chloride under otherwise identical conditions. Figure 11 shows that the percentage or fractional recovery of Fe(III) or Al(III) remains essentially the same i.e., the process is equally effective for concentrating any trivalent cation.

Relative Carryover. Besides Al(III) and Fe(III), undesirable solutes and NOM also get carried over to the recovered solution. Relative carryover (η_R) of substance "i" with respect to Al is defined as the following dimensionless variable

$$\eta_R = \left(\frac{C_R^i}{C_R^{Al}} \times \frac{C_F^{Al}}{C_F^i}\right) \times 100 \qquad (6)$$

where "C" represents concentrations, and the subscripts R and F denote the recovered solution and the WTR feed, respectively. Figure 12 shows the percentage relative carryover i.e., η_R values of DOC, Cu(II), Zn(II), and Mg(II). It is noted that η_R values are nearly zero for DOC and significantly less than aluminum for all divalent cations. For conventional acid digestion process, no selective separation is achieved i.e., percentage η_R values of all the contaminants are essentially the same as that of Al(III).

Rate-Limiting Step and Intramembrane Diffusion. Under the hydrodynamic conditions of the experiments investigated, diffusional resistances resided solely within the membrane phase i.e., ion transport from the bulk liquid to the membrane interface was much faster relative to the intramembrane transport of ions. Donnan membrane is essentially a coupled transport process i.e., transport of a cation across the membrane is balanced by the counter-transport of another cation on an equivalent basis. Considering trivalent Al^{3+} and monovalent H^+ to be the primary transporting cations for the alum recovery process, Figure 13 represents the concentration gradient across the membrane for Al^{3+} and H^+ between the feed side and the recovery
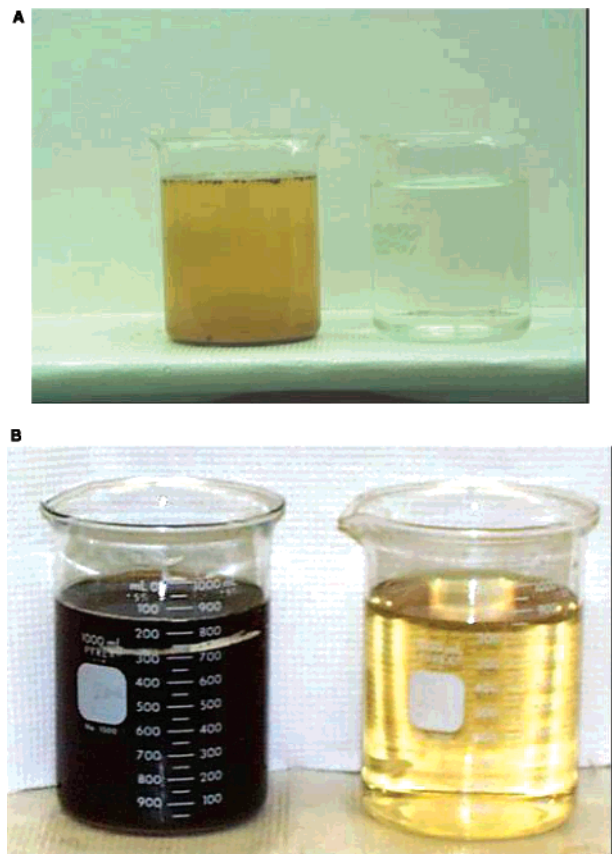

FIGURE 10. A. Visual comparison of recovered alum coagulant from AWTP residuals by acid digestion process (left) and Donnan membrane process (right). B. Visual comparison of recovered ferric coagulant from Baxter Plant residuals by acid digestion process (left) and Donnan membrane process (right).

side. For coupled transport of Al^{3+} and H^+, the interdiffusion coefficient is given as (*30*)

$$\bar{D}_{Al-H} = \bar{D}_H * \bar{D}_{Al} * \left(\frac{z_H^2 q_H + z_{Al}^2 * q_{Al}}{z_H^2 q_H * \bar{D}_H + z_{Al}^2 * q_{Al} * \bar{D}_{Al}}\right) \qquad (7)$$

where $\bar{D}$ refers to the diffusion coefficient in the membrane, "q" refers to the molar concentration of diffusing ions in the
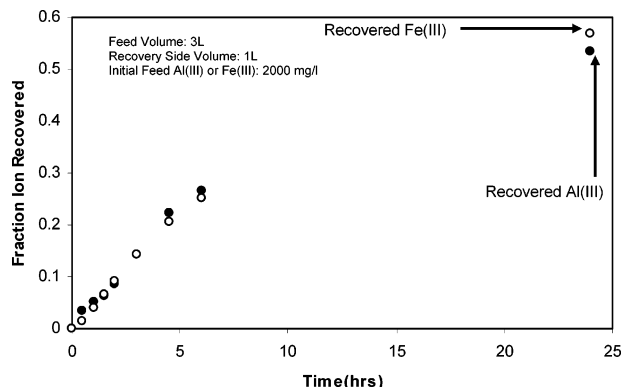
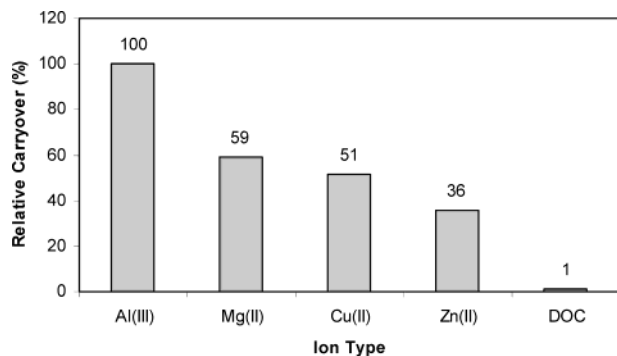**FIGURE 11.** Fractional recovery of ferric and aluminum ions from synthetic solutions.

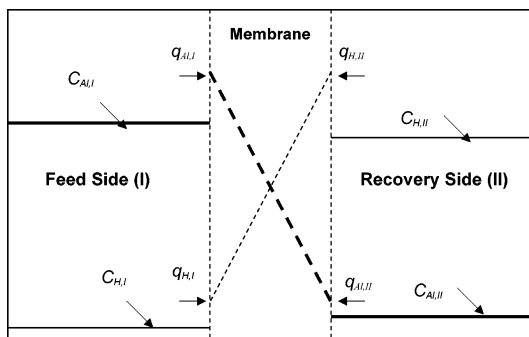**FIGURE 12.** Relative carryover of undesirable solutes and NOM.

FIGURE 13. Instantaneous aluminum and hydrogen ion concentration in the liquid phase and within membrane under intramembrane transport limited condition.

membrane phase, and "z" refers to the charge of the ion. The "Al" and "H" in the subscript refer to the diffusing aluminum and hydrogen ions. Replacing the charges by "3" and "1" for aluminum and hydrogen, respectively, the resulting equation is given as

$$\bar{D}_{Al-H} = \bar{D}_H * \bar{D}_{Al} * \left(\frac{q_H + 9*q_{Al}}{q_H * \bar{D}_H + 9*q_{Al}*\bar{D}_{Al}} \right) \quad (8)$$

The interdiffusion coefficient, $\bar{D}_{Al-H}$, is dependent on the membrane phase Al^{3+} and H^+ concentrations, as can be seen from eq 8. From the concentration data for feed and recovery solutions during alum recovery process in Figure 4, $\bar{D}_{Al-H}$ values were computed using aluminum transport rate or flux (J_{Al}) at different time intervals. Figure 14 shows computed $\bar{D}_{Al-H}$ values from the experimental data at different times during the run. An important observation is that for hydrophilic Nafion 117 membrane, the interdiffusion coefficient values are quite high ($10^{-11}-10^{-10}$ m²/s) and significantly greater than the corresponding self-diffusion coefficient
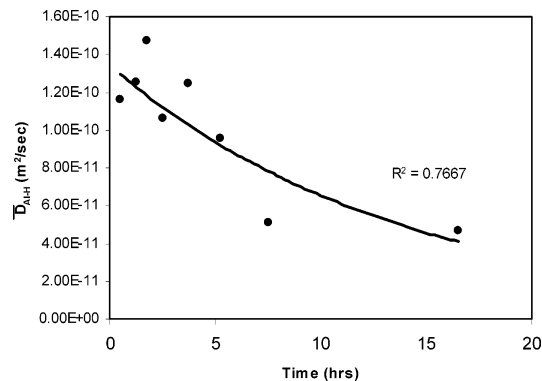

FIGURE 14. Interdiffusion coefficient ($\bar{D}_{Al-H}$) values for aluminum transfer based on Figure 4 data.

values of trivalent and divalent cations (less than 10^{-12} m²/s) reported in the open literature for cation-exchange resins (*31*).

Discussion

For pressure-driven semipermeable membrane processes such as reverse osmosis and nanofiltration, the solvent water molecules permeate through the membrane in preference to electrolytes. On the contrary, for Donnan membrane processes, the specific ions and not the solvent migrate through the membrane under electrochemical potential gradient. The absence of transmembrane pressure gradient and the presence of negatively charged functional groups on the cation exchange membrane are the underlying reasons why high concentrations of NOM and suspended solids had practically no adverse impact in recovering the coagulant selectively from the water treatment residuals. Equally important, aluminum concentration in the final recovered alum was significantly greater than the total aluminum concentration in the parent feed, as demonstrated in Figure 4. Due to its high purity and concentration, the recovered alum may find, apart from the usage as coagulant, other industrial applications such as in synthesis of polyaluminum compounds (*32*).

While Fe(III) is a transition-metal cation, Al(III) is a hard cation with an electronic configuration identical to inert argon i.e., chemical makeup of Al(III) is very different from Fe(III). As demonstrated in Figure 11, the recovery of Fe(III) was similar to Al(III). This observation confirms that only valences of transporting ions, independent of their chemical characteristics, are of consequence in the Donnan membrane process.

Considering electroneutrality for counter transport of H^+ and Al^{3+} and linear concentration gradient across the membrane, the aluminum flux (J_{Al}) at any given time during the process is given as

$$J_{Al} = -\frac{J_H}{3} = -\bar{D}_{Al-H} \frac{\partial q_{Al}}{\partial x} \quad (9)$$

where "x" is the membrane thickness and "q_{Al}" represents the membrane-phase aluminum concentrations. For a given feed composition and specific cation exchange membrane, the kinetics of the alum recovery process is primarily governed by the Al−H interdiffusion coefficient, $\bar{D}_{Al-H}$. Experimentally determined $\bar{D}_{Al-H}$ values shown in Figure 14 are quite high and vary between $10^{-10}-10^{-11}$ m²/s, thus confirming the viability of the process from a kinetic viewpoint. In fact, the $\bar{D}_{Al-H}$ values are significantly greater than self-diffusion coefficients of divalent and trivalent cations within a cation exchanger. For instance, the diffusion coefficient values for these ionic species in cation-exchange resins with 15% cross-linking range between 10^{-12} and 10^{-14} m²/s (*31*). This

observation of high interdiffusion coefficient ($\bar{D}_{Al-H}$) values for Nafion membrane is counterintuitive, and the following provides a scientific explanation for high $\bar{D}_{Al-H}$ values observed.

The composition of the membrane with respect to Al^{3+} and H^+ content (i.e., q_{Al} and q_H) varies across the membrane, influencing the $Al-H$ interdiffusion coefficient as shown below:

$$\bar{D}_{Al-H} = \bar{D}_H {}^* \bar{D}_{Al} {}^* \left(\frac{q_H + 9^* q_{Al}}{q_H {}^* D_H + 9^* q_{Al} {}^* D_{Al}} \right) \qquad (8)$$

The relative distribution of Al^{3+} and H^+ in the membrane governs the value of $\bar{D}_{Al-H}$. Nafion is a strong-acid cation exchange membrane and exhibits significantly greater affinity for ions with higher valence (*33*). Laboratory experiments revealed that binary separation factor, which is a measure of relative affinity for two competing ions for an ion exchanger, was equal to 70 for aluminum over hydrogen for Nafion at 50 mequiv/L solution concentration. Thus, at anytime during the process, q_{Al} is significantly greater than q_H within the ion exchange membrane. Considering the extreme case where hydrogen ion is essentially a trace species compared to aluminum, i.e., $q_{Al} \gg q_H$, equation 8 degenerates into the following:

$$\bar{D}_{Al-H} = \bar{D}_H \qquad (10)$$

Since membrane-phase hydrogen ion diffusitivity ($\bar{D}_H$) is over two orders magnitude greater than aluminum ($\bar{D}_{Al}$), the interdiffusion coefficient value approaches that of $\bar{D}_H$ and is therefore very high. For the alum recovery process, hydrogen ion is a minor species within the membrane. Consequently, the interdiffusion coefficient, $\bar{D}_{Al-H}$, approaches that of faster diffusing hydrogen ions, $\bar{D}_H$. The composition of the membrane changes with the progress of the process, thus altering the $\bar{D}_{Al-H}$ values, but they always remain significantly greater than the self-diffusion coefficient of aluminum ions. From an application viewpoint, this phenomenon leads to higher mass transfer or alum recovery rate. It is postulated that high interdiffusion coefficient values will also be observed for Fe(III) recovery from water treatment plants using iron-based coagulants.

Acknowledgments

Literature Cited

(1) Wallace, R. M. *Ind. Eng. Chem., Process Des. Dev.* **1967**, *6*(4) 423−431.

(2) Ersoz, M; Kara H. *J. Colloid Interface Sci.* **2000**, *232*, 344−349.

(3) Kim, B. M. *AIChE Symp. Ser.* **1979**, *76*(197), 184−192.

(4) Hichour, M.; Persin, F.; Molenat, J.; Sandeaux, J.; Gavach, C. *Desalination* **1999**, *122*, 53−62.

(5) Tongwen, X.; Weihua, Y. *J. Membr. Sci.* **2001**, *183*, 193−200.

(6) Kobuchi, Y.; Motomura, H.; Noma, Y.; Hanada, F. *J. Membr. Sci.* **1986**, *27*, 173−179.

(7) James M. Montgomery Consulting Engineers, Inc. *Water Treatment principles and Design*; John Wiley & Sons: New York, 1985.

(8) Technology Transfer Handbook: *Management of Water Treatment Plant Residuals*; ASCE: New York, 1996.

(9) Cornwell, D. A.; Westerhoff, G. P. Management of water treatment plant sludges. *Sludge and Its Ultimate Disposal*; Borchardt, J. A., Ed.; Ann Arbor Science: Ann Arbor, Ml, 1981.

(10) SenGupta, A. K.; Shi, B. *Jour. AWWA* **1992**, *84*, 96−103.

(11) Driscoll, C. T.; Baker, J. P.; Bisogni, J. J.; Schofield, C. L. *Nature* **1980**, *284*, 161−164.

(12) Lamb, D. S.; Bailey, G. *Bull. Environ. Contam. Toxicol.* **1981**, *27*, 59−67.

(13) Desroches, S.; Dayde, S.; Brethon, G. *J. Inorg. Biochem.* **2000**, *81*, 301−312.

(14) Bishop, M. M.; Rolan, A. T.; Bailey, T. L.; Cornwell, D. A. *J. AWWA* **1987**, *79*(6), 76−83.

(15) Cornwell, D. A.; Bailey, T. L. *The benefits and performance of a full-scale alum recovery facility*; Env. Engg., & Technology, Inc.,: 1994.

(16) Cornwell, D. A.; Zoltec, J. *J. WPCF* **1977**, *49*, 600−612.

(17) Saunders, F. M. *Coagulant Recovery from Alum WTR at North area plant*; Final Report for Bureau of Water, City of Atlanta, GA; 1989.

(18) Stevens, A. A.; Symons, J. M. *J. AWWA* **1977**, *69*, 546−554.

(19) Christman, R. F.; Norwood, D. L.; Millington, J. D. S.; Stevens, J. D.; Stevens, A. A. *Environ. Sci. Technol.* **1983**, *17*, 625−628.

(20) Oliver, B. G.; Visser, S. A. *Water Res.* **1980**, *14*, 1137−1141.

(21) Bregman, J. I. *Environ. Sci. Technol.* **1970**, *4*, 296−302.

(22) Sengupta, A. K. Cyclic Process for Selective Coagulant Recovery from WTR, United States Patent 5,304,309. 1994.

(23) Dhage, S. S.; Paramasivam, R.; Rao, R. R.; Andey, S. P. *J. IWWA* **1985**, *XVII*(2), 193−199.

(24) Helfferich, F. *Ion Exchange*; Dover Publication Inc.: New York, 1995; pp 134−135.

(25) Winston Ho, W. S.; Sirkar, K. K. *Membrane Handbook*; Van Nostrand Reinhold: New York, 1992.

(26) Miyoshi, H.; Yamagami, M.; Katoka T. *Chem. Express* **1990**, *5*(10), 717−720.

(27) Sato K.; Yonemoto T.; Tadaki T. *J. Membr. Sci.* **1990**, *53*, 215−227.

(28) APHA, AWWA, WEF. *Standard Methods For The Examination Of Water And Wastewater* **1992**, *18*, 3, 44−46.

(29) Johnson, P. N.; Amirtharajah, A. *J.. AWWA* **1983**, *75*(5), 232−239.

(30) Cussler, E. L. *Diffusion Mass Transfer In Fluid Systems*; Cambridge University Press: Cambridge, U.K., 1998.

(31) Helfferich, F. *Ion Exchange*; Dover Publication Inc: New York, 1995, pp 305−06.

(32) Gray, K. A.; O'Melia, C. R.; Yao, C. *J. AWWA* **1995**, *87*(4), 136−146.

(33) Helfferich, F. *Ion Exchange*; Dover Publication Inc.: New York, 1995; p 162.