ENVIRONMENTAL ENGINEERING PROGRAM

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Research Title:

Selective Coagulant Recovery from Water Treatment Residuals using the Donnan Membrane Processes

Research Objectives:

The primary objectives of this research were to selectively recover coagulants such as alum from water treatment residuals using a Donnan Membrane Process (DMP) or Donnand Dialysis. This process is driven by an electrochemical gradient across a semi-permeable ion exchange membrane. Laboratory results confirmed that over 70% recovery of alum is possible with essentially no particulate matter, Natural Organic Matter (NOM), or other trace metals.

Background:
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 an electrochemical potential gradient across an 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. Although information on several applications of DMP is available in the open literature (1-2), 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 coagulant alum (Al2(SO4)3.14H2O) (3,4) from water treatment plant sludge or water treatment plant residuals (WTR), which are the end product of coagulation. WTR contain insoluble aluminum hydroxide (50-75%) along with suspended inorganic particles, Natural Organic Matter (NOM) and trace amounts of heavy metal precipitates (5). 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 (6). 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 non-selective; 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 (7). 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 USEPA (8). 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. Donnan membrane process is uniquely capable of recovering alum from WTR in a single-step process using sulfuric acid and a cation-exchange membrane.

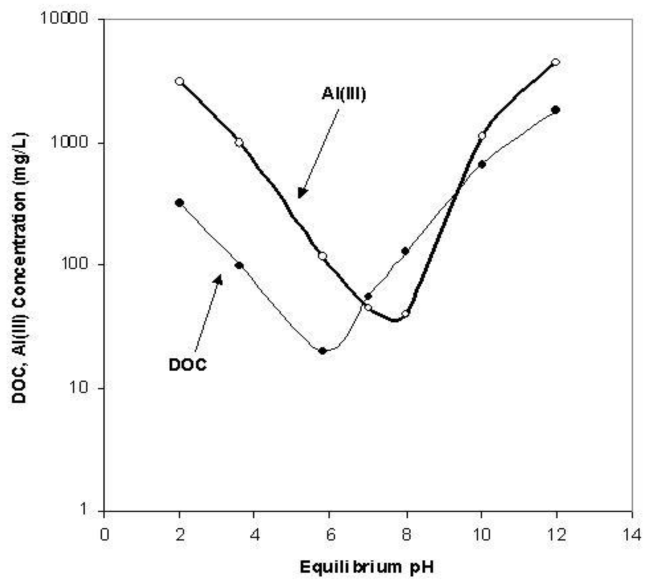

Figure 1 Variation of Dissolved Organic Carbon (DOC) and Aluminum concentration with pH for Water Treatment Residuals (WTR) from Allentown Water Treatment Plant (AWTP).

Theory:

Let us consider solutions of aluminum sulfate (Feed) and sulfuric acid (Recovery) 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 (9). At equilibrium, the electrochemical potential of aluminum ion Al3+ ion ( ) in the Feed solution will be the same as that in the Recovery solution for both aluminum and hydrogen ions, which corresponds to the following Donnan equilibrium condition:

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

If the ratio of hydrogen ion on the recovery (right-hand side) to hydrogen ion on the feed (left-hand side) is 10, it means that the concentration of aluminum ion on the recovery side is 1000 times greater than the concentration of aluminum ion on the feed side. Thus, by maintaining a high concentration of hydrogen ion in the recovery solution, aluminum ions can be driven from the feed to the recovery side even against a positive concentration gradient i.e., from a lower concentration to a higher concentration. **Figure 2** depicts the conceptualized selective alum recovery from WTR, highlighting the following

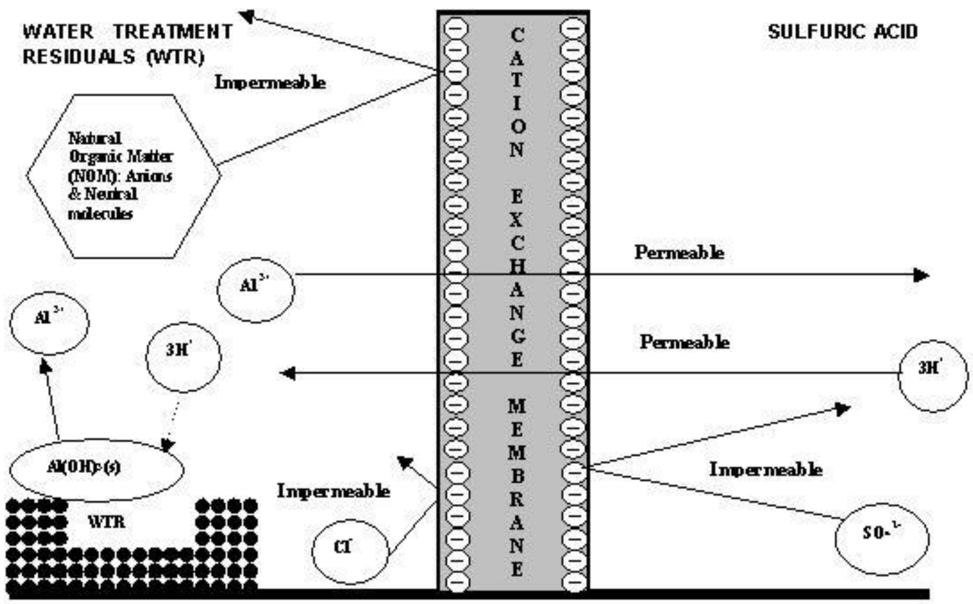

Figure 2 A schematic of Donnan membrane process illustrating selective alum recovery from WTR.

Key Findings:

In the Donnan membrane cell, the feed side of the membrane contained 6.0 liters of the decanted and slightly acidified WTR collected from the AWTP while the recovery side contained 1.5 liters of 10% sulfuric acid solution, separated by a cation-exchange membrane Nafion 117 . At the start, pH of the WTR side was between 3.0-3.5. With the progress of the run, aluminum ions from the WTR side moved to the recovery side through the cation exchange membrane while 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, Al3+, was the predominant aluminum species. **Figure 3** shows the results of the process for a period of twenty-four hours; the percentage aluminum recovery and the concentration of aluminum in the two chambers were plotted against time. It can be seen that over seventy percent recovery (72%) was attained in 24 hours. The noteworthy observation is that the recovered aluminum concentration was 6,650 mg/L as Al and it was significantly greater than the total aluminum concentration (2400 mg/l) present in the parent sludge. It was also noted that the recovery was selective with respect to trace heavy metal ions. 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. Similar results were obtained with WTR received from the Baxter plant (Philadelphia, PA), which utilized FeCl3 as coagulant; where over 75% recovery was made in 24 hours.

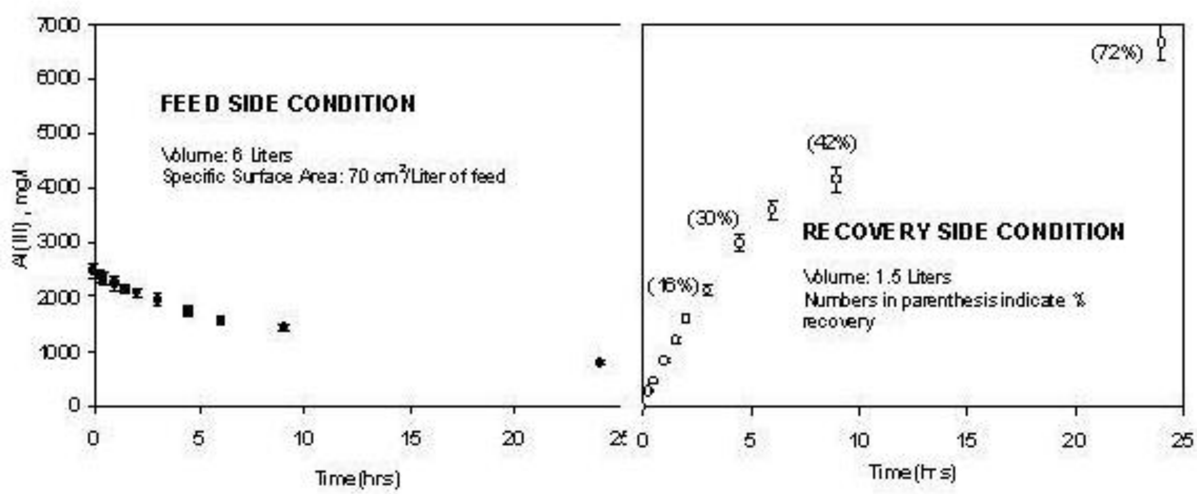

Figure 3 Aluminum recovery from AWTP residuals during Donnan membrane process: (a) decrease in Al concentration in feed; (b) percentage recovery and increase in Al concentration in recovery solution

Figures 4(a,b) show 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.

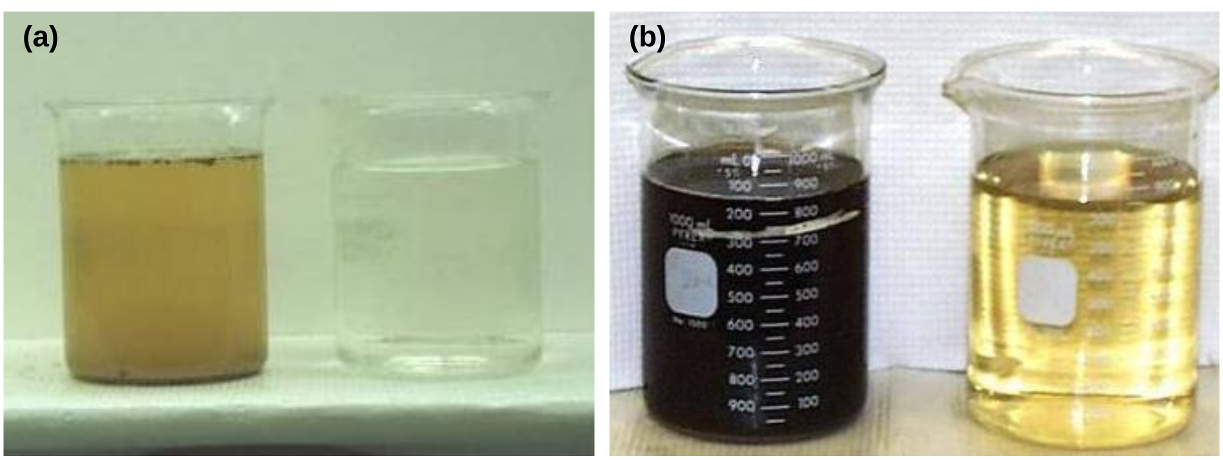

Figure 4 (a) Visual Comparison of recovered alum coagulant from AWTP residuals by Acid digestion process (Left) and Donnan membrane process (Right).

Figure 4 (b) Visual Comparison of recovered ferric coagulant from Baxter Plant residuals by Acid digestion process (Left) and Donnan membrane process (Right).

Conclusions:

In this work, it was worthy to note that : i) aluminum (ferric) hydroxide precipitates could be dissolved and coagulant ions concentrated in the recovery solution ii) negatively charged NOM, sulfate and chloride could not permeate the membrane due to Donnan exclusion iii) the recovered alum was sufficiently pure and reusable in water treatment plants.

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Publications:

1. Prakash, P., SenGupta, A. K. (2003) “Selective Coagulant Recovery from Water Treatment Plant Residuals Using donnan Membrane Process”, *Environ. Sci. Technol.*, 37, 4468-4474.
2. Prakash, P., Hoskins, D. and SenGupta, A.K. "Application of homogeneous and heterogeneous cation-exchange membranes in coagulant recovery from water treatment plant residuals using Donnan membrane process." *Journal of Membrane Science*, 237, (2004), 131-144.
3. Prakash, P. and SenGupta, A.K., "Modeling Al^{3+}/H^+ ion transport in Donnan membrane process for coagulant recovery." *AIChE Jour.,* (2005), 51, 1, 333-344.