

## **Innovative Approaches to RO Concentrate Management: Beneficial Reuse and Concentrate Minimization**

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### **ABSTRACT**

Desalination of brackish waters and reclaimed waters using reverse osmosis (RO) is often limited by the options available for concentrate disposal, particularly in inland areas. Dewatering the concentrate is alternative approach to disposal but the available thermal and membrane technologies are still cost prohibitive for most applications. Beneficial reuse of the RO concentrate represents a sustainable alternative to more traditional concentrate disposal and treatment options because the concentrate becomes a resource rather than a pollutant. This paper presents results from a series of innovative tests utilizing ion exchange (IX), bipolar membrane Electrodialysis (BMED) and Electrochlorination (EC) technologies to recover useful products from RO concentrate that can be utilized at the treatment facility. Two of these technologies including the BMED and the EC are currently in the patent process for this and other applications. Experiments were conducted on RO concentrate obtained from a pilot-scale integrated membrane system (IMS) treating wastewater. The IX experiments focussed on recovering phosphate from RO concentrate using a chelating ion exchange resin and converting the phosphate rich regenerant into struvite, a commercially viable fertilizer. Reasonably long run lengths of up to 700 BVs were obtained with actual RO concentrate using one of the tested resins. BMED was used for generating mixed acids and bases from the RO concentrate solution after suitable pretreatment. Reasonably high concentrations of acids and bases (0.2- 0.5 M) were produced and were shown to be dependent on the concentration and the volume of the used salt solution. It is expected that upto 1 M acid and base concentrations can be produced from this process. Additionally, the RO concentrate was desalted as well. Electrochlorination using RO concentrate was utilized to convert this waste stream into hypochlorite disinfectant of 0.6% similar to that currently being utilized at water treatment plants.

The above processes present the potentially viable alternative of utilizing the RO concentrate for the production of useful products instead of having to dispose of the waste brine into the environment. Costs are currently being developed for implementation of these three strategies and will be presented at the conference.

**KEYWORDS:** Reuse, RO Concentrate, Beneficial Reuse, Bipolar Membrane Electrodialysis, Electrochlorination, Struvite

### **INTRODUCTION**

Membrane treatment is a critical component of water recycling programs being implemented globally to increase limited water supplies. RO treatment is employed when removal of specific

dissolved contaminants and total dissolved solids (TDS) is needed to achieve the target finished water quality. Installation of RO facilities has increased dramatically as the cost of membrane modules continues to decline (Adham et al, 2005). But there is a significant cost associated with the technology when utilized in non-coastal communities. RO treatment produces waste brine that can range from five to 25 percent of the influent flow. While coastal communities can utilize ocean discharge, inland facilities must rely upon conventional alternatives that are not considered environmentally sustainable and are becoming increasingly difficult to permit (Mickley, 2001).

The industry is seeking cost-effective concentrate brine handling alternatives that are more environmentally sensitive. Beneficial reuse of RO represents a promising and sustainable alternative to Zero Liquid Discharge (ZLD) methods that have been applied on a limited scale because of the large energy needs associated with the process. Recovery and beneficial reuse of phosphate and acids and bases from RO concentrate was selected for evaluation after extensive screening of the alternatives currently available.

Bipolar Membrane Electrodialysis is a membrane based electrochemical process, which uses bipolar membranes for separation of ionic species from a salt to produce the respective acid and base. This process has been used in the food industry to produce organic acids like lactic acid, ascorbic acid and salicylic acid with a reasonable amount of success (Wilhelm, 2001; Bazinet et al, 1998). It has also been applied to pure NaCl solutions to produce HCl and NaOH (Mazrou et al, 1998). RO concentrate is mostly made of Na<sup>+</sup> and Cl<sup>-</sup> ions with substantial amounts of divalent ions. However proper pretreatment of the RO concentrate stream is required for beneficial reuse of this stream for production of mixed acids and bases.

Phosphorus removal from wastewater has been studied in detail as wastewater containing phosphorus that is discharged to surface streams can cause major environmental impacts (WERF, 1994). The use of the ion exchange process for this application has also been studied over the last decade (Zhao and Sengupta, 1998). Further, the ion exchange process for phosphate recovery has been enhanced by using the phosphorus recovered in the regenerant stream to produce an excellent nutrient for plants called struvite (Johnston and Richards, 2003). Struvite belongs to a class of chemicals called metal ammonium phosphates, which are insoluble in water and have an excellent biological based slow release mechanism. Struvite is magnesium ammonium phosphate (MgNH<sub>4</sub>PO<sub>4</sub>) and can be formed by addition of ammonia and magnesium to phosphate. RO concentrate from the IMS utilized in this study was expected to have between 10 and 20 mg/L P making struvite recovery from this waste stream a possibility.

Several water treatment plants have been switching to onsite chlorine generation as a disinfectant source due to operational safety concerns and ease of implementation. Conceptually, commercial hypochlorite generators split NaCl using an electrolytic cell to produce hypochlorite. Again, since RO concentrate contains significant amounts of Na<sup>+</sup> and Cl<sup>-</sup> ions, this stream could be beneficially reused through production of hypochlorite

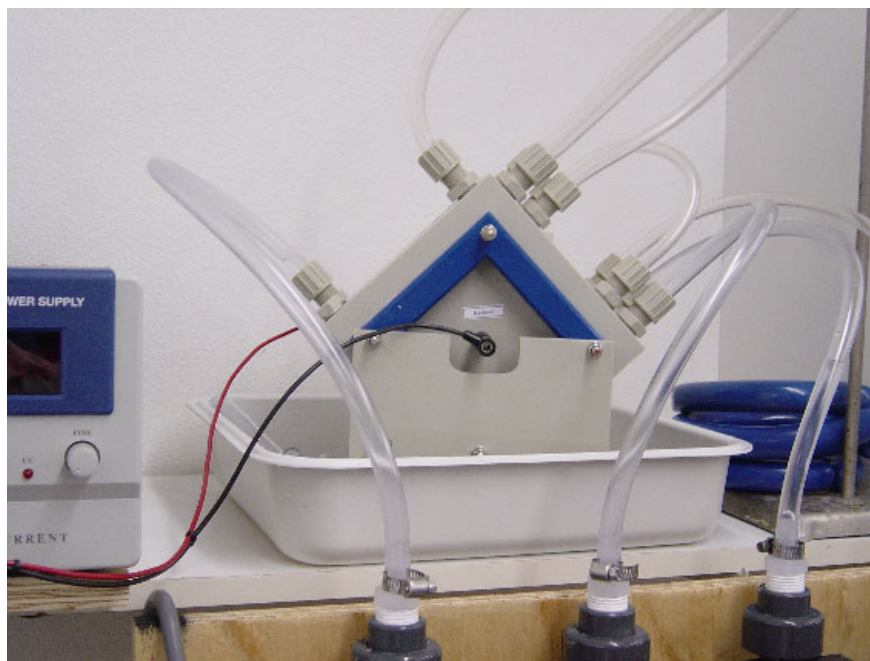
MWH and Sandia National Laboratories recently completed a proof of concept study looking at the above innovative beneficial reuse alternatives for the RO concentrate using bench scale testing. The beneficial reuse alternatives investigated included: production of the fertilizer struvite from the phosphate-rich RO concentrate utilizing ion-exchange and chemical addition; production of mixed acids and bases from the salts present in the RO concentrate using bipolar

membrane electro dialysis; and production of usable hypochlorite utilizing RO concentrate RO as a feed stream by electrolytic reduction. This paper presents the results from this study

## MATERIALS AND METHODS

### TEST EQUIPMENT

**Bipolar Membrane Electro dialysis:** A photograph of the BMED cell used is shown in Figure 1. The operating parameters of this was adjusted after consultation with the manufacturer. There were four streams that passed through the BMED cell with the salt stream being the feed stream and the acid and base stream being the product streams. Additionally, stream of DI water was needed to flush the electrodes. A constant DC current was then maintained across the electrodes.

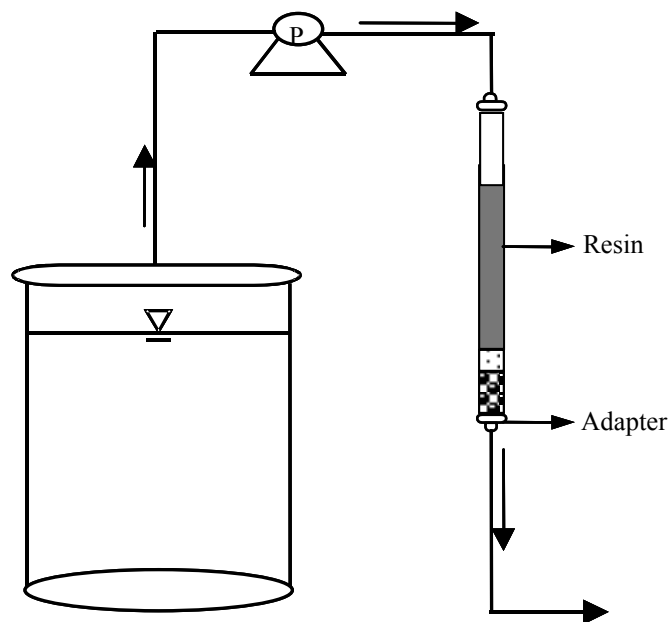


**Figure 1: BMED Cell tested during study**

### Struvite Recovery

Two types of phosphate-selective resins were used in this study; laboratory prepared Cu-loaded Dow-3N and commercial PolyXnp (Solmetex, USA). A chelating resin (DOW 3N) containing only nitrogen donor atoms was used as the parent polymer for preparing the copper (II) loaded polymeric ligand exchanger (PLE). This chelating resin was loaded with Cu (II) in the laboratory; a detailed procedure for which is presented in the test procedure section. In order to avoid leakage of copper from the column a small amount of chelating ion exchanger (IRC- 718, Rohm and Haas) in sodium form was placed at the bottom of the column. In addition to the Cu-

loaded resin, iron nano-particle impregnated phosphate selective resin PhosXnp was also used in this study. Laboratory columns consisted of 1.1 cm (Ace Glass, Vineland, NJ) diameter glass columns approximately 30.5 cm in length with Teflon end caps. Peristaltic pumps were used to control the flowrate. A schematic of the set-up is shown in Figure 2. Three water sources, DI water spiked with phosphate, RO concentrate from pilot unit of the North City Water Reclamation Facility in San Diego, and RO concentrate from the pilot in Rio Rancho, New Mexico were used in the bench scale experiments to evaluate the above mentioned resins. Struvite precipitation experiments were conducted in Imhoff cones held in a wooden holder. Struvite precipitation tests were conducted in DI-water and regenerant solution of the resin bed after exhaustion with RO concentrate.



**Figure 2: Schematic of IX experimental setup**

### Electrochlorination

The Electrochlorination system used consisted of a modular configuration. Key components of the system include electrolyzer cell, salt dissolver, brine proportioning system, metering pumps, hypochlorite storage tank, and power supply. Figure 3 shows the setup including major components of the system. The electrolytic cell is constructed of titanium tubing with CPVC installing unions. The cell consists of two outer mono-polar electrodes and one inner bi-polar electrode. The cell discharge contains a gas separator. The manufacturer suggested capacity of this system is about 2-16 kg/day free available chlorine. The strength of hypochlorite was anticipated to be about 0.8 %. Raw materials required per pound production of chlorine was about 3.5 lbs salt with 2.5 kwh (AC) and 15 gallons of water required.



**Figure 2: Picture of Electrochlorination experimental setup**

## TEST PROCEDURES

### BMED

A series of preliminary tests were conducted to determine the operating conditions such as current density, length of run and batch volume that would be expected from the typical salinities (and ionic compositions) expected in RO concentrate. After optimizing these parameters, tests were conducted with actual RO concentrate from two sources. RO concentrate from two pilot systems was utilized for this testing. The first pilot system from which RO concentrate was obtained consisted of a UF/RO train operating on tertiary treated wastewater at the North City Water Reclamation Facility in San Diego, CA. The second pilot was the one operated on raw wastewater at the WWTP#2 in Rio Rancho, NM and included a MBR/RO train. The concentrate from each pilot was pretreated appropriately to prevent fouling of the ED membranes.

### Struvite Recovery

An ion exchange column was designed with specifications based on similar experiments conducted on wastewater by Zhao and Sengupta (1998). Regeneration of the exhausted ion exchange bed was conducted using a NaCl solution (6 % w/v, or about 1 M) acidified to a pH of 4.3. For struvite precipitation, ammonium chloride (NH<sub>4</sub>Cl) and magnesium chloride

( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) were added to the phosphate solution in the molar ratios of P:  $\text{Mg}^{2+}$ :  $\text{NH}_4^+$  :: 1: 1.5: 1.

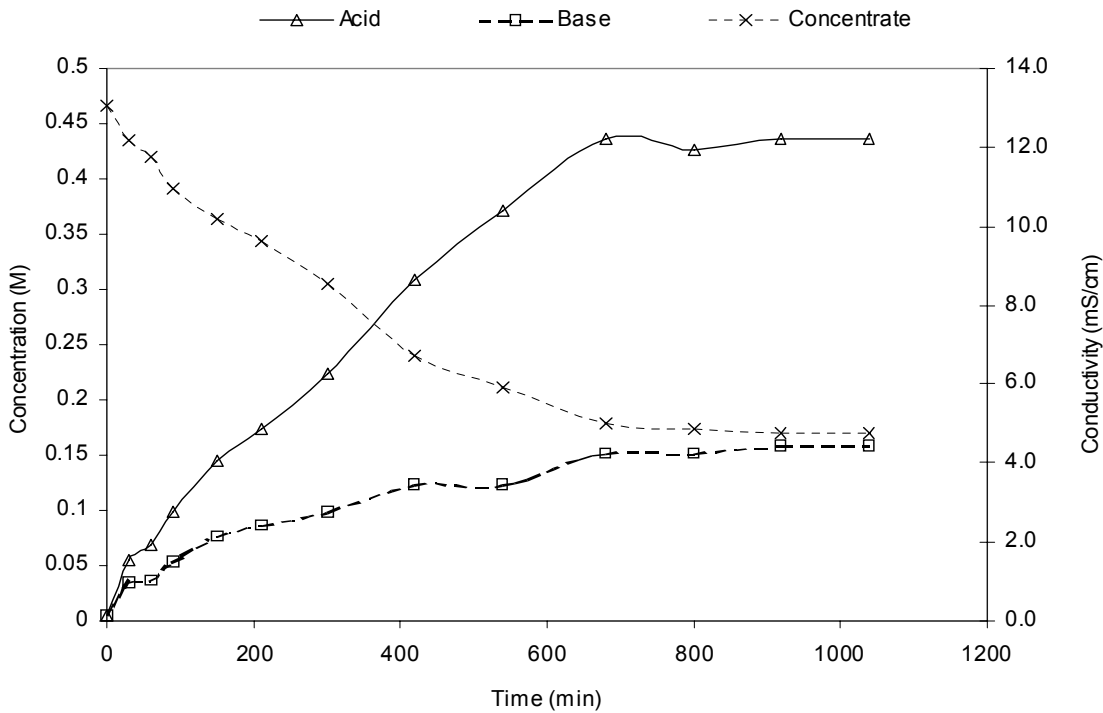
### **Electrochlorination**

The Electrochlorination system was assembled as shown in Figure 3. Commercial food grade sodium chloride solution was mixed with water to make a saturated salt solution (~26 %). Since the electrolytic process produces hydrogen gas, a ventilation system was connected to release hydrogen gas from the chlorine storage tank. The flow-rates of the salt solution and the feed water were adjusted properly to obtain required conductivity of the solution. Current, voltage, resistance, free chlorine, conductivity, specific gravity, and temperature were measured throughout the test.

## **RESULTS AND DISCUSSION**

### **BMED**

Several preliminary tests were conducted with synthetic solutions of salt ( $\text{NaCl}$ ) at high and low concentrations followed by tests with mixed salt solutions representing pretreated RO concentrate and finally with actual pretreated RO concentrate from two sources. These tests were used to select the operating conditions for tests with pretreated concentrate. During tests with pretreated concentrate it was intended to design the tests with actual concentrate to show complete desalination in 8-10 hours so the batch volume was adjusted accordingly. The tests were conducted with RO concentrate from two sources. Results are presented here from one source. These results shown in Figure 4 were obtained with RO concentrate obtained from an IMS system operating on raw wastewater after appropriate pretreatment. The current density utilized was optimized after testing various current densities. These figures show that close to complete desalination of the RO concentrate feed stream is possible in 8 hours. Additionally acid and base concentrations of 0.2 N or higher were obtained. The acid and base concentrations are highly dependent on the volume of the concentrate. Therefore, higher concentrations could be expected in the treatment of larger batches of concentrate and when longer run times are utilized. The water quality composition of the product shows TDS and other major ions except silica concentration were in low levels. Therefore, after production of acid and bases, the product water can be treated again with RO further minimizing the concentrate volume.



**Figure 4: BMED Results on Softened RO concentrate**

**Struvite Recovery**

The side-by-side comparison of Cu-loaded Dow 3N and PhosXnp tested with the Rio Rancho RO concentrate as shown in Figure 5 and suggests that PhosXnp resin is more selective to phosphate and the removal capacity is about an order of magnitude higher than the phosphate removal by the Cu-loaded resin. According to Figure 5, the complete phosphate breakthrough occurred in Cu-loaded column at 170 bed volumes, whereas even after 700BVs, the effluent phosphate concentrate was lower than influent concentration. This data suggests PhosXnp is a phosphate selective resin.

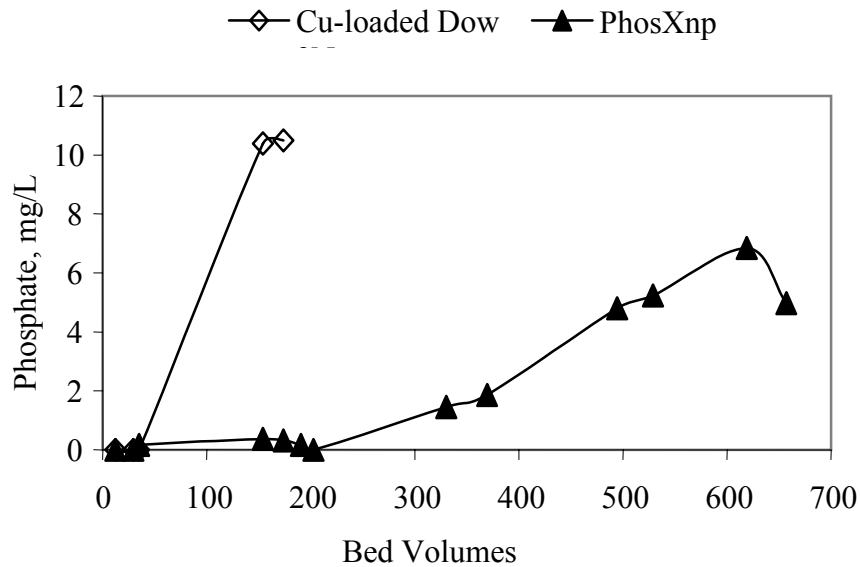


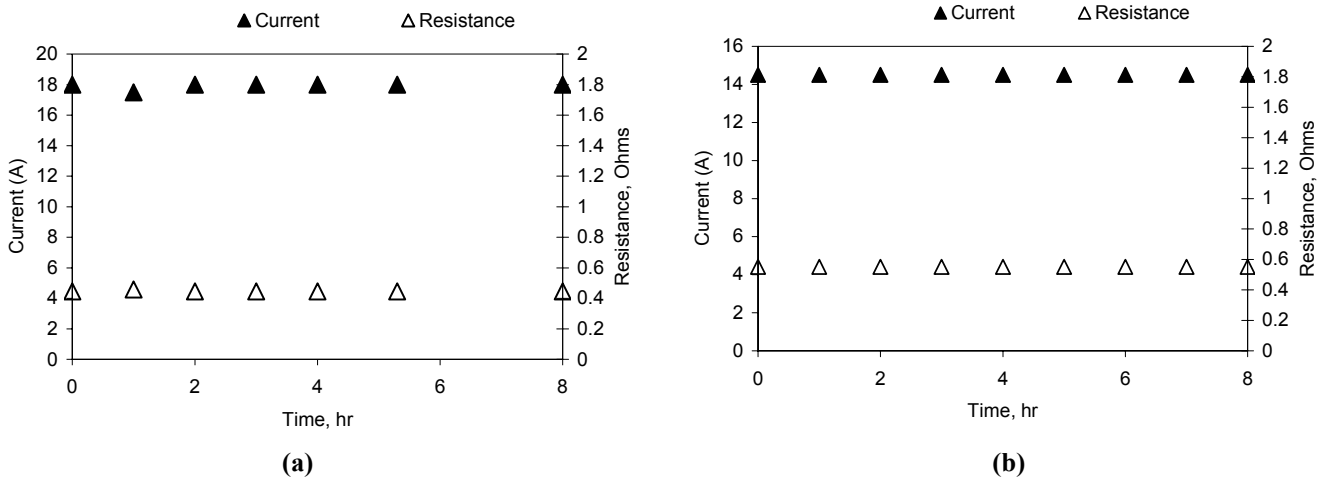
Figure 5: IX Results on RO concentrate using two different phosphate selective resins

The Cu-loaded Dow 3N column exhausted with the Rio Rancho RO concentrate was then regenerated up to 10-bed volumes. From the area within the phosphate elution profile about 78 mg P/L was recovered, which equates to about 85 % of total adsorbed phosphate. About 30-40 % release of adsorbed nitrate, sulfate and chloride was also noticed. These results demonstrate that the phosphate selective resin is regenerable. Even though no regeneration test was conducted with PhosXnp, the manufacture reports about 100 % recovery of phosphate from the exhausted resin (Cinar, 2005).

Two sets of tests were conducted to demonstrate struvite precipitation. A struvite precipitation test was conducted in DI water spiked with 6 % NaCl and 1600 mg/L of total P to determine the appropriate molar ratios of P, Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>. After a series of testing, the optimum molar ratio of P, Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> was observed to be 1:1.5:1. Only the results of experiments conducted with this ratio are included in this report. The test was conducted at three different pHs, since the speciation of phosphate and ammonium varies with the pH of the solution. Phosphate concentrations before and after struvite precipitation were monitored. After establishing the optimum conditions, struvite precipitation tests were conducted in regenerant solution obtained from regeneration of Cu-loaded Dow 3N exhausted with the Rio Rancho RO concentrate. The regenerant solution contained about 78 mg/L of total P. Magnesium, ammonium and phosphate were added in a molar ratio of 1.5:1:1. The test was conducted at a pH of 9.0. A relative mass balance of the major ions such as nitrate, sulfate and phosphate was conducted for 200 mL of the regenerant solution and the data obtained suggests that about 30-40 % elution of adsorbed nitrate and sulfate was noticed during regeneration, where as about 90 % phosphate desorption was observed during regeneration. Additionally, the presence of nitrate and sulfate were also noticed in the supernatant of the precipitation test. This suggests that the precipitate contained nitrates and sulfate compounds. No significant amount of phosphate was noticed in the supernatant solution demonstrating almost 100 % precipitation of phosphate during precipitation.

**Electrochlorination**

The electrochlorination test was conducted with tap water and the Rio Ranch RO concentrate. The system was operated for 8 hours with the tap water and current and voltage were measured and corresponding resistance was calculated. At the end of the run the electrolyzer was cleaned and the RO-concentrate was used to generate chlorine. Figure 6a shows the variation of current and resistance of the system with tap water for 8 hours. According to Figure 6a, during this run the current and resistance were constant. Figure 6b shows the performance of the system operated with pretreated RO concentrate. The system was started operating at a set current and operated for 8 hours. At the end of 8 hours no significant change of current and resistance were noticed. Therefore, it can be concluded that the system can be used to produce chlorine from the RO concentrate without noticeable fouling. The variation in current in the two cases can be attributed to the different conductivities of the two feed solutions (tap water vs. treated RO concentrate). The purpose of the experiment was to demonstrate consistent chlorine production so the flow rates from the salt and the feed solution was not varied leading to this difference in conductivities.



**Figure 6: Electrochlorination Results (a) Variation of current and resistance with tap water (b) Variation of current and resistance with concentrate.**

Figure 7a shows the variation of chlorine concentration from Clor Tec™ T-2 over time with feed from tap water and Figure 7b shows the same result with RO-concentrate. According to Figure 7, about 6,000 mg/L of free chlorine was produced from both tap water and RO-concentrate, which is 0.6 % of free chlorine and similar in magnitude to the suggested chlorine concentration at 0.8 %. It also shows the consistent strength of the produced chlorine solution.

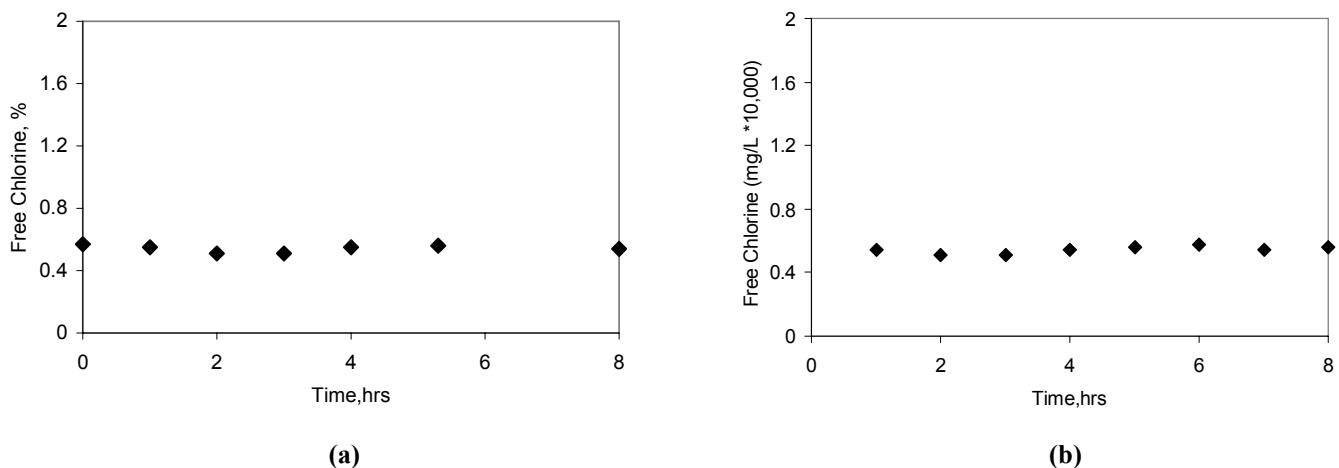


Figure 7: Electrochlorination Results (a) Variation in produced hypochlorite concentration with tap water (b) Variation in produced hypochlorite concentration with tap water with RO concentrate.

## CONCLUSIONS

The following conclusions can be derived from the above results

- Phosphate recovery and struvite precipitation using RO concentrate from a wastewater reuse application was demonstrated to be technically feasible using the PhosXnp resin obtained from Solmetex, Inc.
- The Bipolar Membrane Electrodialysis process was shown to be technically feasible for producing mixed acids and bases of reusable quality from RO concentrate.
- The Electrochlorination process was shown to be technically feasible for producing 0.6 % hypochlorite for the bench scale tests performed and is a technically feasible alternative for RO concentrate reuse. The quality of the hypochlorite produced was similar to that produced with tap water as a source.

## ACKNOWLEDGEMENTS

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