

Energy and Resources Recovery from Reverse Osmosis Desalination Concentrate

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Research background and overview:

The overarching goal of this research project is to develop technologies for beneficial salinity management. Specifically, the project focuses on the energy and resources recovery from reverse osmosis (RO) desalination concentration, which can reduce the cost associated with desalination operation and minimize the environmental impact associated with the disposal of desalination concentrate. The project has been carried out in two phases. The first phase of the study emphasized on harvesting salinity energy from concentrate using an electrochemical capacitor system. The second phase investigated the resource recovery, specifically, phosphorus from RO concentration.

Phosphorous is a valuable element that is essential as a fertilizer in agricultural industry. However, it has been speculated that the world phosphorus production from phosphate rock will peak to its high in the decade of 2030-40 and then the production will inescapably decrease due to the depletion of its natural reserves. Due to the shrinking supply and ever increasing demand the quality of reserves is declining (Runge-Metzger, 1995). Florida is one of the leading producer of phosphorus in the United States (Jasinki, 2005) reported that the phosphate rock reserves in Florida, could be totally depleted by 2050.

RO concentrate has a considerable level of organic phosphorous, mainly due to the application of phosphonate-based antiscalant. In membrane related desalination processes phosphorus-containing chemicals (*i.e.*, organophosphates) are used as antiscalants to prevent scaling of membranes. These antiscalants have excellent chelating properties and are also very effective inhibitor of mineral precipitation, thus raising the saturation point of sparingly soluble salts including calcium carbonate (CaCO_3), calcium sulfate (CaSO_4) and others. It is estimated that the concentration of organic phosphorous in the RO concentrate can reach several mg/L. This is a significant source of phosphorous. However, RO concentrate is typically discharged without recovering the phosphorous from organic phosphate in antiscalant. High phosphorus content due to concentrate disposal can lead to eutrophication in receiving water bodies and degradation of ecological system. For example, a phosphorous concentration as low as 30 $\mu\text{g/L}$ can cause severe eutrophication. In addition, as excellent chelating agents, organic phosphonate compounds can mobilize potentially toxic metals in the receiving water.

Currently, little research has been done to investigate the potential to extract organic phosphonate from RO concentrate, convert it to inorganic phosphorous and recover as a valuable phosphate fertilizer. Technologies for removing phosphorus from the concentrate are still unexplored. Recovering the phosphonate in its antiscalant form has received some attention in the recent years (Mohammadesmaeili, 2010). However, no prior research has investigated the recovery of phosphate as an inorganic fertilizer.

In this project, we proposed a ground-breaking approach to achieve phosphorous recovery from RO concentrate. Granular ferric hydroxide (GFH) is known to be an excellent adsorbent with a higher capacity of adsorption for phosphorus from water due to the strong binding properties (Cornell and Schwertmann, 2013). It has been successfully used as an adsorbent for arsenic removal from wastewater. This affinity of phosphorus to the surface of GFH gives it an edge over adsorption of other anions (Geelhoed et al., 1997 and Genz, 2005), mainly due to interactions of surface charges. Thus, our proposed approach involves the adsorption of organic phosphonate on the surface of GFH from RO concentrate, subsequent desorption of the organic phosphonate from GFH at elevated pH to generate a concentrated solution. Following that, an advanced oxidation step using ultraviolet-based hydrogen peroxide (H_2O_2) was employed to convert organic phosphonate to value inorganic phosphorous mineral as fertilizer. The research objectives are to:

- (1) Examine the time dependence of adsorption of organic phosphonate on GFH
- (2) Examine the impact of ions in RO concentrate on adsorption of organic phosphonate on GFH, for example, calcium (Ca^{2+}) since it is present in high concentrations in RO concentrate.
- (3) Optimize the desorption of organic phosphonate and its conversion to inorganic phosphorous during the separation processes.

Experimental method:

Experiments were carried out in a batch reactor. The system was stirred continuously at 400 rpm to maintain uniform suspension of GFH throughout the batch volume. The GFH dosage was 2.6 g/L while the antiscalant dosage was 1.5 mg P/L. The pH was maintained between 7.6 and 7.8 throughout the experiment. Further, the pH was raised above pH 10 to desorb the antiscalant from the concentrate obtained after centrifuging the solution. Desorbed solutions were subsequently oxidized in UV/ H_2O_2 system with a H_2O_2 dosage equivalent to 50 times of the concentration of organic phosphonate. The photochemical oxidation experiment was carried out for 60 minutes at a wavelength spectrum of 200-600nm using a medium pressure UV lamp. Further, orthophosphate was measured by the standard ascorbic acid method. A UV/vis spectrophotometer was used to measure the concentration of orthophosphate in the solution.

Progress to date:

At the experimental conditions mentioned above, the impacts of adsorption time (i.e., 4 and 24 hours) and the presence of cation (i.e., Calcium) on phosphorous recovery are shown in Figure 1. Experiments were carried out with varying concentrations of calcium. Based on the conditions tested so far, a maximum recovery of 37% of antiscalant has been achieved at a molar phosphorus: calcium ratio of 1:2 with a 24 hours' adsorption experiment. However, the presence of calcium does not show a very significant increase in the recovery. The recovery obtained with 24 hours' adsorption experiment is much higher than the 4 hours' adsorption, suggesting that the recovery percentage depends on adsorption time.

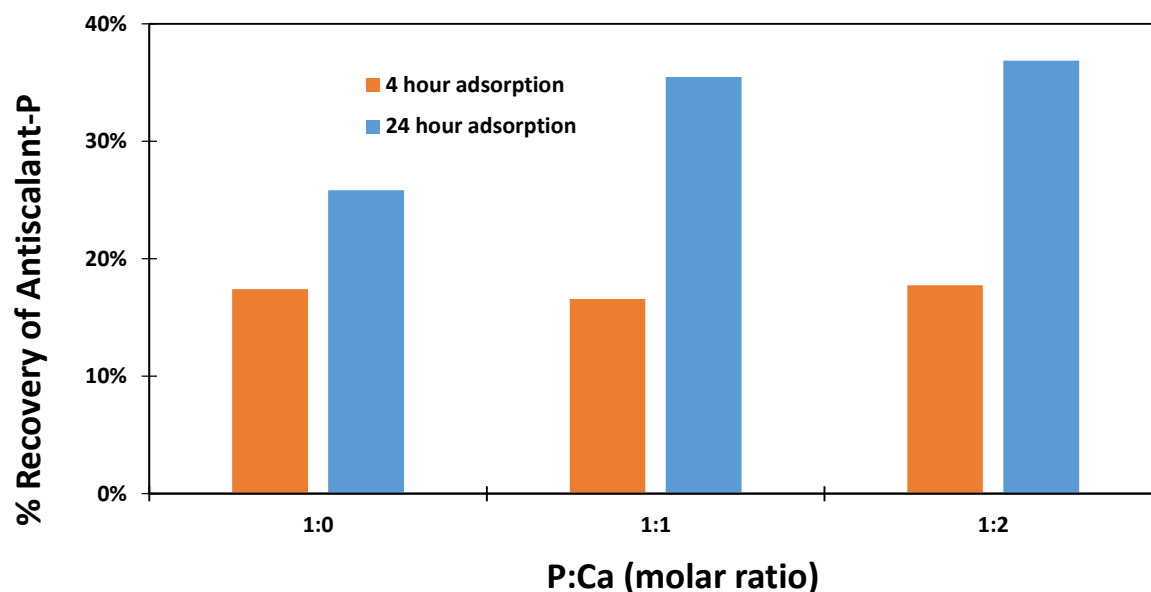


Figure 1: Impact of P-to-Ca molar ratio on the efficiency of recovery of phosphorus for various [P:Ca] ratio as antiscalant. Initial pH: 7.8, GFH: 2.6 g/L. antiscalant: 1.5 mg-P/L. Batch volume: 250 mL

During the recovery process, the distribution of the antiscalant as phosphorus can be divided into three groups:

- (i) Unrecovered antiscalant from the bulk RO concentrate (i.e. remained in the solution)
- (ii) Extracted from the bulk RO concentrate and recovered from the adsorbent (i.e. recovered)
- (iii) Antiscalant that is recovered from the bulk RO Concentrate but could not be desorbed from the adsorbent (i.e. adsorbed on metal oxide)

Figure 2 shows the antiscalant distribution in the end of the process. It is evident from the distribution graph that more than 97% of the antiscalant was removed from the RO concentrate thus bringing down the concentration of phosphorus in the antiscalant from 1500 $\mu\text{g P/L}$ to 40 $\mu\text{g P/L}$. Of the 97% removed, 20% of the antiscalant could be recovered from the solution. Thus, a major portion of antiscalant remains unaccounted for. The possible reason for that could be an inefficient desorption process which led to only a partial recovery of the antiscalant from the GFH.

Another reason could be incomplete transformation of organophosphate to inorganic phosphate. The analysis method relies on measurement on the transformed organophosphate to inorganic phosphate. However, the later hypothesis seems less contributable due to the fact that the

increase in the hydrogen peroxide dosage in the UV-photolysis step for conversion of organic to inorganic phosphate did not change the measured results.

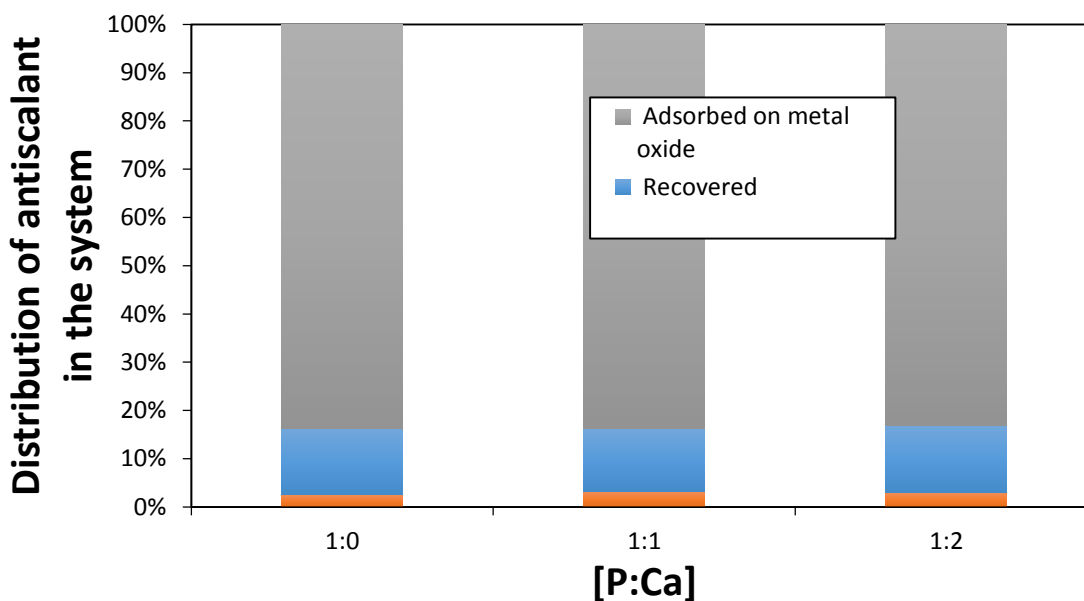


Figure 2: Distribution of antiscalant in the separation process for different P-to-Ca molar ratios. Initial pH: 7.8, GFH: 2.6 g/L. antiscalant: 1.5 mg-P/L. Batch volume: 250 mL. Batch time: 4 hours.

Future plans:

The results indicate that a reasonable removal of antiscalant (final concentration of 40 $\mu\text{g-P/L}$) can be achieved by this process. Thus this can prove to be a promising technique for removing antiscalant (phosphorus) from the reverse osmosis concentrate. However, the downstream process still needs optimization to improve the recovery of the removed phosphorus.

Task 1:

To increase the ionic strength of the system by adding concentrated NaCl. Increasing the ionic strength can suppress the double layer and hence can reduce the bond between the adsorbed species. Reverse osmosis concentrate also has a chloride concentration of around 500 mg/L. Different dosage of NaCl will be investigated.

Task 2:

Study the effect of presence of other species such as Mg^{2+} and SO_4^{2-} . Similar to Calcium, other entities may or may not have an effect on the recovery process. Thus trying these species with typical concentrations found in the RO concentrate (41 mg/L Mg^{2+} and 268 mg/L SO_4^{2-}) will give an insight to the extent of removal based on realistic conditions.

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