Use of Desalinated Reject Water as a Source of Magnesium for Phosphorus Recovery

Kazi P. Fattah, Sina Shabani, and Aqeel Ahmed

Abstract—In this study, the formation potential of struvite has been assessed using synthetic centrate mixed with reject water of a local desalination plant. $NH_4H_2PO_4$, $MgCl_2.6H_2O$, and NH_4Cl were mixed in specific concentrations to simulate centrate of a wastewater treatment plant coming from centrifuge of anaerobic digesters. Due to the lack of adequate magnesium in domestic wastewater, the prepared synthetic centrate was further mixed with the reject water of MED and RO units of the desalination plant since it is rich in magnesium which is required for formation of struvite. Significant removal of phosphorus was observed through precipitation of phosphorus compounds after stirring the samples in a batch reactor.

Index Terms—Magnesium, phosphorus recovery, struvite, wastewater

I. INTRODUCTION

Phosphorus and nitrogen are considered as nutrients which are needed for living organisms to metabolize; however, excess amount of such nutrients can cause eutrophication of water bodies [1]. One of the primary sources of phosphorus in natural water bodies is through the effluent of the wastewater treatment plants; that is because human sewage contains high concentration of phosphorus. In wastewater treatment plants, especially those employing anaerobic digestion of their sludge or where enhanced biological phosphorus removal (EBPR) process is carried out typically have high levels of phosphorus within their treatment plant pipelines post dewatering facilities [2]. The problem caused by excess amount of phosphorus in wastewater treatment plants is the of struvite formation (magnesium ammonium phosphate ,MgNH₄PO₄.6H₂O). Struvite is formed as white crystals that are made of equal molar concentrations of magnesium, phosphorous as well as ammonium (MgNH₄PO₄.6H₂O) [3]. The equation below represents the reaction that takes place in forming struvite.

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 .6H_2O$$

Removal of phosphorus and ammonia is possible in the presence of magnesium through precipitation of struvite [4]. Under specific environmental conditions of temperature, pH, alkalinity, phosphorous, ammonium and magnesium concentrations, struvite precipitation can be controlled.

With the advancement of treatment processes and the

required discharge regulations in reduced phosphorus discharge to the water bodies, many wastewater treatment plants have secondary and tertiary phosphorus removal processes. The result is the increase in internal phosphorus concentrations, which has increased occurrences of struvite formation. The precipitation of struvite can lead to problems such as freezing of the valves, clogging of the pipes, and fouling of the pumps. Previous studies show that accumulation of struvite on pipe walls and equipment surfaces of anaerobic digestion significantly increases operational problems and maintenance costs of wastewater treatment plants [5] and [6]. The most common practice of removing uncontrolled formation of struvite is using concentrated acid solutions to be flushed through pipes, or in extreme cases of significant blockages due to struvite, the replacement of the entire section of affected pipeline [7]. One study shows that digested sludge pipe line's bore was reduced from 0.3 to 0.15 meter due to formation of struvite [8]. Another case shows that in 12 weeks, a 150 mm pipe made of rubber reduced to 60 mm in the discharge line of centrate [9]. Although struvite might be considered as a main problem occurring in wastewater treatment plants, it can be used in the production of fertilizers and soil conditioners [6]. There is a significant demand for phosphorus as a fertilizer for agricultural purposes. If phosphorus recovery happens in form of Struvite, it can be used as a slow-release fertilizer which will not leach like conventional fertilizers. In addition, struvite will remain on the soil for a notable period [10]. Struvite solubility should be minimal in order to remove struvite by precipitation, and higher pH values (8.0-9.0) minimize the solubility of struvite [3]. One study showed that initial pH of more than 8.1 was effective in formation of struvite [11]. Stirring and aeration will increase the pH of the solution through loss of CO₂ which is a favorable condition for struvite formation [12]. The simplest methods for inducing struvite formation are controlling pH level and magnesium concentration [9]. The purpose of this research is to assess the formation potential of struvite by mixing synthetic centrate and reject water from desalination.

Magnesium plays a vital role in struvite precipitation. As shown in Table I, majority of previous studies on recovery of phosphorus used chemicals such as magnesium salts for their source of magnesium [13]-[17]. All these chemicals are not economically efficient. On the other hand, magnesium is lower in concentration in comparison to phosphorus and ammonia resulting in an excessive need of adding magnesium to reach the required equilibrium for precipitation of struvite [18]. One study shows that sea water can be a suitable source of magnesium for such experiments [19]; however, using membrane filtration can be another problem to cost

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effectiveness of the whole process. United Arab Emirates has 23 % of the total production of desalinated water in the world [20]. Having the reject water from the desalination plant of, a rich and sustainable source of magnesium was used in this study which has almost no cost in comparison to previous sources of magnesium. In addition to a free source of magnesium, recovery of magnesium from the reject water will reduce the amount of magnesium that would otherwise have been discharged into the ocean.

TABLE I: LITERATURE ON SOURCES OF MAGNESIUM AS A REAGENT

No.	Source	Authors
1	BMP *	Quintana et al,2008[13]
2	Magnesium Oxide	Quintana et al,2005[14]
3	Magnesium Chloride	Korchef et al, 2011[15]
4	MgCl ₂ & MgSO ₄	Hug et al, 2013[16]
5	Magnesium Chloride	M.I. Ali, 2007 [17]

*Byproduct of Magnesium Production

II. RESEARCH OBJECTIVES

The purpose of this research is to assess the potential for phosphorus removal using desalinated reject water as a source of magnesium. The formation potential of struvite is assessed by mixing synthetic centrate and the reject water from a local desalination plant.

III. MATERIALS AND METHODS

A. Preparation of Synthetic Feed and Magnesium Source

Synthetic centrate samples were prepared to simulate the common values of phosphorus, nitrogen, and magnesium present in a centrate of anaerobic digester. The chemicals used and final targeted concentrations of the synthetic feed are shown in Table II. Desalination plant process reject water was used in the experiments for the source of magnesium. Reject water was collected from one of the multi-effect desalination (MED) and one reverse osmosis (RO) operating units at the water treatment plant. The concentration of magnesium in the MED and RO reject waters were 1555 mg/L and 2795 mg/L, respectively.

TABLE II: CHEMICAL AND FINAL CONCENTRATIONS OF SYNTHETIC FEED USED IN THE EXPERIMENTS

Chemical used	Final Targeted concentration
(NH4) ₂ HPO ₄	Phosphorus – 110 mg/L as P
NH ₄ Cl	Ammonium – 1250 mg/l as N
MgCl ₂ .6H ₂ O	Magnesium – 2 mg/L

IV. EXPERIMENTAL APPROACH

Synthetic centrate prepared in the lab was mixed with the reject water for and then samples were collected in 15 minutes intervals. The amount of reject water to be added was based on the Mg:P molar ratios of 2:1 and 8:1. Two pH set points were tested in the study - 8.3 and 8.5 – the MED reject water.

These two numbers were chosen to minimize the need for high caustic addition but at the same time provide a pH environment high enough for struvite precipitation to occur. For the RO reject, the pH was lowered to 8.0 to as the magnesium concentration was significantly higher. Caustic solution 0.1 N was used to adjust the pH value of the mixed water to the desired pH set point. Samples were tested for phosphorus and magnesium concentrations. A summary of the conditions is provided in Table III.

TABLE III: SUMMARY OF EXPERIMENTAL CONDITIONS	
Test 1 – pH 8.3, 500 ml synthetic feed, 50 ml MED solution.	
Test $2 - pH 8.5$, 500 ml synthetic feed, 200 ml MED solution.	
Test 3 – pH 8.0, 200 ml synthetic feed, 10 ml RO	
Test 4 – pH 8.0, 200 ml synthetic feed, 13 ml RO	
Test 2 – pH 8.5, 500 ml synthetic feed, 200 ml MED solution. Test 3 – pH 8.0, 200 ml synthetic feed, 10 ml RO Test 4 – pH 8.0, 200 ml synthetic feed, 13 ml RO	

V. RESULTS AND DISCUSSION

A. Influence of Reaction Time of Phosphorus Removal

Results from Test 1 and 2 (Fig. 1) showed a decrease of 42.6% and 50%, respectively, of phosphorus during the first 15 minutes of the experiment. No significant reduction in phosphorus was observed in continuing the tests beyond the first 15 minutes. Therefore, in order to reduce the removal process time, it is sufficient to carry out the process in short durations.

B. Influence of pH on Phosphorus Removal

Although the influence of pH on phosphorus removal is well documented [3], no significant difference in phosphorus removal was observed in the experiments. This could be due to the numerous "other" factors that strongly influence phosphorus removal via struvite precipitation. These factors, such as conductivity, may have contributed to diminishing reduction values. The influence of other factors in phosphorus removal is being investigated at present.

C. Magnesium Recovery

Fig. 2 shows the magnesium concentration levels before and after each trial of the experiments. For the first trial of the experiment initial magnesium of 338 mg/L reduced to 138 mg/L. In the second trial of the experiments after 15 minutes the magnesium concentration level went from 843 to 554 mg/L and in the second 15 minutes it reduced further to 554 mg/L. It can be observed that significant magnesium is still left unused. One of the reasons for the low recovery could be the influence of other ions such as calcium and sodium, which are present in significant numbers in the reject water.

Table IV shows the results of the third trial in which 200 ml was used as the synthetic feed mixed with 10 ml of reject water from the reverse osmosis unit of the desalination plant to provide magnesium. The pH of the mixed sample was controlled at 8.0 in the beginning of the experiment using 0.1 NaOH solution. Samples were taken at the same time intervals of 15 and 30 minutes of mixing using a magnetic stirrer. The results showed 47.15 % removal of phosphorus after 15 minutes followed by a further removal of 55.26 % after 30 minutes of mixing. The entire experimental plan was the same

for the fourth trial except the volume of reject water of reverse osmosis unit which was increased to 13 ml. Unlike what was expected, removal of phosphorus was not more efficient by increasing the volume of reject water by 3 ml. Results showed a percentage removal of 44.51 % and 53.50% for 15 and 30 minutes of mixing time intervals, respectively. Other parameters checked are given in Table IV and Table V which are being used for further investigation of the results.



	TABLE IV: RESULTS C	F THIRD TRIAL	
Trial 3	T15	T30	

Phosphorus	60.25 mg/L	51 mg/L	
рН	8.05	8.04	
Temperature	23.8 °C	23.9 °C	
Conductivity	17.03 mS	17.00 mS	
TDS	8.51 g/L	8.50 g/L	
Salinity	10%	10%	

TABLE V: RESULTS OF FOURTH TRIAL			
Trial 4	T15	T30	
Phosphorus	63.25 mg/L	53 mg/L	
pН	8.06	8.04	
Temperature	23.8 °C	23.8 °C	
Conductivity	18.43 mS	18.44 mS	
TDS	9.22 g/L	9.22 g/L	
Salinity	11%	11%	

VI. CONCLUSION

The recovery of phosphorus is essential for a sustainable future as it is used for the manufacturing of fertilizer and thus directly related to food production. Results of the experiments conducted in the present study showed that phosphorus recovery in form of struvite is applicable using two types of wastes – a synthetic centrate and desalinated reject water. Centrate of wastewater treatment plants and reject water of desalination plants can be mixed together under specific physical and chemical conditions in order to recover phosphorus through chemical precipitation of phosphorus. The cost of such a recovery of nutrient is significantly low since the materials used in these experiments are only wastes of wastewater and desalination treatment plants. This idea can be a huge step forward to the concepts of sustainability and zero waste. For future research ideas some parameters like temperature, pH, calcium effect, and reject water of other desalination methods can be analyzed under the same experimental conditions

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