

# Phosphate Recovery from Municipal Wastewater through Crystallization of Calcium Phosphate

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## ABSTRACT

Phosphate concentrations in municipal and agricultural wastewaters continuously increase because of the growing use of detergents and fertilizers. Thus, it seems that phosphate recovery from wastewater as calcium phosphate would be attractive due to the vast applications of calcium phosphate in industry. In the current experimental study, the phosphate recovery by addition of calcium chloride to a synthesized wastewater was investigated under alkaline conditions. The crystallization experiments showed that using seed particles, the concentration of phosphorus can be reduced from 50 to 5.5 ppm in presence of ions of magnesium and carbonate as common impurities in wastewaters.

(Keywords: crystallization, phosphate removal, recovery, wastewater treatment,  $\text{Ca}_3(\text{PO}_4)_2$ )

## INTRODUCTION

Phosphorus in different compounds is found in natural waters and wastewaters (Rand et al., 1975). Due to industrial, domestic, and agricultural activities the phosphorus input to the surface waters is continuously increasing (Henry et al., 1989).

A phosphorus concentration rise to more than 0.1 mg P/l may cause eutrophication phenomenon in which excessive growth of organisms such as algae decreases the soluble oxygen concentration in waters and causes detrimental effects on aquatic life (Henry et al., 1989 and Foy et al., 1998).

A method of phosphate removal from wastewaters is the addition of flocculants such as ferric chloride and alum to precipitate

compounds containing phosphorus. Around 70-95% of phosphorus can be removed depending on the points of flocculent introduction. This method suffers from high costs of chemical flocculants and has been substituted by biological methods of phosphate removal (Foy et al., 1998). In a biological treatment, the wastewater is aerated for about two hours until a higher pH is reached and phosphates are crystallized (Suzuki et al., 2002).

Another method of phosphate removal is the use of DHV crystalactor process, in which a fluidized bed crystallizer containing sand seed is used and phosphorus in wastewater, due to addition of materials such as lime, calcium chloride, magnesium hydroxide, and magnesium chloride, crystallizes in different compounds such as calcium and magnesium phosphates (Giesen, 1999). Using this method, dissolved phosphorus in wastewater may be reduced from 9 to 0.5 mg/l (Foy et al., 1998).

A preliminary literature survey showed that most municipal wastewaters have around 25-50 ppm of phosphorus (Giesen, 1999 and Sekler et al., 1996) and an economical recovery of phosphate from wastewater necessitates a phosphorus concentration of about 50 ppm (Foy et al., 1998).

The present study aims at investigating the feasibility of phosphate removal by crystallization of calcium phosphate from municipal wastewaters using seed crystals of calcium phosphate and addition of a  $\text{CaCl}_2$  solution to provide calcium ions.

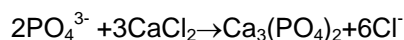
It is pertinent to note that  $\text{CaCl}_2$  is produced through the Solvay process as a by-product. A local petrochemical complex has experienced many difficulties in disposal of calcium chloride produced in this process.

## EXPERIMENTAL DETAILS

The experiments detailed in this paper were carried out at room temperature in a two liter glass crystallizer equipped with a magnetic stirrer. The synthetic solution, containing 50 ppm phosphorus, was prepared by dissolving 0.68 g of  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  in 900 cc distilled water. A specified mass of calcium phosphate powder as initial seed particles, was added to the solution.

A calcium chloride solution was prepared by dissolving 0.767 g of  $\text{CaCl}_2$  in 700 cc distilled water. This solution was added drop-wise at the flow rate of 3.8 cc/min to the crystallizer. The amount of  $\text{CaCl}_2$  was in excess so that a molar ratio of  $\text{Ca/P} = 3.86$  was supported. Due to addition of  $\text{CaCl}_2$  solution to the phosphate solution and consequent dilution and precipitation, the pH of the solution was decreasing which was compensated by the addition of caustic soda.

The reaction between  $\text{CaCl}_2$  and phosphate ions in wastewater in the presence of an alkaline material such as caustic soda for pH adjustment results in the precipitation of calcium phosphate as (Skoog and West, 1976):



Lime milk may also be used in place of calcium chloride and caustic soda to provide both the calcium ions and alkalinity required (Sekler et al., 1996). However, due to very low solubility of lime in water, a huge volume of lime milk would be consumed which consequently necessitates a larger crystallizer. Otherwise, in case of using a suspension of lime, the solid  $\text{Ca}(\text{OH})_2$  in the crystallizer would associate with the calcium phosphate product and reduces its purity. Solubility of  $\text{Ca}(\text{OH})_2$  at 25 °C is 0.159 g/100g  $\text{H}_2\text{O}$  (Perry and Chilton, 1973).

Due to the complex composition of real municipal wastewaters and the sensitivity of the crystallization process to impurities present in the solution, at the present study a synthetic wastewater was used (Sekler et al., 1996 and Song et al., 1999). Municipal wastewater contains many compounds which may affect the precipitation process. However, generally, the influence of magnesium and carbonate ions on calcium phosphate precipitation has been reported (Sekler et al., 1996 and Abbona et al., 1990).

Therefore, to simulate the precipitation process of calcium phosphate from real municipal wastewaters, appropriate amounts of  $\text{MgCl}_2$  and  $\text{Na}_2\text{CO}_3$  were added to the synthetic wastewater prior to reaction initiation. The amount of  $\text{Na}_2\text{CO}_3$  was adjusted so that the concentration of carbonate ion in the remaining solutions not to exceed 12 mg/l (Sekler et al., 1996).

During the course of these experiments at specified time intervals, samples were taken from the solution and analyzed for the phosphate and calcium concentrations by calorimetry and atomic absorption methods, respectively.

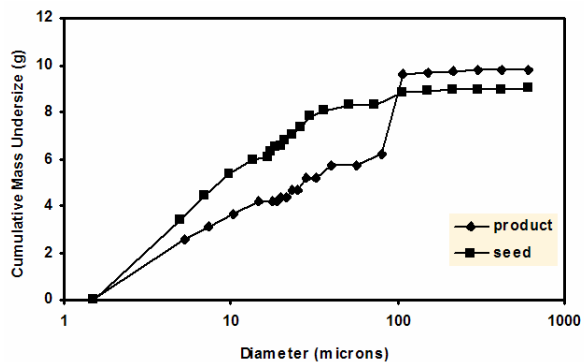
The size distribution of particles was determined using hydrometry method. This method is based on measuring the suspension density of particles in a fluid and its changes due to settling of particles. A one liter suspension of calcium phosphate particles in distilled water was provided in a graduated glass cylinder. A certain volume of 4% sodium hexametaphosphate solution was added as dispersant. The density of the mixture at certain time intervals was measured by hydrometer 152H and using related data the size distribution of particles was calculated.

## RESULTS AND DISCUSSION

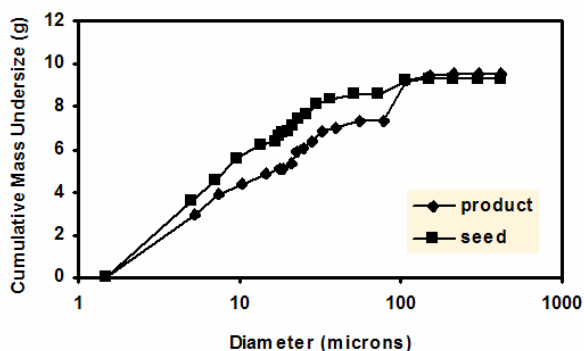
Results of particle size analysis of initial seed and final product in the presence of various amounts of magnesium ion are shown in Figures 1-3.

As the figures show, the product particles are coarser than initial seed particles, indicating that calcium phosphate mass produced through the reaction has been deposited on the seed particles. The addition of  $\text{CaCl}_2$  with a very slow flow rate prevented spontaneous release of a large amount of super-saturation.

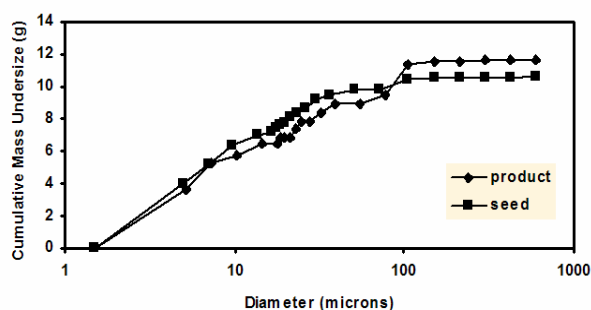
Good mixing of the suspension and the presence of enough surface area due to the addition of seed particles caused a considerable portion of releasing super-saturation to be consumed on growth rather than on primary nucleation. The mass of seed introduced to the solution and the mass of final precipitates collected at the end of experiments are shown in Table 1.



**Figure 1:** Size Distribution of Calcium Phosphate Particles Produced at the Conditions of No Magnesium Ions and  $[\text{CO}_3^{2-}] = 12$  ppm.



**Figure 2:** Size Distribution of Calcium Phosphate Particles Produced at the Conditions of Molar Ratio of  $\text{Mg}/\text{P} = 0.5$  and  $[\text{CO}_3^{2-}] = 12$  ppm.



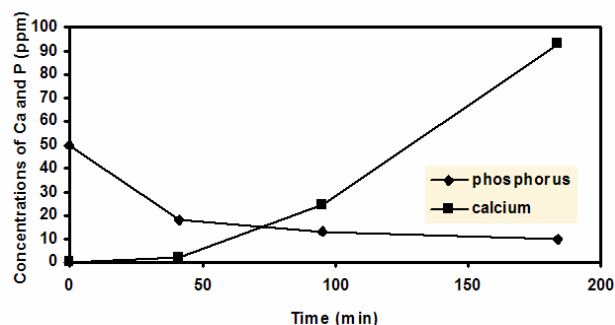
**Figure 3:** Size Distribution of Calcium Phosphate Particles Produced at the Conditions of Molar Ratio of  $\text{Mg}/\text{P} = 2$  and  $[\text{CO}_3^{2-}] = 12$  ppm.

**Table 1:** Masses of Initial Seed and Final Product in Different Runs of Precipitation Experiment.

Run	1	2	3
Mass of seed (g)	10	10.4	11.8
Mass of product (g)	10.15	10.6	12

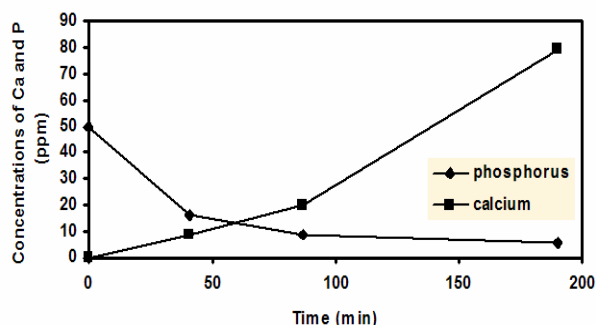
Comparison of these values of masses confirms the mass deposition on initial seed particles. The mass of phosphorus deposited in Runs 1, 2, and 3 were calculated as 81, 89, and 89 percent of the phosphorus in the feed solutions, respectively. It is notable that some product particles have probably been washed out during the filtration and were not been collected from the filter paper; thus, the deposition is likely to be more than that calculated.

Results of concentration measurements of calcium and phosphorus in the solution at various times are shown in Figures 4, 5, and 6.

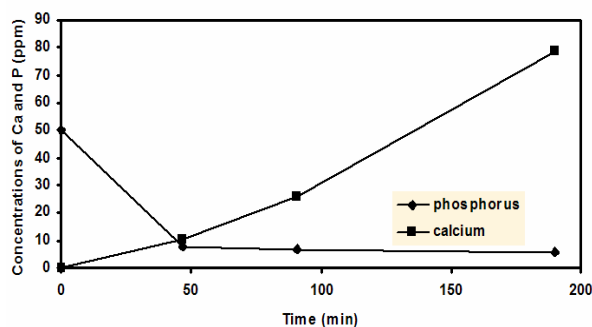


**Figure 4:** Variations in Concentrations of Phosphorus and Calcium with Time at the Conditions of Molar ratio  $\text{Mg}/\text{P} = 0$ ,  $[\text{CO}_3^{2-}] = 12$  ppm, and  $\text{pH} = 7.61 - 8.91$ .

As time passes and the concentration of calcium ion increases, the concentration of phosphorus in the solution decreases, due to precipitation of  $\text{Ca}_3(\text{PO}_4)_2$  which has a low solubility product. It is pertinent to note that solubility product of  $\text{Mg}_3(\text{PO}_4)_2$  is  $10^{-25}$ , several orders of magnitude larger than that of  $\text{Ca}_3(\text{PO}_4)_2$  which is  $2.83 \times 10^{-30}$ . Therefore, at the conditions of these experiments, it is less likely that magnesium phosphate precipitates in place of calcium phosphate.



**Figure 5:** Variations in Concentrations of Phosphorus and Calcium with Time at the Conditions of Molar ratio Mg/P=0.5,  $[\text{CO}_3^{2-}] = 12$  ppm, and pH=7.91-8.56.



**Figure 6:** Variations in Concentrations of Phosphorus and Calcium with Time at the Conditions of Molar ratio Mg/P=2,  $[\text{CO}_3^{2-}] = 12$  ppm, and pH=9.19-9.28.

The final concentration of P in the solution in absence of  $\text{Mg}^{++}$  was 9.5 ppm but in presence of  $\text{Mg}^{++}$  with molar ratios of Mg/P=0.5 and 2 was about 5.5 ppm. This suggests a higher removal and recovery of P when  $\text{Mg}^{++}$  is present in the solution.

Since the pH of solutions used in the experiments of this study was maintained in the range 7-10, thus the product of precipitation reaction would be  $\text{Ca}_3(\text{PO}_4)_2$ . This precipitate was separated from the mother solution without delay, therefore, there was not enough time the precipitate to convert to hydroxy apatite (Boister et al., 1990).

Calcium phosphate particles produced in this process may be used as a fertilizer or a feed material for fertilizer production. Since calcium

phosphate has a low solubility, it dissolves very slowly in water and may be used as a slow release fertilizer (Giesen, 1999).

## CONCLUSION

A decline of more than 80% in the concentration of phosphorus due to addition of  $\text{CaCl}_2$  to a synthetic municipal wastewater indicated that phosphorus removal and recovery is feasible. Size enlargement of calcium phosphate product due to seeding and slow release of supersaturation suggests that filterability of product may be improved.

Experiments carried out in the presence and in the absence of magnesium ions in solution showed that  $\text{Mg}^{2+}$  enhances the removal efficiency of phosphorus.

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## SUGGESTED CITATION

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