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Phosphate Recovery by Crystallization Process Using Magnesium Ammonium Phosphate Crystals as Seed Material

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Abstract. Phosphate is alarmingly depleting in a global scale and this has drawn so much attention in the area of wastewater treatment with the primary goal recovering phosphate. Fluidized-bed crystallization (FBC), being the most effective method, was used to recover phosphate from wastewater in a form magnesium ammonium phosphate (MAP) with the same crystal as seed. The process was examined at different influent flow rate ranging from 4-12 $mL\text{-}min^{-1}$ for phosphate concentration of 110 $mg\text{-}L^{-1}$. The effect of influent flow rate was investigated by measuring the conversion from liquid to solid phase. As the flow rate is increased from 4-12 $mL\text{-}min^{-1}$, the rate of phosphate removal also increases. The conversion also depends on the inlet flow, which also increases from 66.39-74.18% as the flow rate is increased. Highest conversion of about 74% was attained at 12 $mL\text{-}min^{-1}$ inlet flow rate. SEM and XRD analysis revealed that the recovered solids were aggregates of struvite (MAP) crystals.

Keywords: struvite, magnesium ammonium phosphate (MAP), fluidized-bed crystallization, Influent flow rate

1. Introduction

Phosphate is an important compound to agricultural and industrial development. Inorganic phosphates are commonly mined from non-homogeneous, non-renewable phosphorite or rock phosphate [1]. The result of which will deplete the supply of the mineral in the next 50 to 100 years [2], [3]. During the last decades, sustainable measures in recovering phosphate has gained so much attention to reduce dependence on phosphate finite resource, reduce water pollution and increase communities' phosphorus security [1].

Of the various treatment technologies, chemical precipitation and crystallization are widely used treatment methods to recover phosphate from wastewater. If efficiency and product recyclability is considered, seeded fluidized bed crystallization (FBC) remains superior [4]. Currently, sand is the most popular seed that has been used in FBC process due to its inexpensiveness and availability, however, the pellets produced are impure [5]. To address this problem, FBC using seeds of the same crystal material might be used to produce pure crystal pellets.

Phosphate is commonly precipitated and crystallized as simple metal salts such as calcium orthophosphate, however, if other ions are present in the waste stream it is more desirable to form complex phosphate salts having high selectivity on phosphate and simultaneously removing other pollutants in wastewater, magnesium ammonium phosphate hexahydrate (MAP, struvite) being the most common [1]-[7]. Struvite is a biogenic sparingly soluble mineral that has been used as fertilizer to high value crops. The crystallization of struvite is described Eqn. 1.

$$Mg^{2+} + HPO_4^{-2} + NH_4^{+} + OH^{-} + 6H_2O \rightarrow MgNH_4PO_4\ 6H_2O + H_2O \quad (1)$$

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Several studies have been made for struvite crystallization in an FBC but no study has been employed on the system that uses the same crystal material as seed for an FBC process. In this study, the effect of influent flow rate on fluidized-bed crystallization of MAP onto the surface of struvite seeds was investigated. The recovered product can be used as substitute to phosphate rock used in phosphoric acid industry and phosphorus smelting or it can be directly used as slow-release fertilizer [8].

2. Material and Methods

2.1. Chemicals and analytical methods

110 mg-$L^{-1}PO_4^{3-}$ solution was prepared from KH_2PO_4 (99%, Panreac), 165 mg-L^{-1} NH_4^+ was prepared from NH_4Cl (99.8%, Merck) and 110 mg-L^{-1} Mg^{2+} solution was prepared from $MgCl_2.6H_2O$ (99%, Panreac). 1.0 M HCl (37%, Merck) and 1.0 M NaOH (99%, Merck) were used for pH adjustment.

Collected solids after each run were filtered and dried at 37°C for two days prior to characterization. The morphology of MAP crystals were examined using scanning electron microscopy (SEM) QUANTA 200 Mode. The MAP pellets were also analyzed and identified by X-ray diffraction (XRD) using a DX-2000 SSC model diffractometer with CuK_α radiation as source. The crystallite thickness was calculated from the XRD result.

2.2. Fluidized bed crystallizer

A 1.35 L cylindrical vessel (Fig. 1) was used as crystallizer for MAP. The FBC column was equipped with pH transmitter for controlling the pH inside the reactor and peristaltic pumps for reagent dosing and recirculation.

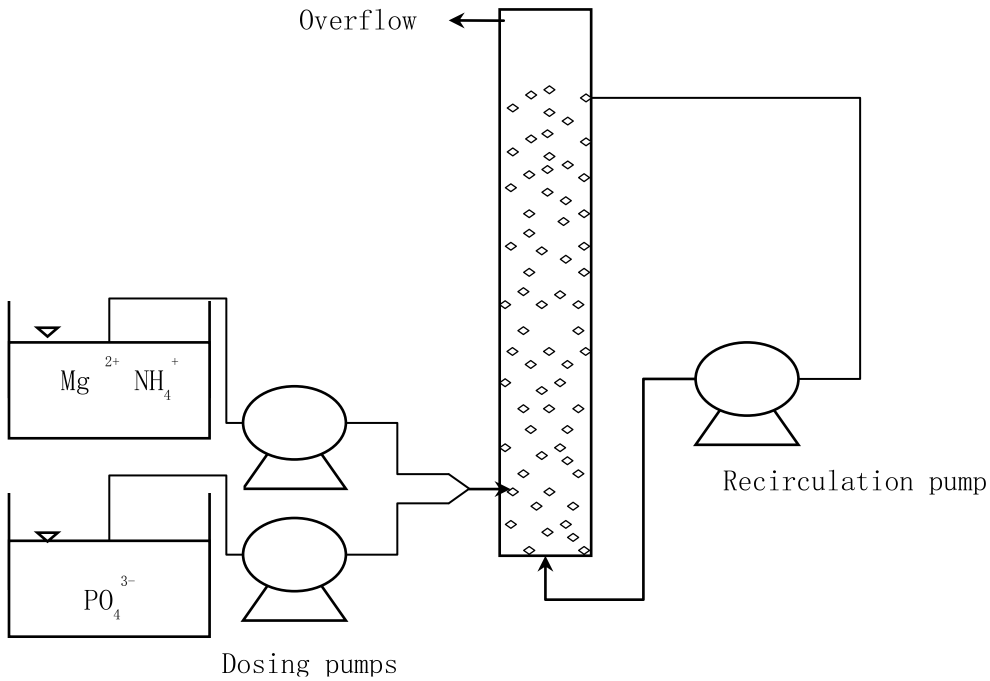

Fig. 1: Fluidized-bed crystallization set-up

2.3. FBC experiments

Synthesized MAP seeds (2 g-L^{-1}) were introduced into the reactor filled with reverse osmosis water. The precipitant and phosphate solution were injected in the system at a specified flow rate. The temperature of the solution ranged from 25-29°C and pH was maintained at 8.5. Samples were obtained from the overflow at different time intervals ad were filtered using 0.45 μm membrane. Samples were mixed with HNO_3 prior to phosphomolybdenum blue scanning. The system is allowed to run for 11 hours.

3. Results and Discussion

3.1. Removal efficiency and conversion from liquid to solid phase

The concentration-time profile of dissolved phosphate in the outlet stream is shown in Fig. 2. Phosphate conversion rates significantly increased with higher influent flow rates. Therefore, inlet flow rate is a significant factor in phosphate removal in an FBC since minor adjustments in flowrate significantly change the rate of conversion from solid to liquid phase. The time it takes to raise the concentration of phosphate in the FBC decreases with increasing influent flow. It can be seen from Eq. 1 that elevated amounts of reagents will shift the reaction to the right, producing more MAP crystals. Since the rate of the reaction is concentration dependent [9], high influent flow rate decreases the time to reach maximum conversion.

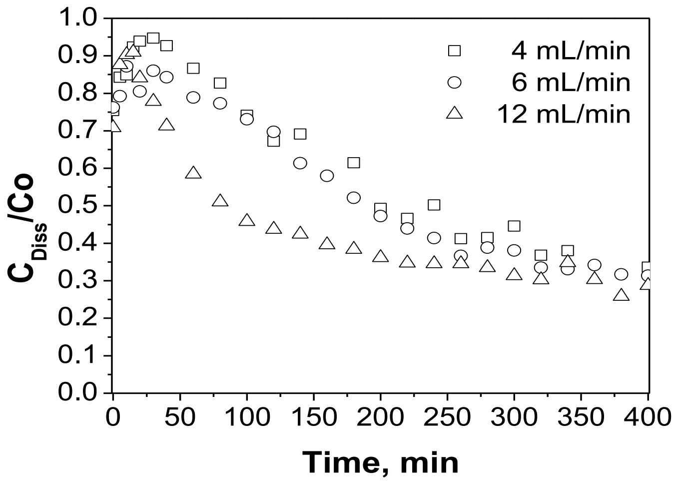

Fig. 2**:** Variation of dissolved phosphate concentration in the outlet steam with time at different influent flow rate

It is important to study the influence of inlet flow to be used in FBC because the flowrate is related to the residence time and reactor volume. Given the same reactor volume, raising the influent flow rate will decrease the residence time of the reagents. It seems that conversion from liquid to solid phase for influent flowrate ranging from 4-12 mL-min^{-1} increases from 66.39-74.18% (Table 1), implying that a larger quantity of wastewater can be treated at a given time for a specific reactor volume and desired conversion.

Table 1: Maximum removal efficiency and crystal conversion at different influent flow rate

Inlet flowrate, ml/min	Projected Residence time, min	Maximum crystal conversion
4	357.50	66.39%
6	238.33	68.68%
12	119.17	74.18%

3.2. Solid characterization

The morphology of the solids formed at different influent flow rate are shown in Fig. 3. As observed the crystals formed at 4 and 6 mL/min are comparable and are smaller relative to the ones produced at 12 mL/min. This is due to the fact that at the same influent phosphate concentration, the amount of reagents available to induce crystal growth with supersaturation as the driving force is much higher at elevated influent flow rate. If the system is allowed to run for seven days at an influent flow rate of 12 mL/min, crystals will grow bigger and will aggregate together forming a more stable solid that will not disintegrate when dried (Fig 3-d). The crystal orthorhombic crystal structure of MAP can be seen from the SEM micrographs and this structure is validated from the XRD results. The characteristic peaks of MAP (Struvite) were found in all samples (Fig. 4), which proved that the solids are indeed struvite with the following lattice parameters: a = 6.94500 Å, b = 11.20800 Å, c = 6.13550.404 Å, α=90^o, β=90^o and γ=90^o.

The peak intensities in XRD pattern reflect the total scattering from the each plane in the phase's crystal structure, and are directly dependent on the distribution of particular atoms in the structure.

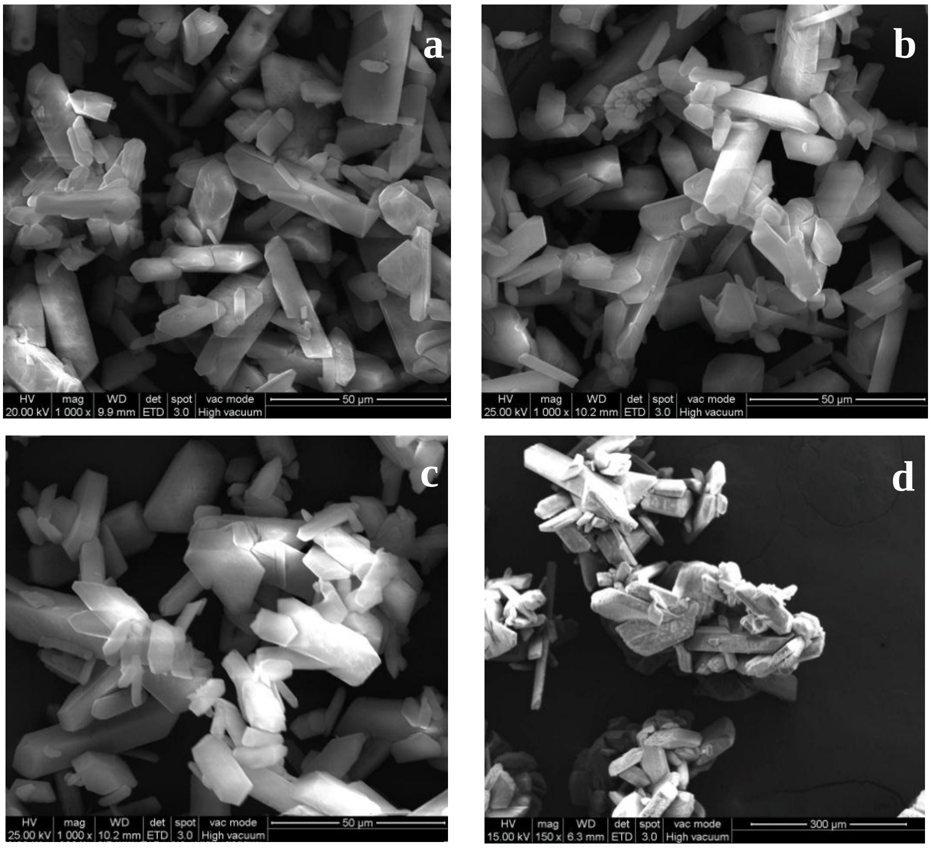

Fig. 3: SEM micrographs showing the morphological structure of MAP at different influent flow rate: (a) 4 mL min $^{-1}$ (1000×); (b) 6 mL min $^{-1}$(1000×); (c) 12 mL min $^{-1}$(1000×); (d) crystal aggregate at 12 mL min $^{-1}$ after 7 days (150×)

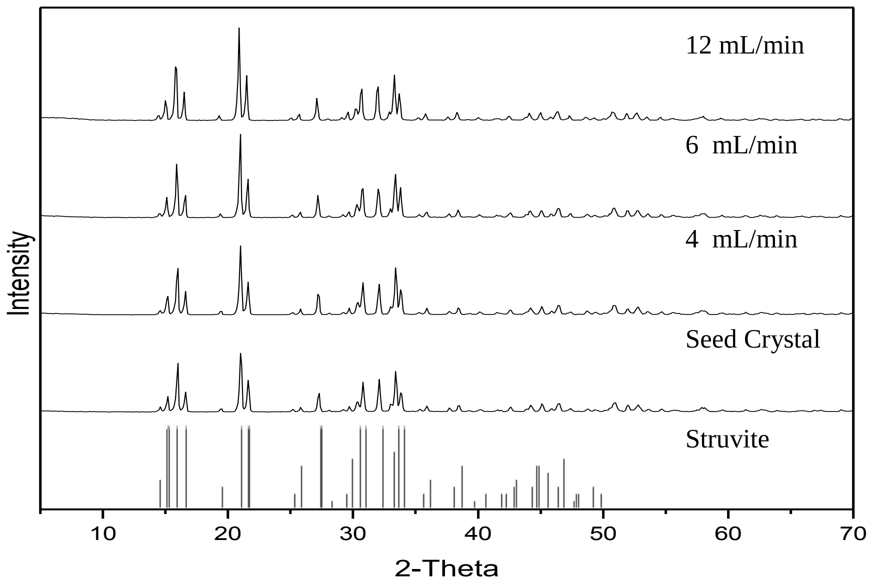

Fig. 4: XRD result of MAP at different influent flow rate

The relative intensity together with the peak width is also related to the crystallite thickness. The calculated crystallite thickness (Table 2) for the seed crystals have a dominant size of 43.9 nm; observed to have grown ranging from 51.0 – 62.4 nm upon dosing with reagents at the rate of 4-12 mL-min^{-1}. The crystallite size was observed to be invariable for 4 and 6 mL-min^{-1} and highest at 12 mL-min^{-1}, which is expected for high reagent concentration is achieved at higher influent flow rate.

Table 2: Calculated crystallite thickness with varying influent flowrate

Influent Flowrate/ solid	Crystallite Size, nm	
	Size range	Dominant size
Seed	21.1-70.1	43.9
4 mL/min	25.6-71.2	53.9
6 mL/min	21.7-67.5	51.0
12 mL/min	20.7-71.4	62.4

4. Conclusions

Fluidized bed crystallization of struvite was tested at different influent flow rate ranging from 4-12 mL-min^{-1}. The rate of phosphate conversion from liquid to solid phase depends on the inlet flow and is observed to increase with high flow rate. For MAP crystallization treating 110 mg-L^{-1} at seed dose of 2 g-L^{-1}, the highest conversion from liquid to solid phase of around 74% was observed at 12 mL-min^{-1}. The SEM and XRD results confirmed that the crystals produced were aggregates of magnesium ammonium phosphate hexahydrate or struvite. Therefore, struvite-seeded MAP crystallization at the influent flow rate studied in an FBC has a potential in recovering phosphate from wastewater.

5. Acknowledgements

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