

## Effects of various process parameters on struvite precipitation kinetics and subsequent determination of rate constants

M. S. Rahaman, N. Ellis and D. S. Mavinic

### ABSTRACT

In this paper, struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) precipitation kinetics were studied with different operating conditions (varying supersaturation, pH, Mg:P ratio, degree of mixing and seeding conditions) and relevant rate constants were determined by fitting a slightly modified first-order kinetic model to the experimental data obtained. The rate of change of ortho-P concentration in the bulk solutions increases with increasing supersaturation ratio. The estimated rate constants are 2.034, 1.716 and  $0.690 \text{ hr}^{-1}$  for the supersaturation ratio of 9.64, 4.83, and 2.44, respectively. Kinetic parameters were also evaluated for the Mg:P ratio between the ranges of 1.0 and 1.6, indicating higher phosphorus removal efficiency with increasing Mg:P ratio. The rate constants were found to be 0.942, 2.034 and  $2.712 \text{ hr}^{-1}$  for Mg:P ratios of 1.0, 1.3 and 1.6, respectively. The experimental observations for kinetic study of struvite precipitation with different stirrer speeds clearly show that the mixing intensity used had little effect on the intrinsic rate constants. K values found to be 2.034 and  $1.902 \text{ h}^{-1}$  for 100 and 70 rpm, respectively. Seeding, with 250–500  $\mu\text{m}$  of seed crystals during the struvite precipitation kinetics test, was found to have very little effect on the ortho-P removal.

**Key words** | kinetics, P-recovery, struvite, supersaturation

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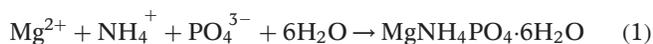
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### INTRODUCTION

Magnesium ammonium phosphate hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), more commonly known as struvite, is a white crystalline substance consisting of equal molar amount of magnesium, ammonium and phosphate, as well as six water of hydration. The simplified form of the reaction involving the struvite formation is as follows:



Struvite precipitation is a well recognized problem in anaerobic sludge digesters, where it precipitates in digester supernatant recycle lines, especially at the elbows and the suction side of pumps. It has also been observed in the sludge derived from the anaerobic digestion of animal farming liquid wastes and agricultural wastes (Booram *et al.* 1975). In recent years, extensive research has been conducted by

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several researchers with respect to recovering phosphorus from wastewater through struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) crystallization. The UBC fluidized bed MAP (Magnesium Ammonium Phosphate) crystallizer, is found to be very effective in recovering phosphorus (80–90% recovery) from anaerobic digester supernatant (Adnan *et al.* 2003). In order to implement this process in the plant scale operation, an efficient design and scale-up method has to be developed. A good estimation of process kinetics can help design the reactor and establish optimum process conditions.

Several articles have been published with regards to the effectiveness of the struvite crystallization process in recovering phosphorus from wastewaters. However, adequate information in terms of kinetics of struvite precipitation is still lacking in the literature. Olinger *et al.* (1999) studied kinetic effects on preferential struvite

accumulation in wastewater. The authors found struvite nucleation as a reaction controlled process and thus strongly dependent on the degree of supersaturation level. At the same time, crystal growth rate was found to be transport-limited and depended heavily on the mixing strength. In further research, the same group of researchers found that the first order kinetic relationship suited well to the disappearance of ortho-phosphate from bulk solutions and a rate constant was estimated as  $4.2 \text{ h}^{-1}$ , by fitting the first order kinetic model (Ohlinger *et al.* 2000). Nelson *et al.* (2003) studied the effect of pH in the range of 7.5 to 9.5 and Mg:P ratios between 1:1 and 1.6:1 on struvite precipitation in anaerobic swine lagoon liquid. For all Mg:P ratios, the minimum concentrations of  $\text{PO}_4\text{-P}$  occurred between pH 8.9 and 9.25. The authors described the rate of ortho-P decrease by a first-order kinetic model, and estimated rate constants as 3.7, 7.9 and  $12.3 \text{ h}^{-1}$  at pH 8.4, 8.7 and 9.0, respectively. On the other hand, Bouropoulos & Koutsoukos (2000) studied the kinetics of spontaneous precipitation of struvite in aqueous solutions supersaturated with respect to struvite species concentrations and reported kinetics following a second-order dependence on the solution supersaturation, implying a surface controlled mechanism. Ven Rensburg *et al.* (2003) investigated the reaction kinetics and design parameters of struvite production, using a draft-tube type reactor. The authors devised an equation in order to estimate the struvite production rate and found that rate constant ( $k_2$ ) increased with increasing struvite concentration and mixing intensity in the reactor. Quintana *et al.* (2005) studied the kinetics of phosphorus removal and struvite formation by the utilization of by-product of magnesium oxide production from both synthetic and real anaerobic digester liquor. The authors have demonstrated that a first-order kinetic model adequately represented the rate of phosphorus removal and found an increase in reaction rate constant ( $k$ ) and a decrease in the equilibrium concentration ( $C_e$ ) with increasing Mg:P molar ratio. It was also observed that the kinetic constants for real wastewater were higher ( $0.018\text{--}0.024 \text{ min}^{-1}$ ) than those obtained for synthetic liquor ( $0.0009\text{--}0.017 \text{ min}^{-1}$ ). Yoshino *et al.* (2003) observed that the reaction kinetic was influenced by the mixing intensity and constituent species concentrations of struvite in bulk solutions.

As can be found in the literature, various process parameter such as supersaturation ratio, pH, Mg:P ratio, degree of mixing, temperature and seeding conditions are likely to affect the struvite precipitation process. Therefore, in this paper, struvite precipitation kinetics was studied at different operating conditions to determine the rate constants by comparing the experimental data with a suitable kinetic model.

## MATERIALS AND METHODS

### Synthetic liquor preparation

In this study synthetic supernatant containing the constituent ions of struvite was used. The reagent salts used to prepare the synthetic liquor were commercial grade magnesium chloride hexahydrate, diammonium hydrogen phosphate and ammonium chloride. Commercial grade sodium hydroxide was used for pH adjustment. Bulk solutions were adjusted over a range of  $\text{PO}_4$  concentration to reflect typical low strength anaerobic digester supernatant ( $< 40 \text{ mg/L}$ ).

### Methods

A six-station Phipps & Bird™ jar tester was used to investigate the struvite formation kinetics. Three sets of experiment were run for this current study. In the first set of experiments four replicate runs, each having identical initial concentrations of  $\text{PO}_4\text{-P}$ , Mg and  $\text{NH}_4\text{-N}$  were conducted. Among all these four replicates, the only parameter varied was the supersaturation ratio and the changes in SSR were done by adjusting the solution pH values. In the second set three replicate runs of experiment, each having same SSR were carried out. Among these three, the first two runs were identical in terms of all the process variables, except 10 g of struvite seed crystals were added in the second run. In third run ion species concentrations, with respect to those in the first ones were varied to get different Mg:P ratio. In the last set of experiments only two replicate runs were carried out with two different Mg:P ratio and a constant stirrer speed of 70 rpm was maintained. The experimental conditions for all nine runs are shown in Table 1. In each experimental run, 1.5 liter of synthetic supernatant was transformed into a 2 L jar. The solution pH was adjusted accordingly to ensure

**Table 1** | Operational conditions for various experimental runs

Process parameters	Run#1	Run#2	Run#3	Run#4	Run#5	Run#6	Run#7	Run#8	Run#9
Initial PO <sub>4</sub> -P Conc. (mg/L)	30.5	30.5	30.5	30.5	30.5	30.5	30.5	30.5	30.5
Initial Mg Conc. (mg/L)	31	31	31	31	38	38	24	38	31
Initial NH <sub>4</sub> -N Conc. (mg/L)	600	600	600	600	500	500	760	500	600
Mg:P molar ratio	1.3	1.3	1.3	1.3	1.6	1.6	1.0	1.6	1.3
pH	8.51	8.2	7.91	7.6	8.51	8.51	8.51	8.51	8.51
Supersaturation ratio (SSR)	9.64	4.83	2.44	1.13	9.97	9.97	9.91	9.97	9.64
Stirrer speed (rpm)	100	100	100	100	100	100	100	70	70
Temperature (°C)	20	20	20	20	20	20	20	20	20

\*In run # 6, 10g of struvite seed crystal in the size range of 250–500 $\mu$ m was added.

desired supersaturation ratio with a constant Mg:P ratio. All the experimental runs were performed in a temperature controlled room set at 20 °C. The pH in each jar was raised to a desired value by adding 6 M sodium hydroxide (NaOH) solution. The experiment was conducted for 240 min with 15 min sampling interval for the first 60 min, and 30 min interval for the rest of the period. Samples were filtered immediately through a 0.45  $\mu$ m mixed cellulose ester membrane filter and preserved for chemical analysis.

### Analytical techniques

The filtered samples were analyzed for magnesium, ammonia and ortho-phosphate. Analyses for ortho-phosphate and ammonia were performed using flow injection method on a LaChat QuikChem 8,000 instrument. Magnesium analysis was performed by flame atomic absorption spectrophotometry, using a Varian Inc. SpectrAA220 Fast Sequential Atomic Absorption Spectrophotometer. pH measurements were performed using a Beckman  $\Phi$ 44 pH meter, equipped with an Oakton pH probe.

### Treatment of data

As demonstrated in the literature, first order kinetic model represents the struvite formation in aqueous solutions. In this present study, the kinetic data were fitted to a

slightly-modified, first-order kinetic model, as proposed by Nelson *et al.* (2003). The model expresses the relationship between the disappearance of a reactant ( $-dC/dt$ ) and its instantaneous concentration above the equilibrium value (Equation 2). A constant of proportionality,  $k$ , referred as the rate constant, is introduced. By mathematical manipulation of Equation 2 and integration, it generates the linear form of the first-order reaction kinetics (Equation 3). As described by the first order reaction kinetics, a plot of  $\ln(C - C_{eq})$  against time generates a straight line with slope  $-k$ .

$$-dC/dt = k(C - C_{eq}) \quad (2)$$

$$\ln(C - C_{eq}) = -kt + \ln(C_0 - C_{eq}) \quad (3)$$

## RESULTS AND DISCUSSION

### Influence of supersaturation ratio and pH on struvite precipitation

Supersaturation ratio (SSR) is defined as the ratio of conditional solubility product ( $P_s$ ) to the equilibrium conditional solubility product ( $P_{s_{eq}}$ ). Conditional solubility product represents the solubility product in actual conditions and equilibrium counterpart means its value at equilibrium state. Therefore,

$$SSR = P_s/P_{s_{eq}} \quad (4)$$

And the conditional solubility product is expressed as

$$Ps = [C_{TMg}][C_{TNH3}][C_{TPO4}] \quad (5)$$

$Ps_{eq}$  is highly pH dependent as found by various researchers (Ohlinger *et al.* 1998). With an increase in pH value, the concentration of phosphate ion increases, while the concentrations of Mg and  $NH_4$  decrease; thus establishing a range of solubility limits. An increase in the concentrations of the any constituent ions would increase the conditional solubility product, whereas at a higher pH, the values of  $Ps_{eq}$  would decrease. So the prevailing SSR in the process fluid can be increased by increasing the concentration of struvite constituent ions or by increasing the pH of the bulk solutions. In this study, the SSR of the reaction solutions were changed by adjusting the pH value. To investigate the effects of SSR on the formation of struvite, the disappearance of the ortho-P ions were monitored during the experimental run. As shown in Figure 1, the results clearly indicate that SSR plays an important role in the struvite precipitation kinetics. With increasing SSR, the removal of  $PO_4$  increases with the equilibrium being achieved faster for the SSR ranging from 9.64 to 1.13. The desired SSR values were achieved by adjusting solution pH values (from 7.6 to 8.5). Therefore it can also be inferred that the higher phosphorus removal

efficiency could be achieved by increasing pH values from 7.6 to 8.5. Subsequently, the reaction rate constants were estimated by fitting the experimental data in the modified first-order kinetic model (Figure 2). The estimated rate constants were 2.034, 1.716 and  $0.69 \text{ hr}^{-1}$  for supersaturation ratio of 9.64, 4.83, and 2.44, respectively. Similar trend in the variation of rate constants with respect to pH (means SSR) was observed by Nelson *et al.* (2003). They estimated the rate constants 3.7, 7.9 and  $12.3 \text{ h}^{-1}$  for the pH values of 8.4, 8.7 and 9.0. The rate constant reported by the group,  $3.7 \text{ h}^{-1}$  at pH 8.4 is higher than the calculated rate constant ( $2.034 \text{ h}^{-1}$ ) at pH 8.5 in the present work. The lower rate constant reported in the present study may be due to the difference in initial concentrations of the constituent ions, which, in turn affects the SSR. Also, the rate constant in this current study was determined for synthetic liquor whereas Nelson *et al.* (2003) performed their experiments with real swine liquor. It has also been observed by Quintana *et al.* (2005) that the  $k$  values in real liquor were higher than those obtained with the synthetic liquor.

#### Effect of Mg:P ratio

Magnesium is another important constituent ion for struvite precipitation. Hence, it also affects the supersaturation level

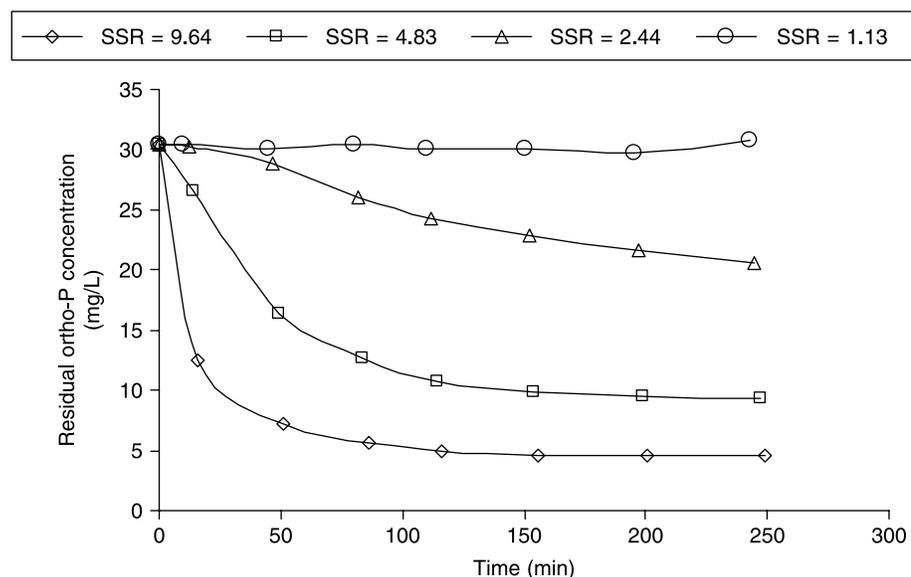
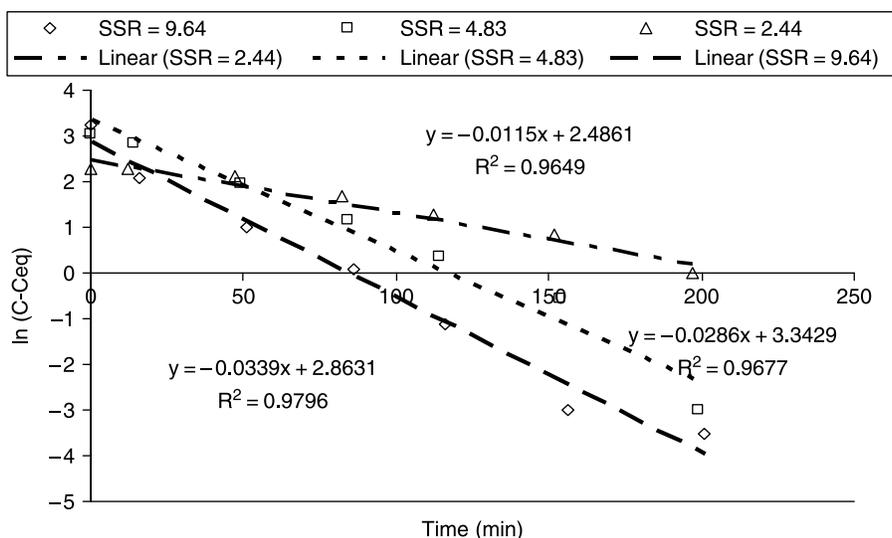


Figure 1 | Variation of ortho-P concentrations with the reaction time.



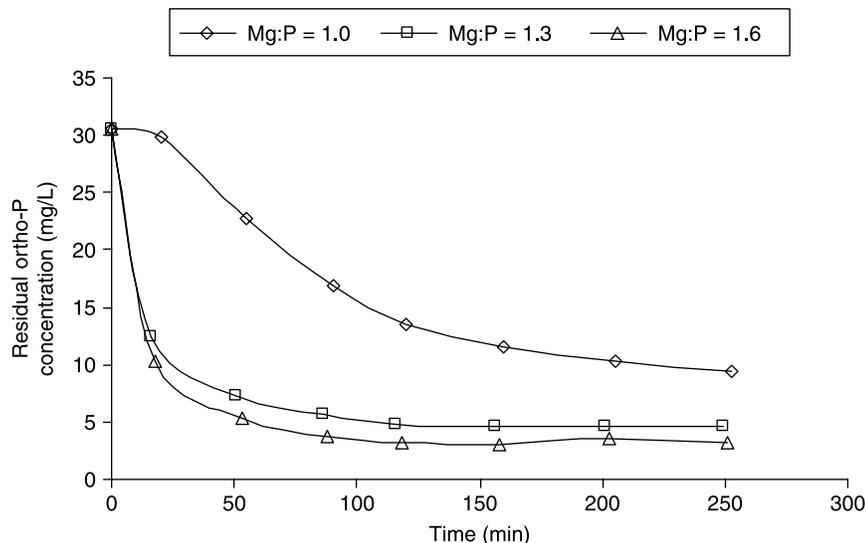
**Figure 2** | Linear form of the first order kinetic of struvite precipitation with different SSR values.

and the progress of precipitation process. In many cases of struvite formation from anaerobic digester supernatant, the addition of magnesium from an external source is necessary as struvite forms in a theoretical Mg:N:P molar ratio of 1:1:1 and many domestic wastewaters do not contain Mg ions required to fulfill the stoichiometric requirements for struvite formation. Although unwanted struvite can be formed at any Mg:P molar ratio, for intentional struvite crystallization the Mg:P ratio should be at least unity. Higher magnesium can increase the P-removal from reaction solutions. At a given pH, any increase in the Mg:P ratio would increase the degree of saturation with respect to struvite formation, which, in turn, would enhance the phosphorus removal (Adnan *et al.* 2004). In this current study, Mg:P ratio in the range of 1.00 to 1.60 was investigated and results for phosphorus removal, with respect to time, is illustrated in Figure 3. It was found that better removal of phosphorus was achieved with higher Mg:P ratio in the range of studied ratios. A similar trend was observed by many other researchers (Adnan *et al.* 2004). In general, Mg:P ratio of 1.1 ~ 1.6 was considered as optimum in most of the cases of investigation (Adnan *et al.* 2004). As can be observed in Figure 3, a rapid decrease in PO<sub>4</sub>-P concentration was observed during the first 50 minutes for Mg:P ratios of 1.3 and 1.6. However, a gradual decrease in PO<sub>4</sub>-P concentration was observed in case of Mg:P ratio of 1.0. Thus, the molar ratio had a strong

influence on the decrease of phosphorus concentration. However, the difference in the reduction between Mg:P ratios of 1.3 and 1.6 was minimal. Data were plotted as ln(C - Ce) versus time in order to obtain the kinetic values. As can be seen in Figure 4, a plot of ln(C - Ce) versus time generates straight lines with different slopes; this means that the rate of reaction with different Mg:P ratios varied and the straight lines suggest the proposed first order kinetic model fit reasonably well with the experimental observations. Kinetic parameters were also evaluated for different Mg:P ratio (1.0, 1.3 and 1.6) and the results showed that the higher the ratio, the better the phosphorus removal efficiency for the range of Mg:P ratio investigated. The rate constants are found to be 0.942, 2.034 and 2.712 hr<sup>-1</sup> for Mg:P ratios of 1.0, 1.3 and 1.6, respectively (Figure 4).

### Effect of degree of mixing

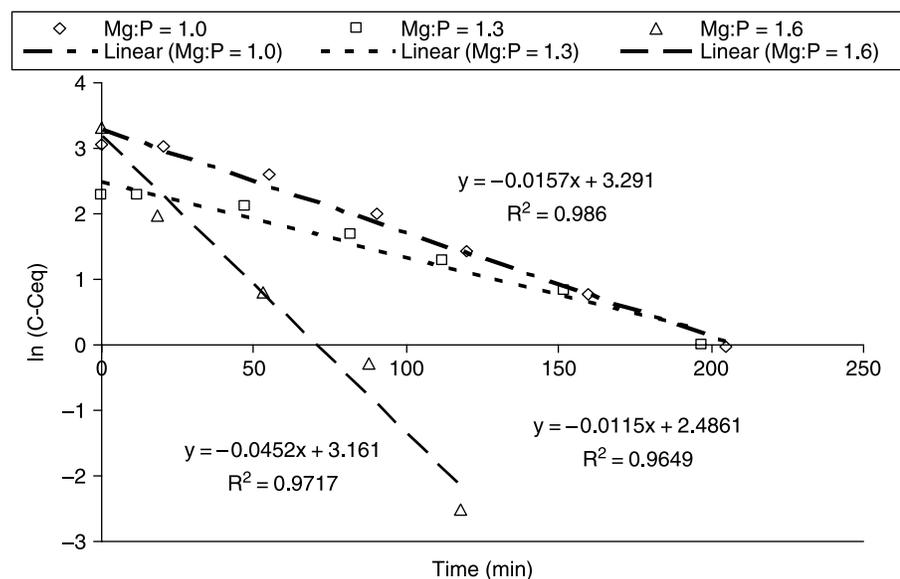
Figure 5 shows the residual phosphorus concentration with respect to time for two different mixing speed (100 and 70 rpm). The experimental observations clearly indicated that mixing intensity had little effect on the intrinsic kinetics of struvite precipitation for the range of mixing speed tested. In the precipitation process, crystal formation is taken place in two different stages: nucleation and growth. At the optimum pH, the induction time is affected by the process



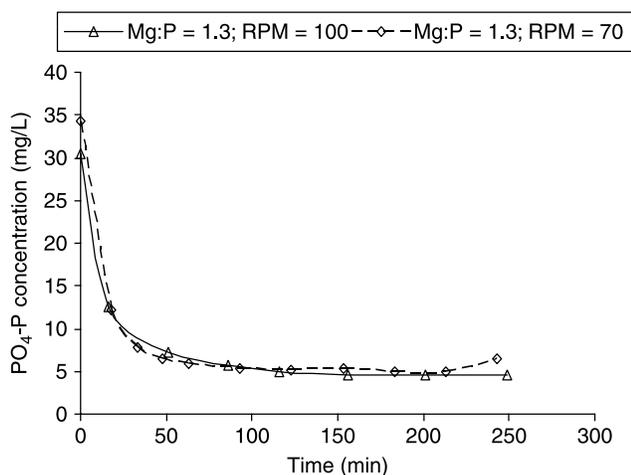
**Figure 3** | Variation of ortho-P concentration with the reaction time for different Mg:P ratios.

fluid turbulence (Ohlinger *et al.* 1999). Therefore, the induction time decreases as the stirring speed increases and the nucleation of struvite becomes rapid. Once the nuclei are formed, struvite crystal growth on the existing nucleation sites is primarily controlled by the mixing energy. The reason for the insignificant influence of mixing strength in this current study may be due to fact that the mixing energy might be in excess of the optimum value for the set process parameters in the experiment. As excessive mixing

strength may cause the break down of the crystals and thus the settability and the removal of phosphorus is decreased. Findings in this experiment make sense as Wang *et al.* (2006) reported that the optimum mixing strength ( $G$  value) was  $76 \text{ s}^{-1}$  for unseeded synthetic animal lagoon wastewater and no significant increase in phosphorus removal were obtained when mixing strength was greater than  $76 \text{ s}^{-1}$ . In this study, the different mixing strength ( $G$  values) used was 97 and  $165 \text{ s}^{-1}$ , both of which were greater than



**Figure 4** | Linear form of the first order kinetic of ortho-P removal for different Mg:P ratios.

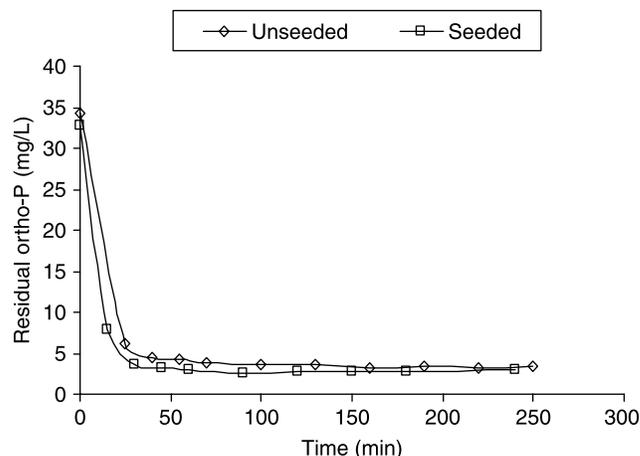


**Figure 5** | Variation of ortho-P concentration with the reaction time for different stirrer speeds.

the optimum mixing strength found by Wang *et al.* (2006). Subsequently rate constants were determined by fitting the experimental results with modified first-order kinetic model. The precipitation rate constants were estimated as 2.034 and 1.902  $\text{hr}^{-1}$  for 100 and 70 rpm, respectively.

### Effect of seeding

Kinetic experiments were also conducted to reveal the effect of seeding with struvite seed crystals (initial size range of 250 to 500  $\mu\text{m}$ ) in the reactive solutions and it was found that the seeding had very little effect on the intrinsic kinetics of struvite precipitation. The effects of seeding have been studied by several investigators to enhance the struvite crystallization and postulated that the seeding material should pose sufficient size and crystal structure that mimic the precipitating substances. Seeding is considered to enhance the struvite crystallization by providing the adequate reaction surface. Therefore, specific surface area of the seed could be one of the factors influencing the P removal (Ohlinger 1999). A seed with larger specific surface area and therefore, a smaller size could promote P-removal. However, as seen in Figure 6, the difference in P removal between seeded and unseeded condition was not significant. A similar observation was reported by Adnan *et al.* (2004). The reason behind this phenomena could be that the reaction equilibrium was reached very fast and nuclei were formed which had much greater surface area



**Figure 6** | Variation of ortho-P concentration with the reaction time for seeded and unseeded conditions.

than the seed crystals, since seed crystals are of much bigger size and the amount added was small (10g of 250 ~ 500  $\mu\text{m}$  struvite crystal). It is very likely that the surface area provided by the seed crystals might be very small in compare to that of the fresh produced nuclei. Seeding would obviously influence the precipitation process. But for the species concentrations of struvite in this current study, equilibrium reached before the growth could be taken place on the surface of the seed particles.

### CONCLUSIONS

The experimental results reveal that supersaturation plays an important role in the struvite precipitation kinetics. Since the desired SSR of bulk solutions was achieved by adjusting the pH values, it can be inferred that pH is also important factor influencing the precipitation reaction kinetics. The rate of disappearance of ortho-P in the bulk solutions increases with increasing SSR values. The estimated rate constants are 2.034, 1.716 and 0.69  $\text{h}^{-1}$  for supersaturation ratios of 9.64, 4.83 and 2.44, respectively, with a constant Mg:P ratio of 1.3 at 20°C. The results for struvite precipitation kinetics with varying Mg:P ratio reveal that the higher the ratio (in the range of 1.0–1.6), the better is the ortho-P removal efficiency. The rate constants are found to be 0.942, 2.034 and 2.712  $\text{h}^{-1}$  for Mg:P ratios of 1.0, 1.3 and 1.6, respectively. The experimental observations for kinetics of struvite precipitation

with different stirrer speeds clearly show that the mixing intensity used in this study had little effect on the intrinsic rate constants. K values found to be 2.034 and 1.902 h<sup>-1</sup> for 100 and 70 rpm, respectively. Seeding, with 250–500 μm of seed crystals, during the struvite precipitation kinetics test was found to have very little effect on ortho-P removal.

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