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Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates

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A B S T R A C T

Struvite crystallization is a promising method to remove and recover phosphorus from wastewater to ease both the scarcity of phosphorus rock resources and water eutrophication worldwide. To date, although various kinds of reactor systems have been developed, supporting methods are required to control the struvite fines flushing out of the reactors. As an intrinsic property, aggregation is normally disregarded in the struvite crystallization process, although it is the key factor in final particle size and therefore guarantees phosphorus recovery efficiency. The present study developed a method to analyze the characteristics of struvite aggregates using fractal geometry, and the influence of operational parameters on struvite aggregation was evaluated. Due to its typical orthorhombic molecular structure, struvite particles are prone to crystallize into needle or rod shapes, and aggregate at the corners or edges of crystals. The determined fractal dimension ($D_{pf}$) of struvite aggregates was 1.52–1.31, with the corresponding range of equivalent diameter ($d_0$) at 295.9–85.4 μm. Aggregates formed in relatively low phosphorus concentrations (3.0–5.0 mmol/L) and mildly alkaline conditions (pH 9.0–9.5) displayed relatively compact structures, large aggregate sizes and high aggregation strength. Increasing pH values led to continuous decrease of aggregate sizes, while the variation of $D_{pf}$ was insignificant. As to the aggregate evolution, fast growth in a short time followed by a long steady stage was observed.

Introduction

Excess nitrogen and phosphorus (P) discharged into the environment lead to eutrophication and are toxic to aquatic species in the receiving waters, and are therefore regarded as pollutants. Moreover, phosphorus rock is an important and non-renewable resource, making a major contribution to agricultural and industrial development. Due to the scarcity of phosphorus rock resources, recovering P as struvite ($\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$) from wastewater, such as swine wastewater and sludge anaerobic supernatant, has gained importance as a means of capturing and recycling P (Gilbert, 2009). The recovered product is preferred as a good fertilizer in agriculture for its slow release rate and much lower impurity levels than other phosphate fertilizers (Rahman et al., 2011).

To date, various kinds of reactors have been developed at laboratory, pilot and full scales and have shown great potential in recovering struvite (Le Corre et al., 2009; Forrest et al., 2008). However, issues remain on the degree of crystal growth and the formation of crystal fines. Struvite fines produced are easily flushed out of the reactor and decrease the P recovery efficiency, so that supporting methods are normally required to control the fines. Harris et al. (2008) used quartz and periclase grains as seed materials so that the grain surfaces could serve as nucleation sites for struvite precipitation. Le Corre et al. (2007) applied ferric chloride, aluminum sulfate, and polyDADMAC as coagulants to agglomerate struvite fines into large particles.
Other researchers used stainless steel meshes or improvements in hydraulic and saturation conditions to collect suitable crystal sizes (Forrest et al., 2008; Song et al., 2007; Perera et al., 2009). Actually, aggregation is unavoidable in the crystallization or precipitation of sparingly soluble salts (Kim et al., 2011), and is also observed in the struvite crystallization process (Le Corre et al., 2007; Huang et al., 2006). Aggregation is the key factor to determined the final particle size. However, since it is unpredictable and hard to measure, the aggregation process is often disregarded in comparison with other processes, such as nucleation and crystal growth (Kim et al., 2011; Moussaouiti et al., 1996). Disregarding aggregation may lead to inaccurate characterization of the physical properties of the powder product, including crystal size distribution and shape, and can involve errors in the estimation of nucleation and crystal growth rates (Kim et al., 2011; Moussaouiti et al., 1996). As for the struvite crystallization process, little information is available regarding the structure of struvite aggregates and their size distribution. Fractal geometry, which was founded by Mandelbrot in 1975, has often been used to describe the irregular structures of geometric objects, such as sediments, flocs, latex, and conditioned water treatment residuals, as presented in Table 1. Aggregates generated in crystallization processes have been shown to be fractal, since they possess self-similar and scale-invariant properties (Liu et al., 2000; Helalizadeh et al., 2006). The aggregate structure can be described by the fractal dimension, a parameter expressing the degree of aggregate compactness by which primary particles fill the space within the nominal volume occupied by an aggregate. The present study therefore presented a method to analyze the characteristics of struvite aggregates using fractal geometry. The influence of process parameters, including P concentration, pH value and shear rate on struvite aggregation was investigated, and the evolution of struvite aggregates was also identified. The outcomes will be important in providing further information on the practical application of improving particle size and aggregate compactness in the struvite recovery process.

### Table 1 | Boundary fractal dimension of different materials

<table>
<thead>
<tr>
<th>Object</th>
<th>$D_{pf}$</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin flocs</td>
<td>1.06–1.23</td>
<td>He et al., 2012</td>
</tr>
<tr>
<td>Lime softening flocs</td>
<td>1.22–1.38</td>
<td>Vaheidi and Gorczyca, 2011</td>
</tr>
<tr>
<td>Cohesive sediment</td>
<td>1.25–1.36</td>
<td>Stone and Krishnappan, 2003</td>
</tr>
<tr>
<td>Conditioned water treatment residuals</td>
<td>1.50–1.80</td>
<td>Dong et al., 2011</td>
</tr>
<tr>
<td>Conditioned sludge</td>
<td>1.34–1.48</td>
<td>Chu et al., 2004</td>
</tr>
<tr>
<td>Struvite aggregates</td>
<td>1.31–1.52</td>
<td>Present study</td>
</tr>
</tbody>
</table>

$D_{pf}$ is a two-dimensional boundary fractal dimension, calculated by regression analysis of the logarithm of the projected areas versus the logarithm of their corresponding perimeters.

1. **Materials and methods**
2. **1.1 Solution preparation**

P concentration levels of the solutions (3–15 mmol/L) adopted in this study were representative of swine wastewater and sludge digestion supernatant produced in China, as described by MEPC (2002) and Wang et al. (2010). Stock solutions containing $\text{NH}_4^+\cdot\text{N}, \text{PO}_4^{3-}\cdot\text{P}$ and $\text{Mg}^{2+}$ were prepared by dissolving $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{MgCl}_2\cdot6\text{H}_2\text{O}$ into deionized water, respectively. These solutions were stored at 4°C for further experiments.

3. **1.2 Determination of the states for struvite crystal formation**

There are three states for crystal formation, undersaturated, metastable and over saturated (Le Corre et al., 2009). Crystallization is impossible in the under saturated state. In the metastable state, the solution is saturated and crystallization occurs heterogeneously, which means that crystal formation is induced by seed addition. As to the over-saturated state, spontaneous crystallization occurs rapidly and abundantly without the need for seeding. In industrial phosphate production, the spontaneous crystallization technique is widely practiced due to high productivity and smoother continuous operation in controlled supersaturation. To define the states of solution where struvite crystallization can occur spontaneously, preliminary experiments were conducted to identify the minimum limit of spontaneous precipitation, based on the method described by Ali and Schneider (2006). The experiments were carried out in a dark room using a light scattering device (red laser pointer) in which laser light passed through reactive solution. Synthetic solutions of different concentrations were prepared by mixing $\text{MgCl}_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ and setting the molar ratio of $\text{Mg}:\text{N}:\text{P}$ at 1:1:1. Reactive solutions were slowly brought up to saturation level by adding 2 mol/L NaOH until the first appearance of a crystal cloud was detected. The corresponding pH value at crystallization occurrence was recorded as the minimum pH for spontaneous precipitation. Subsequent experiments were conducted in the over saturated region.

Saturation index (SI) was used to describe the saturation
state of precipitating system, as described by Ye et al. (2011). The calculation of SI is as follows:

\[ \text{SI} = \log \frac{\text{IAP}}{K_{sp}} \]  

(1)

where, IAP is the free ionic activities product, and \( K_{sp} \) represents the thermodynamic solubility product of the precipitate phase. When SI is below 0, the solution is supersaturated and precipitation occurs spontaneously; when SI is equal to 0, the solution is in equilibrium; when SI is above 0, the solution is under saturated and no precipitation occurs. The calculation of SI for solid and dissolved phases of minerals was performed by the equilibrium speciation model PHREEQC (Interactive Version 2.15.0.2697). PHREEQC allows users to create a personal thermodynamic database in which possible solid phases can be formed. Due to the absence of struvite in the original PHREEQC database, the reaction equilibrium of struvite with its solubility product constant \( (pK_{sp} 13.36) \) (Iqbal et al., 2008) was added for consideration.

1.3 Jar test

Standard jar tests were conducted on a program-controlled jar test apparatus (TA6-4, Wuhan Hengling Technology Ltd., China) and the temperature was kept at 23–25°C. The relationship of velocity gradient \( (G) \) to the stirring speed was calculated as described by Cao et al. (2011). In each experiment, after a certain amount of \( \text{NH}_4\text{H}_2\text{PO}_4 \) and \( \text{MgCl}_2 \) stock solutions (molar ratio of Mg:N:P at 1:1:1) was dosed in the standard beaker (1 L working volume), the liquor was then mixed rapidly at 400 r/min, and the pH value was quickly increased to the desired level by adding 2 mol/L NaOH. Since pH measurement is generally employed as a common method to estimate the struvite precipitation process (Le Corre et al., 2009; Kabdasli et al., 2006), reaching a stable pH value at the designed level was considered as the achievement of struvite precipitation and the beginning of the aggregation process. In the aggregation stage, the solution was mixed continuously at 400 r/min for 45 sec, followed by a slow stirring phase at 100 r/min for 45 min. At the end of the test, a sample was withdrawn immediately from below the water surface (2.5 cm) for geometric analysis on aggregates, and the zeta potential was measured using a zeta meter (MALVERN Instrument Nano ZS Zeta, UK). Considering the optimum pH for struvite precipitation is 9.0–9.5 (Song et al., 2007; Ryu et al., 2008), experiments concerning the influence of P concentration on struvite crystal aggregation were conducted at pH 9.0 with the range of initial P concentrations at 3–15 mmol/L. The investigation on the influence of pH variation was carried out by setting pH values from 9.0 to 10.5.

In struvite recovering reactors, regions of high shear are very common, which may lead to the breakage of aggregates and lower recovery efficiency. As a physical property, aggregate strength may significantly affect the efficiency of solid/liquid separation. Aggregate strength can be measured in terms of the relationship between the increase of shear force and the decrease of aggregate size. The empirical relationship has been reported as (Cao et al., 2011):

\[ \log d = \log C - \gamma \log G \]  

(2)

where, \( d \) (µm) is the average aggregate size; \( C \) is the aggregate strength coefficient; \( \gamma \) is the stable aggregate exponent; and \( G \) (sec\(^{-1}\)) is the average velocity gradient in the system. A test for aggregate strength was performed by increasing the shear rate in the jar tester during the slow phase. Different P levels coupled with different pH values, including P 3.5 mmol/L pH 9.5, P 5.0 mmol/L pH 9.0, P 6.0 mmol/L pH 9.5 and P 8.0 mmol/L pH 9.0, were adopted. Stirring speeds of 80, 160, 240, 320, 400 r/min were employed and the respective \( G \) values of each shear rate were 10.5, 27.3, 47.1, 69.3 and 93.6 sec\(^{-1}\), respectively.

For aggregation evolution experiments, three P concentrations (3.5, 6.0 and 9.0 mmol/L) with pH set at 9.5 were employed. After the achievement of the precipitation process, the suspension was mixed at 400 r/min for 45 sec following aggregate evolution for 45 min. Samples were carefully withdrawn at intervals for aggregate geometry analysis.

1.4 Aggregate morphology and fractal dimension

The aggregate samples resulting from the process were carefully and evenly introduced into a glass square dish for image recording using a wide mouthed pipette. A digital Nikon ECLIPSE 80i microscope (Nikon Instruments Co. Ltd., Japan) was applied to obtain images of the aggregates in the dish. Image processing software of Nikon NIS-Elements BR 2.30 (Nikon Instruments Co. Ltd., Japan) was used to obtain the characteristics of aggregates, including area, equivalent diameter, perimeter, macroaxis and minor axis. The holes inside the image were deducted from the area by the software. The size distribution of the aggregates was determined through statistical analysis on the equivalent diameter of aggregates using Excel 2007 (Microsoft Co. Ltd., USA) software.

Fractal dimensions can be defined in linear, planar or volumetric terms, i.e., one-, two-, or three-dimensional fractal dimension, respectively (Chakraborti et al., 2003). Since the three-dimensional fractal dimension cannot be directly determined, two-dimensional fractal dimension is often used to characterize the fractal properties of aggregates (He et al., 2012; Chakraborti et al., 2000). The two-dimensional boundary fractal dimension \( (D_{fr}) \) for the aggregates was calculated by regression analysis of the logarithm of their projected areas \( (A) \) versus the logarithm of their corresponding perimeters \( (P_i) \) (Dong et al., 2011;
2 Results and discussion

2.1 Effect of P concentration

Figure 1 provides several images of struvite aggregates in the operational conditions. The microphotographs exhibited distinct differences between crystal habits and aggregates formed under different P concentrations. Needle-shaped crystals with relatively small sizes were observed in low P concentrations, compared to some fork-shaped crystals with large sizes formed in high P concentrations. Aggregates formed in low P concentrations displayed a relatively more compact structure. The equivalent diameter ($d_{0.5}$) distribution of the aggregates in the experimental runs is illustrated in Fig. 2. Higher diameter values and wider size distribution were observed for the aggregates generated at low P concentrations. Aggregates formed in differing P concentrations. The fractal dimension was used to quantify the aggregate structure, and subsequently served as a mathematical parameter for tracking differences among aggregates formed in different operational conditions. The fractal characteristics of these aggregates and their corresponding linear regression plots are illustrated in Fig. 3. The calculated $D_{pf}$ values, combined with mean $d_{0.5}$, zeta potential and SI are summarized in Table 2. A decrease of $D_{pf}$ from 1.52 to 1.39 with a corresponding decline of $d_{0.5}$ from 295.9 to 108.6 μm was observed as initial P concentrations increased from 3.0 to 5.0 mmol/L. Slight variations of $d_{0.5}$ and $D_{pf}$ were detected when P doses further increased to 7.0–15.0 mmol/L. Corresponding to the constant increase of P concentrations, SI exhibited a trend with values continuously increasing. As to zeta potential, it appeared to be irrelevant to aggregate size and $D_{pf}$ in the operational runs.

It has been known that the most basic crystal morphology of struvite is a typical hemimorphic morphology, which is correlated with the atomic arrangement (Prywer and Torzewska, 2009). The struvite crystal structure consists of $\text{PO}_4^{3-}$ and $\text{NH}_4^+$ tetrahedral and $\text{Mg}([\text{H}_2\text{O}]_{6}^{2+}$ octahedral species. The rectangular $ac$ or $bc$ crystallite facets ($a$, $b$, $c$ are the three-dimension coordinate axes) are rich in $\text{Mg}([\text{H}_2\text{O}]_{6}^{2+}$ or positive charge as compared to $ab$ crystal facets (Prywer and Torzewska, 2009). Accordingly, negatively charged additives will adsorb preferentially onto the $ac$ or $bc$ crystallite facets, thus giving rise to electrostatic inhibition of rectangular facet-to-facet particle adsorption. As to $\text{PO}_4^{3-}$ and $\text{NH}_4^+$ tetrahedral species in the structure, they are held by hydrogen bonds. When the contents of $\text{PO}_4^{3-}$ and $\text{NH}_4^+$ increase, they are prone to absorb and extend on the crystallite in a $c$-axis orientation, which suggests that the increase of SI in the solution leads to the crystal growth of needle or rod-like shapes. Similar findings on struvite crystal shapes have been reported by other.
Fig. 3  Double-logarithmic plots of perimeter (Pi) and area (A) for struvite aggregates at pH 9.0 under different P concentrations.
Table 2  Experimental details of struvite aggregates at pH 9.0 under different initial P concentrations

<table>
<thead>
<tr>
<th>P (mmol/L)</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>7.0</th>
<th>9.0</th>
<th>11.0</th>
<th>13.0</th>
<th>15.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent diameter $(d_{0.5}, \mu m)$</td>
<td>295.9</td>
<td>134.1</td>
<td>108.6</td>
<td>85.4</td>
<td>96.6</td>
<td>102.0</td>
<td>89.7</td>
<td>91.5</td>
</tr>
<tr>
<td>$D_{pf}$</td>
<td>1.52</td>
<td>1.41</td>
<td>1.39</td>
<td>1.36</td>
<td>1.35</td>
<td>1.35</td>
<td>1.33</td>
<td>1.31</td>
</tr>
<tr>
<td>Zeta potential (mV)</td>
<td>–8.27</td>
<td>–1.60</td>
<td>–2.13</td>
<td>–2.77</td>
<td>–3.30</td>
<td>–2.45</td>
<td>–4.69</td>
<td>–5.32</td>
</tr>
<tr>
<td>Saturation index (SI)</td>
<td>1.09</td>
<td>1.35</td>
<td>1.56</td>
<td>1.86</td>
<td>2.08</td>
<td>2.26</td>
<td>2.40</td>
<td>2.53</td>
</tr>
</tbody>
</table>

In the experiments with high initial P concentrations, some fork-shaped crystals were observed. This was because in the high degree of supersaturation conditions, more crystal nuclei formed and agglomerated spontaneously, leading to volume diffusion and supersaturation on the crystal surface unevenly (Prywer and Torzewska, 2009; Ronteltap et al., 2010). As for zeta potential, the struvite crystal has a high negative charge from –26 to –20 mV at alkaline pH (Le Corre et al., 2007). However, experimental results showed that the zeta potential approached zero (Table 2). This was due to the decrease of electrostatic repulsion among crystal particles by aggregation (Warmadewanthi and Liu, 2009).

Little literature exists on $D_{pf}$ values of aggregates in the struvite crystallization process. As shown in Table 2, the $D_{pf}$ in the experiments ranged from 1.31 to 1.52, somewhat higher than the typical values of $D_{pf}$ for aggregates in the range of 1.1–1.4 (He et al., 2012; Xiao et al., 2011). This is because classic aggregation models, including the diffusion-limited aggregation model and its several variations (He et al., 2012; Harif and Adin, 2007), are based on the assumption that primary particles are impermeable spheres, and any other addition of particles will make an aggregate structure more porous and loose (He et al., 2012; Chakraborti et al., 2003; Gmachowski, 2007). Therefore, according to classic models, the fractal dimension of an aggregate will decrease as the aggregate cluster size increases. However, the present study displayed behavior inconsistent with the classical models. Large struvite aggregates resulted in high $D_{pf}$ levels (Table 2). Such a result was thought to closely associate with the struvite crystal structure. It has been known that the surface atomic structure is expected to affect the existence and strength of the agglomerative bond between two crystallites (Brunsteiner et al., 2005). As mentioned above, the increase of P concentration in the solution will extend the crystallite in the c-axis orientation and lead to the crystal growth of needle or dendrite shapes. Such crystal evolution indicates that the supersaturation on the crystal surface is uneven, with the highest at the corners and edges and the lowest at the center (Prywer and Torzewska, 2009). Since crystals are prone to aggregate at the smaller crystal faces possessing relatively higher supersaturation (Brunsteiner et al., 2005; Simons et al., 2004), high SI conditions may obligate struvite crystals to aggregate at the corners or edges. Thus, aggregates with loose and porous structure and small equivalent sizes will be obtained, as shown in Fig. 1. Accordingly, through controlling composition concentrations one can adjust the solution SI, and achieve appropriate $D_{pf}$ values and struvite aggregate sizes. This outcome can appropriately explain the effects of SI on struvite particle sizes as reported previously (Korchef et al., 2011; Ronteltap et al., 2010).

2.2 Effect of pH value

Considering that struvite aggregates formed in low P concentrations have a relatively compact structure, the investigation of solution pH was conducted by setting the initial P level at 3.0 mmol/L and pH values at 9.0–10.5. Figure 4 presents the types of aggregates obtained in the operational experiments. The data showed distinct differences between crystal habits and aggregates, both in morphology and size. Needle-shaped crystals were observed at pH below 10.0, compared to rod-shaped crystals formed at pH 10.2 and 10.5. Aggregate size distribution analysis was carried out as a complementary procedure to image analysis. Figure 5 displays the undersize frequency of aggregate sizes obtained at different pH conditions.

![Fig. 4](image-url)  Geometric morphology of struvite aggregates at P 3.0 mmol/L under different pH conditions.
A trend was detected in which high solution pH levels corresponded to small aggregate sizes. Frequencies of aggregate sizes under 200 μm were 30.6%, 57.8%, 66.2%, 81.7% and 93.1%, corresponding to solution pH values at 9.0, 9.5, 9.8, 10.0 and 10.5, respectively. \( d_{0.5} \) combined with \( D_{pt} \), SI and zeta potential are summarized in Table 3. Enhancing pH values led to continuous decrease of \( d_{0.5} \) from 295.9 to 105.3 μm, SI from 1.09 to 0.36 and zeta potential from –2.70 to –8.31 mV, whereas \( D_{pt} \) showed a different variation range. The largest \( D_{pt} \) of 1.52 was observed at pH 9.0, followed by insignificant \( D_{pt} \) variation at 1.43–1.45 when solution pH increased.

pH is a particularly important parameter in struvite crystal formation and aggregation. For struvite precipitation, increasing pH levels made solution SI drop continuously (Table 3), and led to crystal habits changing from needle shape to rod shape, as shown in the present study (Fig. 4) and reported by other literature (Wilsenach et al., 2007; Ronteltap et al., 2010; Warmadewanthi and Liu, 2009). Different from the profile of \( d_{0.5} \) variation, \( D_{pt} \) was stable at 1.43–1.45 despite pH changes, except for 1.52 at pH 9.0. It was observed that the aggregates formed at low pH conditions were made up by more crystals, whereas the small aggregates obtained at high pH conditions included fewer crystals (Fig. 4). Although the large aggregates in low pH solutions had larger \( d_{0.5} \) and displayed more open and irregular shapes, their structures were as compact as those of the small aggregates obtained in pH 10.2 and 10.5 conditions. Hence, \( D_{pt} \) showed an insignificant variation range in the pH test.

### 2.3 Effect of shear rate

The mean diameter of aggregates under different P concentrations and pH levels was plotted against the shear rate on a log-log scale (Fig. 6). The fitted aggregate strength coefficients \((C)\) and stable aggregate exponents \((\gamma)\) are shown in Table 4. The strength of aggregates can be indicated by the value of log\(C\), which is the intercept of the fitted line. Therefore, for a given condition with different shear rates, larger log\(C\) implies stronger aggregation (Cao et al., 2011; Bache, 2004). The value of \(\gamma\) provides information on the variation of aggregate sizes on exposure to increasing shear rate. A larger \(\gamma\) means that the aggregates are prone to be broken into smaller sizes when shear rate increases (Cao et al., 2011; Jarvis et al., 2005). In the present study, high P concentrations combined with high pH values resulted in the decline of log\(C\) values, implying that the aggregates formed in low P levels and mildly alkaline conditions had relatively high aggregation strength. Similarly, small \(\gamma\) values were observed in the conditions with high P and

**Table 3** Aggregate sizes and fractal dimension of MAP at P 3.0 mmol/L under different pH conditions.

<table>
<thead>
<tr>
<th>pH</th>
<th>( d_{0.5} ) (μm)</th>
<th>( D_{pt} )</th>
<th>( R^2 )</th>
<th>SI</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>295.9</td>
<td>1.52</td>
<td>0.95</td>
<td>1.09</td>
<td>–2.70</td>
</tr>
<tr>
<td>9.5</td>
<td>179.2</td>
<td>1.43</td>
<td>0.97</td>
<td>1.03</td>
<td>–5.58</td>
</tr>
<tr>
<td>9.8</td>
<td>157.5</td>
<td>1.45</td>
<td>0.95</td>
<td>0.89</td>
<td>–9.36</td>
</tr>
<tr>
<td>10.2</td>
<td>125.4</td>
<td>1.45</td>
<td>0.96</td>
<td>0.61</td>
<td>–7.54</td>
</tr>
<tr>
<td>10.5</td>
<td>105.3</td>
<td>1.43</td>
<td>0.97</td>
<td>0.36</td>
<td>–8.31</td>
</tr>
</tbody>
</table>

**Fig 5** Undersize frequency of struvite aggregates at P 3.0 mmol/L under different pH conditions. \( d_{0.5} \), the equivalent diameter of aggregates.

**Fig 6** Aggregate strength plots for aggregates formed at different conditions. \( d_{0.5} \), average equivalent diameters; \( G \), shear rate.
Table 4 Aggregate strength coefficient (C) and stable aggregate exponent (γ) for aggregates formed under different conditions

<table>
<thead>
<tr>
<th>Run</th>
<th>P 3.5 mmol/L, pH 9.5</th>
<th>P 5.0 mmol/L, pH 9.0</th>
<th>P 6.0 mmol/L, pH 9.5</th>
<th>P 8.0 mmol/L, pH 9.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log C )</td>
<td>2.698</td>
<td>2.385</td>
<td>2.185</td>
<td>2.053</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>0.419</td>
<td>0.202</td>
<td>0.170</td>
<td>0.041</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.956</td>
<td>0.781</td>
<td>0.956</td>
<td>0.918</td>
</tr>
</tbody>
</table>

pH levels, which suggested that the aggregates formed at low P concentrations as well as low pH conditions were easily broken into smaller fragments under increasing shear force.

Figure 7 presents the average \( d_{0.5} \) and \( D_{pf} \) of aggregates exposed to various shear rates (\( G \) 10.5–93.6 sec\(^{-1}\)). Under different shear rates, aggregates formed at low P concentrations as well as low pH conditions distributed over wide diameter ranges, compared to narrow regions of aggregates obtained at high P levels as well as high pH values. With regard to \( D_{pf} \), the increase of shear rates resulted in a slight decrease of \( D_{pf} \) values obtained in conditions with low P levels and low pH. \( D_{pf} \) calculated at high P levels and high pH conditions kept relatively stable, despite shear rate variation. The decrease of \( D_{pf} \) suggested that the broken struvite aggregates were difficult to rearrange to a compact structure.

2.4 Evolution of aggregates

To clearly illustrate the aggregate size evolution, the overall aggregation process was divided into two phases, i.e., transitional phase, when struvite crystals evolved from nucleation and crystal growth stage to aggregation, and steady phase, where aggregate size did not significantly increase and fluctuated in a certain range. All the curves shown in Fig. 8 appeared to have a similar form. \( d_{0.5} \) rapidly increased at the beginning (less than 2 min) despite P concentration variation, and then further increase in size was restricted, resulting in a steady state. This result suggested that the transitional phase in struvite aggregation process had a short period, i.e., struvite evolved from crystal nuclei to aggregates rapidly.

Similarly, the total process of \( D_{pf} \) variation was divided into two phases, transitional phase and steady phase. As shown in Fig. 8, \( D_{pf} \) increased quickly to a significant extent (within 2 min), and stayed steady to the end of the experiments. Generally, in the aggregation process, the destabilized particles interact with each other and aggregate to form compact micro-flocs, resulting in \( D_{pf} \) increase. When the process proceeds, the formation of aggregates is dominated by adsorption, entrapment and bridging of micro-flocs, which results in non-compact structure.

Fig. 7 \( d_{0.5} \) (a) and \( D_{pf} \) (b) of struvite aggregates under different shear rates.

Fig. 8 Variation in aggregate size with aggregation time at pH 9.5 under different P concentrations.
structures indicated by the decline of $D_{pf}$ values (Cao et al., 2011; He et al., 2012; Chakraborti et al., 2003). However, struvite aggregates exhibited a different evolution process (Fig. 8), compared to the classic aggregation model. This was attributed to the struvite structure and crystal habits formed in the experimental conditions as discussed in the previous section. Hence, a relatively integral process of struvite crystal aggregation was elucidated as shown in Fig. 9. Due to the typical orthorhombic structure, struvite particles are prone to crystallize into needle or rod shapes, and aggregate at the corners or edges of crystals. Under appropriate conditions (supersaturation, pH, shear rate etc.), the individual crystals collide with each other, leading to adhesion between the crystals. The decrease of SI or solution pH promotes an increasing contribution of aggregation. With the growth of aggregates, cluster-cluster aggregation gradually starts to dominate the evolution process, giving rise to more fractal aggregates with more elongated shape and rougher surface (Figs. 1 and 4). Finally, the production of more irregular structures will be impeded by other aggregates. Consequently, $D_{pf}$ reaches a steady state. Similar phenomena were also observed by Stone and Krishnappan (2003) and He et al. (2012) in cohesive sediments and kaolin flocs.

![Fig. 9 Schematic illustration for the formation of struvite aggregates at constant pH.](image)

3 Conclusions

As an intrinsic property, aggregation is normally disregarded in struvite crystallization process, although it is the key factor for final particle size and therefore guarantees the efficiency of phosphorus recovery from wastewater. In this study, fractal geometry was applied to determine the characteristics of struvite aggregates, and the influence of operational parameters was evaluated. Due to their typical orthorhombic structure, struvite particles are prone to crystallize into needle or rod shapes, and aggregate at the corners or edges of crystals. Controlling operational conditions to low P concentrations and mildly alkaline pH would result in compact structures, large aggregate sizes and high aggregation strength. The change in pH throughout the process caused a shift in electrostatic potential, and consequently a shift in morphology and aggregate size. Increasing pH enhanced electrostatic repulsion among crystals and led to continuous decrease of $d_{0.5}$, whereas insignificant variation of $D_{pf}$ was observed. Struvite aggregates evolved with fast growth in a short time and stayed steady to the end of the experiments. Further experiments will focus on improving struvite aggregation under real wastewater conditions, and the means to enhance the fractal dimension of aggregates will be developed.

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