



Effects of organic substances on struvite crystallization and recovery

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ABSTRACT

The effects of organic substances on struvite crystallization and recovery from synthetic wastewater were investigated. Experiments were completed during trials lasting 5 days using a pilot reactor with two concentric stainless steel meshes as seed material. Various concentrations of organics were added to synthetic CO₂-saturated solutions and the pH was elevated from an initial value of 6.5 using a degassing technique. The results showed the presence of glucose, humic acid, and citric acid could reduce the struvite mass accumulating rates as compared to solutions without organic additives. In addition, glucose as an additive could significantly promote the removal rate of phosphorus as opposed to the other two. The mechanisms of the inhibitory effects are specially focused on the fact citric acid is able to complex with Mg²⁺, and NH₄⁺ in solution, while humic acid or glucose are able to adsorb onto the crystal surface. The recovered precipitates were analyzed using X-ray diffraction and were proven to have high purities. The morphologies of the precipitates were examined using scanning electron microscopy and found struvite particles aggregated together showing an irregular block shape, with the exception of particles recovered from solutions with humic acid, which showed a triangle-like shape.

Keywords: Organic substances; Struvite; Accumulation device; Nutrients removal and recovery

1. Introduction

The large-scale generation and discharge of nutrient-rich wastewater, such as wastewater from swine farms, is a threat to humans and the environment due to its potential to cause eutrophication or blue-green algal blooms in receiving waters [1–3]. As a result, increasingly stringent environmental regulations for nutrient removal have been introduced. Therefore, technically feasible and economically beneficial nutrient removal technologies are required for the mandated pollution control. Both phosphate and ammonia can be

recovered from nutrient-rich wastewater simultaneously in the presence of magnesium by crystallization to the form of magnesium ammonia phosphate salt known as struvite (MgNH₄PO₄·6H₂O) [4,5]. This process is a sustainable option for nutrient removal due to its high removal efficiency, solid–liquid separation capability, and the potential reuse of struvite as a slow-release fertilizer. Therefore, struvite crystallization is considered as a superior technology for nutrient recovery from wastewater [6,7].

The key factors driving struvite nucleation and growth as well as the specific crystallization mechanisms have been widely investigated and well-summarized in the literature, including optimal pH [8],

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temperature [9], stir rate [10], the supersaturation level [11] as well as the effects of foreign ions such as Ca^{2+} [12] and K^+ [13]. In certain wastewater, the levels of organic substances are relatively high and can be converted into various kinds of compounds during the anaerobic digestion, of which humic acids are the main components. Furthermore, glucose and citric acid are sometimes used as additives to either increase the concentration of the organic substances in reactant solutions or to act as low-molecular-weight organic ligands to influence the crystallization morphology [14,15]. However, few studies have focused on the influence of organic substances on the struvite crystallization process from wastewater. A previous study showed that both citrate and phosphocitrate were found to be effective growth inhibitors, remarkably lengthening the induction time of struvite crystallization. This effect was attributed to the adsorption of the citrate or phosphocitrate on the struvite crystal surface, successfully blocking the active crystal growth sites [16]. Meanwhile, Tamm–Horsfall glycoprotein was seen to promote struvite crystallization in feline urine [17]. In a recent study, three organic acids were used to examine the effects of organic compounds on phosphorus recovery by struvite crystallization. Results found that a high concentration of citric acid could significantly affect the phosphate removal efficiency and morphology, but succinic acid and acetic acid had little influence on the crystallization process [18]. Therefore, for successful nutrient removal and recovery from wastewater, it is vital to assess the effects of organic substances on struvite crystal formation and growth.

The struvite crystallization process is not more widely used due to a combination of factors, including the unknown economic value of the process, the need for a high level of pH control, and the challenge of collecting crystal particles. The wastewater supersaturation with regard to struvite increases drastically upon elevation of the solution pH. To achieve the desired pH, aeration by CO_2 degassing can be used to increase the pH value of the reactant wastewater [19]. This technique could provide a much gentler pH increase and insure the purity of the struvite precipitates, thus reducing the need to adjust solution pH by the addition of alkali [20]. To deal with the challenge of separation or collection of the struvite particles, attempts have been made to either seed the reaction or to develop accumulation devices [21,22]. Several studies have demonstrated a strong adhesion force between struvite and a metallic surface [23,24], and that a metallic support can successfully accumulate struvite with high purity [25,26]. As mentioned above, it has been reported that some organic substances have an inhibitory impact on the phosphate

crystallization process due to their adsorption on the crystal particles, but whether or not the adhesion properties of struvite were also affected are yet to be discussed. In summary, it is essential to investigate whether organic substances could interfere with the struvite mass accumulation rates while utilizing CO_2 degassing to elevate pH.

In this work, the effects of various organic additives on the mass accumulation rates of struvite were measured using a stainless steel mesh accumulator submerged into the aeration column of a pilot reactor and were examined using a demonstration reactor for phosphate, magnesium, and ammonia removal from synthetic wastewater. The objective of this study was to test the effects of organic substances on the formation of struvite crystals as well as the accumulation performance in recovering struvite from synthetic wastewater. In addition, the morphology and purity of precipitates recovered from reactant solutions were observed.

2. Materials and method

2.1. Reactor design

Based on the results of previous work, utilizing stainless steel mesh as an accumulating device [25,26], a pilot reactor was chosen for struvite crystallization and recovery experiments (Fig. 1). The reactor consisted of a cubic column with a cone-shaped bottom, and had a total effective volume of 50 L including a 40 L aeration column for the reaction and a 10 L cone-shaped piece at the bottom for sedimentation. A coarse air diffuser was affixed to the bottom of the aeration column to provide air for increased blending power as well as CO_2 degassing.

A seed system composed of two concentric meshes was designed for use as a substrate to accumulate struvite. Both meshes consisted of woven 0.35 mm stainless steel wire (Grade AISI 304, Ra(roughness) = 1.6 μm) with 1 mm hole size, designed to fit in the aeration column of the reactor (Fig. 1). Specifically, the external mesh was 84 x 30 cm and the internal mesh was 42 x 30 cm. The two pieces of mesh could be removed independently to study the accumulation efficiency of the system under the various conditions summarized in Table 1.

2.2. Materials and experimental design

Ten trials were conducted to study the effects of organic matter on the crystallization process and the scaling rate of the accumulating devices (Table 1). Three types of organics, that is humic acid, glucose,

(M6, Thermo, USA). The pH was measured using a pH meter (pHs-3C, Leici, China). The submerged system was removed and left to dry at room temperature for 7 days before being weighed to determine the mass of struvite accumulated. Struvite crystals were then recovered by light brushing and characterized using scanning electron spectroscopy (KYKY-2800, China). The compositions of the crystals were analyzed using X-ray diffraction (XRD, Bruker D8, Germany).

All aforementioned analyses were performed in triplicate and the averages were calculated. Statistical analysis of experimental data was performed using SPSS 11.0 (SPSS Inc., USA).

3. Results

3.1. Evolution of pH in the reactor

The variations of pH in the effluent for different synthetic wastewaters are shown in Fig. 2. An increase in solution pH was clearly observed during the precipitation step as compared with the initial pH. This effect is attributed to the removal of carbonate from the solutions by aeration. With the addition of glucose (Runs 1–3), the trends in pH values vary only slightly, with the final pH measured at about 8.3, and furthermore had no significant difference when compared to the control (Run 10), which had no added organics. For the addition of humic acid (Runs 4–6), a higher final pH value was achieved with the increase in concentration from 10 to 100 mg L⁻¹, increasing from 8.08

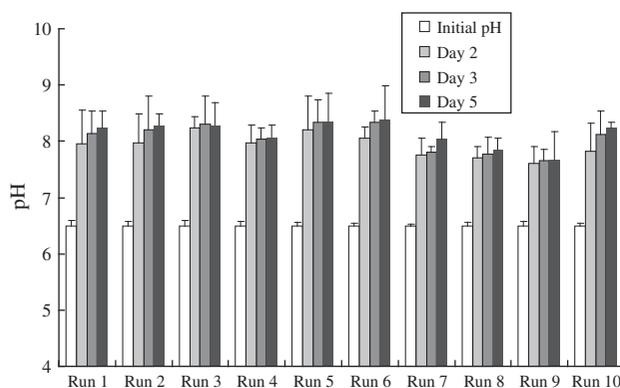


Fig. 2. The variation of pH in the effluent of the reactor in different Runs (the glucose as additives with concentrations of 10, 50, and 100 mg L⁻¹ in Runs 1–3, respectively; the humic acid as additives with concentrations of 10, 50, and 100 mg L⁻¹ in Runs 4–6, respectively; the citric acid as additives with concentrations of 10, 50, and 100 mg L⁻¹ in Runs 7–9, respectively; without organics in Run 10).

to 8.39. With the addition of citric acid (Runs 7–9), the final pH shifted to a lower level from 8.04 to 7.67 for each increase in concentration.

3.2. Effects of organic substances on removal efficiencies

The removal efficiencies of magnesium, ammonia, and phosphate for different organic additives in the supersaturated solutions at a given initial concentration are shown in Fig. 3. It can be seen that there was an increase in the phosphorus removal rate from 61.7 to 67.3% over Runs 1–3 corresponding to increasing levels of glucose. These phosphorus removal rates were much higher than those of any other Runs. The removal efficiencies of PO₄³⁻ decreased slightly from 50.2 to 46.6% in Runs 4–6 where humic acid was used, and the same trend was also observed in solutions with added citric acid (Runs 7–9).

The removal efficiencies of Mg²⁺ and NH₄⁺ increased slightly in Runs 1–3, from 29.1 to 36.1% and from 31.2 to 33.2%, respectively. The removal efficiencies of Mg²⁺ and NH₄⁺ did not differ much in Runs 4–6. However, the efficiencies of Mg²⁺ and NH₄⁺ showed a decreasing trend in Runs 7–10, from 30.5 to 25.1%, and 30.2 to 21.2%, respectively. In addition, it was found that the removal efficiencies of phosphorus were almost double that of ammonia and magnesium, meaning that the molar ratios of the removed nutrients were 1:1:1, since the initial molar ratio of Mg:N:P was 2:2:1 in synthetic wastewater.

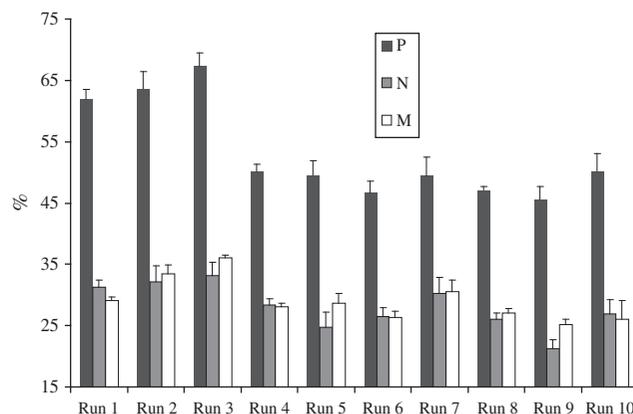


Fig. 3. The removal efficiencies of Mg²⁺, NH₄⁺, PO₄³⁻ during the crystallization in synthetic solutions with different organic substances (the glucose as additives with concentrations of 10, 50, and 100 mg L⁻¹ in Runs 1–3, respectively; the humic acid as additives with concentrations of 10, 50, and 100 mg L⁻¹ in Runs 4–6, respectively; the citric acid as additives with concentrations of 10, 50, and 100 mg L⁻¹ in Runs 7–9, respectively; without organics in Run 10).

3.3. Struvite mass accumulation rates on a stainless steel structure

Because the mass rate of struvite accumulation on a surface is a useful criterion for optimizing the recovery in the precipitation reactor, a custom accumulation device made of stainless steel wire mesh was used and its efficiency was examined. During the 5 d submergence in the aeration column, differing weights of struvite crystallized and accumulated on the struvite-accumulation device.

The amount of recovered struvite and recovery rates varied among experiments, as shown in Table 2. The largest amount of struvite collected, 31.55 g, was achieved in Run 3. In the absence of organic additives (Run 10), the metallic mesh was able to collect up to 30.33 g of struvite. With the increasing concentrations of humic acid (Runs 4–6), the recovery amount declined from 16.44 to 14.24 g, about a half of that in Run 10. The amount of struvite accumulated from the synthetic solution decreased from 25.35 to 22.04 g in Runs 7–9 due to the effects of the added citric acid. The inhibitory effect of the citric acid had been investigated in former studies [18], which showed a reduction in the initial rates of struvite precipitation and an increase of induction times. However, the results observed in Runs 1–3 were in contrast to those of other runs. Higher glucose concentrations lead to an increased potential to accumulate struvite due to a higher concentration of struvite particles in the solutions, from 24.38 to 31.55 g collected.

3.4. Characterization of the struvite

Since XRD analysis may be the only qualitative method for judging struvite purity, this method was

used and the resulting diffractogram is shown in Fig. 4. The XRD pattern of the precipitates accumulated up from the solutions with organic substances and matched well with the standard peaks of struvite attained from the ICCD (International Centre for Diffraction Data, PDF2–2004), which identified the precipitated crystals as pure struvite. It was noted that the relative intensities of the precipitates showed differences in comparison with the reference struvite pattern, and that the differences were related to the different organic additives in the supersaturated solutions. This finding suggests changes in the texture of the crystalline material and more specifically changes in the crystallite size.

The morphologies of the precipitates were identified using SEM. The micrographs, seen in Fig. 5, show that for added glucose and citric acid, as well as in the absence of organic substances in the solution, precipitates in the form of struvite aggregates with irregular block patterns were observed (Fig. 5(a), (c), and (d)). However, the recovered solids from solutions with humic acid were triangular plate-like structure, differing significantly from the other collected solids (Fig. 5(b)).

4. Discussion

Struvite particles can be formed according to the chemical Eq. (1) under the condition that the ion activity product of struvite exceeds the solubility product. Understandably, the pH value of the reaction solution can greatly influence the existing species as well as the activity of each struvite component [27]. Therefore, the pH of solution is a primary factor affecting phosphorus recovery by the struvite crystallization process [28].

Table 2
The amount of precipitates accumulated by stainless meshes in synthetic solutions

Types of organic substances	Concentration (mg L ⁻¹)	Amounts of precipitates (g)		
		Internal mesh	External mesh	Combined system
Without organic substances	0	12.16 ± 1.73	18.17 ± 2.11	30.33 ± 3.84
Glucose	10	9.79 ± 1.47	14.59 ± 1.83	24.38 ± 0.36
	50	10.00 ± 1.51	17.25 ± 1.97	27.25 ± 3.48
	100	15.25 ± 1.88	16.30 ± 2.03	31.55 ± 3.91
	100	5.76 ± 0.88	10.19 ± 1.05	15.95 ± 1.93
Humic acid	10	6.81 ± 0.89	9.52 ± 1.11	16.33 ± 0.22
	50	5.76 ± 0.88	10.19 ± 1.05	15.95 ± 1.93
	100	5.56 ± 0.78	8.68 ± 0.93	14.24 ± 1.71
Citric acid	10	8.89 ± 1.12	16.46 ± 1.89	25.35 ± 3.01
	50	8.61 ± 1.09	15.57 ± 1.86	24.18 ± 0.77
	100	8.51 ± 1.06	13.53 ± 1.75	22.04 ± 2.81

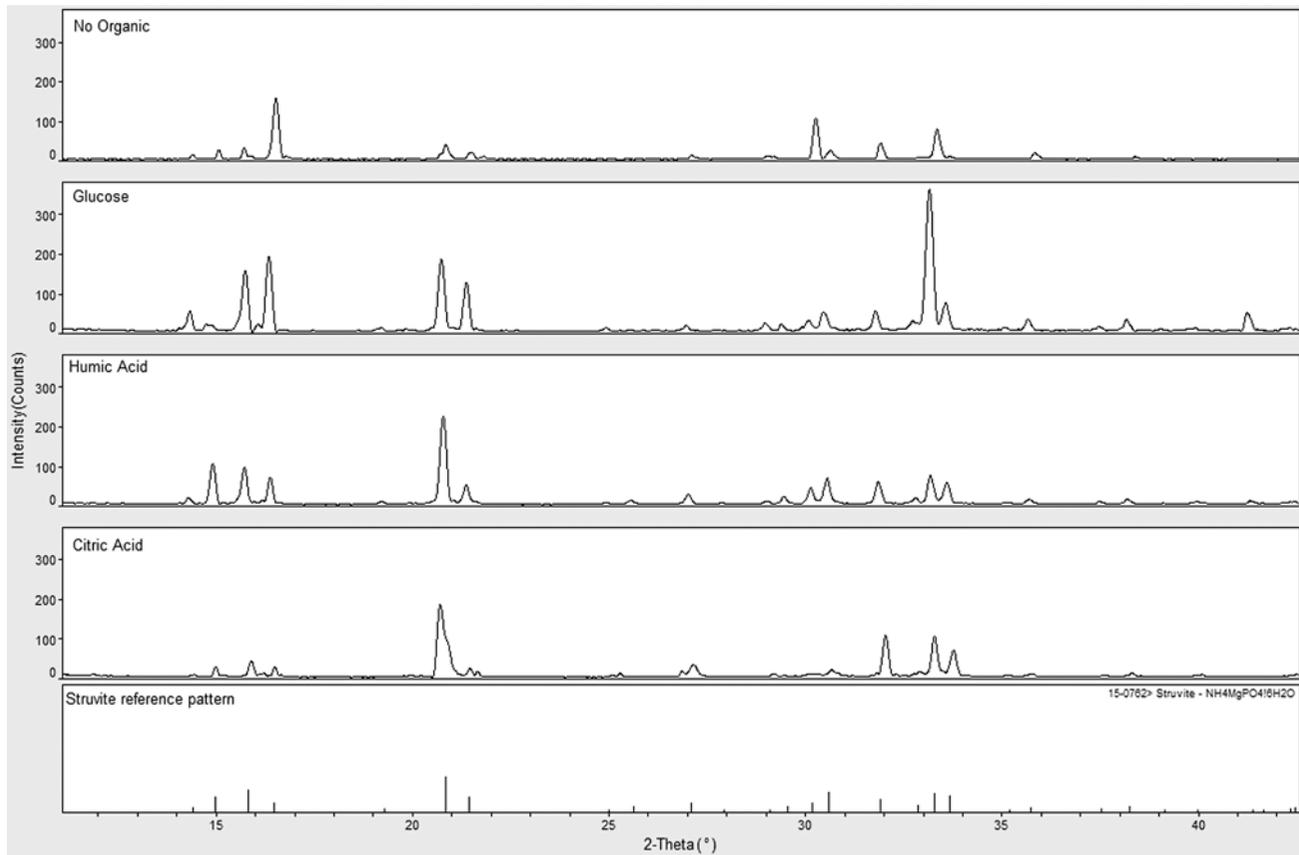
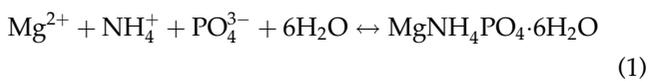


Fig. 4. XRD pattern of the precipitates obtained from the accumulation mesh in comparison with the reference diffraction pattern for struvite.



Elevating pH through degassing with CO_2 has been used in many studies and has proved to be an efficient means of pH manipulation as compared to the addition of alkali to the solution. The results of previous research in this area revealed that the CO_2 degassing technique could lead to a maximum pH above 8 from an initial pH of 6.5, with the struvite formation occurring at pH slightly greater than 8 [28]. However, when the citric acid was used as the additive in the solution, the maximum solution pH achieved was below 8 (Runs 8–9). Previous research suspected that the citric acid could complex with Mg^{2+} and NH_4^+ to form $[\text{C}_3\text{H}_5\text{O}(\text{COO})_3]_2\text{Mg}_3$ (Stability constant of coordination compounds, $\log K_1 = 3.29$) and $\text{C}_3\text{H}_5\text{O}(\text{COO})_3(\text{NH}_4)_3$ (hydrolysis equilibrium constant, $K_{\text{ha}1} = 8.04 \times 10^{-7}$, $K_{\text{hb}1} = 3.36 \times 10^{-5}$), respectively (as shown in Eqs. (2) and (3)). This reaction

would reduce the concentration of Mg^{2+} and NH_4^+ in the solution, and therefore inhibit the process shown in Eq. (1) as well as release a proton [18]. In this work, the concentrations of Mg^{2+} , PO_4^{3-} , and NH_4^+ remained stable in Run 9 (the highest concentration of citric acid tested) during the first two days of the reaction (data not shown), but the stainless meshes still accumulated a considerable amount of struvite. This result was further supported by the finding that a low concentration of citric acid could reduce the initial rates of precipitation and prolong the induction time of the struvite formation, a finding that may be ascribed to a lesser consumption of Mg^{2+} and NH_4^+ to form complexes due to the low citric acid concentration [15]. According to the above hypothesis, the inhibitory effects observed may be not compounded by the fact that citric acid may be adsorbed onto the active sites of crystal nuclei, thus blocking the crystal growth and increasing the required supersaturation level for the struvite crystallization reaction and resulting in the decline of the P removal efficiency [29,30].

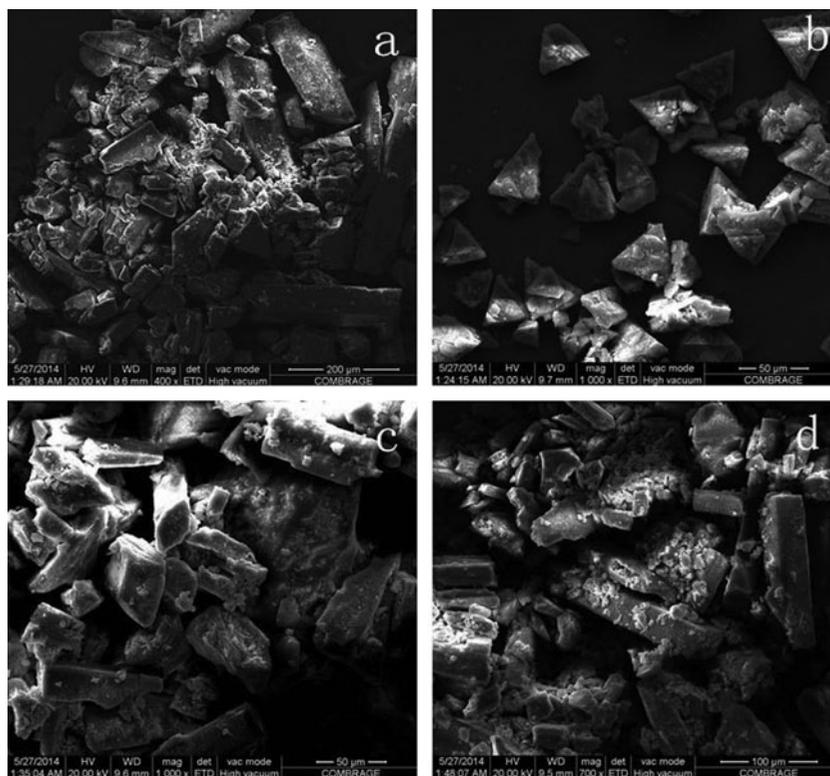
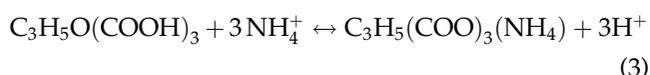
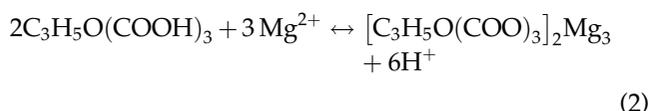


Fig. 5. SEM of precipitates recovered from synthetic solution with glucose (a), humic acid (b), citric acid (c), and without organic substances (d).



Furthermore, it has been observed that high concentrations of citric acid almost completely inhibited the reaction from the beginning, which could be due to the citric acid entirely enveloping the crystal nucleus and suppressing the growth of crystals [18]. For solutions with humic acid or glucose, the final pH did not differ much as compared to solutions without organic additives.

The degree to which the adhesion properties of stainless steel meshes can be affected by the presence of organics in solution have not previously been discussed. In the present study, the metallic struvite extraction system consisting of two circular stainless steel meshes was submerged into the synthetic wastewater solutions with added organic substances in order to test the mass accumulation rates. In Runs 1–3, the removal efficiencies of phosphorus were

much higher than in Run 10 (where no organic substances were added). However, the accumulation amounts of Runs 1–2 were less than that measured for Run 10, meaning that glucose could promote the crystallization rate but decrease the adhesion force between the struvite and stainless mesh or inhibit the continued crystal growth. The results of previous research demonstrated that the measured rates of crystal growth were significantly reduced in the presence of low concentrations (10^{-6} mol L $^{-1}$) of glucose, but that crystallization did not stop at high glucose concentrations (10^{-3} mol L $^{-1}$) for the crystallization of calcium phosphate [31]. Also, it has been suggested that adsorption of glucose on the hydroxyapatite surface has a relatively high affinity for the substrate [31]. It is supposed that the adsorption of glucose on the struvite surface weakens the adhesion properties between the crystal particles and metal surface, thereby slowing crystal growth. The removal efficiencies of Mg^{2+} , NH_4^+ , and PO_4^{3-} did not differ significantly between Runs 4–6 and Run 10. However, the accumulation system could only recover in Runs 4–6 around half of what was recovered for Run 10, with the recovered precipitates displaying a brown color as opposed to white. This result may indicate that the acids with

larger molecular weights could physically cover the crystal surface. The reason for this is most likely that the active groups of humic acids, such as carboxyl, hydroxyl, amino, and carbonyl, would have adsorbed onto the seed crystals, thereby blocking sites for further crystal growth and scaling [32]. Furthermore, the findings of another study showed that dissolved humic acid could inhibit the calcite or calcite phosphate crystallization rate by simply covering the active sites rather than by forming a complex with the seed crystals [33,34]. It can be concluded that the mechanism for the inhibitory effect of humic acid on struvite crystallization was not the same as the effects due to citric acid. The citric acid could be used as an effective inhibitor because both the removal efficiencies and mass accumulation rates decrease in correspondence with increasing concentrations. However, the mass accumulation rate was not largely decreased because the organic ligand of citric acid did not actually bind to the active growth sites of newly formed crystal nuclei; therefore, not greatly influencing the adhesion properties.

In previous studies, the effects of organic substances in wastewater on struvite crystallization were not fully discussed, but focused instead on the influence of these substances on the purity of precipitates. Results showed that only small amounts of organic substances attach to struvite crystals during crystallization, meaning that the organic additives did not significantly affect the purity of the struvite. When crystallizing struvite in urine, the levels of hormones and pharmaceuticals in solution held nearly constant, meaning that the obtained precipitates were clean [35]. Meanwhile, succinic acid, acetic acid, and citric acid at low concentration (≤ 2 mM) were proven to have little effect on the composition of crystalline product. Moreover, the stainless steel meshes used as seed material in the pilot reactor during the treatment of swine wastewater were able to recover high purity struvite during a long-term operation [26]. According to the above-mentioned examples, it can be concluded that the organic substances had little influence on the struvite composition. In this study, the precipitates were proven to be high purity struvite, meaning that the three types of organic additives used could not significantly affect the struvite purity, and that the organics could attach to the crystals, for example, the color of precipitate collected from Runs 4–6 was brown.

The struvite crystal is a type of rhombic system, and can crystallize into two major crystal forms: distinctive orthorhombic structure or needle-like structure with varying thickness and length [36,37]. Using SEM, the precipitates were observed to be aggregated, and

the particles collected from solutions with glucose, citric acid, and the absence of organic substances had the same morphology, irregular block shape. Crystals collected from solutions with humic acid did not fit this pattern, but instead had a triangular plate-like structure. In a previous study, results demonstrated that the shape of the reaction products was greatly affected by citric acid [18]. The crystal morphology was seen to change from regular needle-shaped to irregular block, and finally transformed to rectangular block with increasing concentration. The reason for this observation may be that the different concentrations of citric acid affected the nucleation, aggregation, and growth rate of the crystals, resulting in the formation of different shaped products. On the contrary, the increasing concentration of citric acid did not influence the shape of aggregates in this work. On the other hand, it was demonstrated that the morphology of struvite was not affected by the addition of glucose, but this could promote the size of the precipitates [15]. The shape of particles recovered from solutions with humic acid was triangle-shaped, which was quite distinct from the others precipitates, and may be due to its ability to block active sites and adsorb to the newly formed crystallites, thus influencing their growth and transformation. Moreover, the morphology of the precipitates could also be affected by the reaction crystallization process, and some previous researches revealed that the solids could present the tubular forms and trough shape [38,39] or an agglomeration of single orthorhombic crystals in continuous mode [22]. It was supposed that this was the net effects of the impurities present in the wastewater and technological parameter of reaction crystallization process.

5. Conclusions

The impacts of organic substances on struvite crystallization and accumulating have been investigated using a pilot reactor. In the present study, it was found that the presence of some organic substances could interfere with the adhesion prosperities between the struvite and stainless steel meshes, with citric acid as the exception. Humic acid and citric acid could inhibit both the struvite formation and crystal growth; however, a higher concentration of glucose in the solution could be a promoter of struvite formation due to high P removal efficiencies. The recovered solids were proven to be pure struvite using XRD analysis. SEM of the aggregates showed irregular block shapes for all collected precipitates except those collected from synthetic wastewater solutions with added humic acids.

Acknowledgments

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