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Optimization of struvite crystallization to recover nutrients from raw swine wastewater

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ABSTRACT

For the nitrogen and phosphorus resource recovery from raw swine wastewater, laboratory-scale batch experiments were carried out to investigate the effects of pH value, magnesium dosage, and phosphate dosage on struvite crystallization. The crystallization process of the struvite was observed under inverted microscope, and the composition and morphology of the precipitates were characterized by X-ray diffraction and scanning electron microscope. It has been found that the optimal parameters were a Mg^{2+}/NH_4^+ molar ratio of 1.6, a PO_4^{3-}/NH_4^+ molar ratio of 1.3, and a pH of 10.0. The results showed that a large number of crystals had been formed in 5 min under optimal conditions, the precipitates were orthorhombic crystal systems with 10–20 μm in length, and they were proved to be struvite. When pH value reached 11.5, there were few crystals in the precipitates, and $Mg(OH)_2$ was formed instead of struvite.

Keywords: Struvite crystallization; Ammonium; Phosphate; Magnesium; Swine wastewater

1. Introduction

Nitrogen (N) and phosphorus (P) are often referred to as the primary macronutrients; however, they can provoke water eutrophication when they are present in excess. In most countries, removing ammonium and phosphate is usually obligatory before discharging wastewater into water bodies, and special attention is given to phosphate removal and its recycling as a raw material for the phosphate industry [1]. Struvite (MAP, $MgNH_4PO_4{\cdot}6H_2O$) precipitation has been widely investigated on the treatment of wastewater which is rich in ammonium or phosphate, such as rare-earth wastewater [2], landfill leachate [3], coking wastewater [4], semiconductor wastewater [5,6], human urine [7], and urease [8], and it can simultaneously remove and recover P and N from wastewater. Furthermore, struvite is a high-quality fertilizer because of its slow release rate of nutrients, low frequency of application, and low heavy metal content compared to P rocks, which help make it environmentally friendly [9–11].

Struvite precipitates in a 1:1:1 M ratio following the equation [12]:

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + OH^- + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \quad (1)$$

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Struvite precipitation depends on different factors such as pH, Mg^{2+}:PO_4^{3-} molar ratio, Mg^{2+}:NH_4^+ molar ratio, and temperature [13,14]. In addition to PO_4^{3-} and NH_4^+, swine wastewater contains a certain concentration of Mg^{2+}. Once the pH of swine wastewater rises to an appropriate value, PO_4^{3-}, Mg^{2+}, and NH_4^+ become crystallized, forming struvite [15]. Many researchers claimed that struvite precipitation was a valid alternative for the removal of PO_4^{3-} and NH_4^+ from the swine wastewater [16,17]. However, previous studies have focused on the operational parameters and optimization of solution conditions [18,19], the characterization of nucleation [16], and the struvite formation kinetics and thermodynamics [20]. These characteristics of struvite precipitation were evaluated by using synthetic swine wastewater or pretreated swine wastewater [16,21]. As stated in many studies, untreated swine wastewater is a very complex media in which parameters such as the presence of foreign ions can strongly influence the precipitation process. Up to now, few attempts have been made to explore the struvite crystallization from raw swine wastewater.

In this paper, the chemical processes controlling the precipitation of struvite in raw swine wastewater were investigated, and the operational parameters were optimized. The crystallization process of the struvite was observed under inverted microscope, and the composition and morphology of the precipitates were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The aim of this work was to better understand the mechanisms of the struvite crystallization from raw swine wastewater, which would provide references for the process control in struvite precipitation recycling of P and N.

2. Materials and methods

2.1. Swine wastewater

The swine wastewater used during this study was collected from a piggery in Zengcheng, Guangdong province, PRC. The swine wastewater was stored in a 25-L container at 4℃ until required. Prior to utilization, the swine wastewater was screened by a sieve with 0.5-mm mesh openings to remove large solids. The characteristics of the wastewater are summarized in Table 1.

2.2. Batch experiments

In comparison with NH_4^+, swine wastewater generally contains lower concentrations of Mg^{2+} and PO_4^{3-} (see Table 1). For the effective removal of NH_4^+, some Mg^{2+} and PO_4^{3-} are required to be added. $Na_2HPO_4{\cdot}12H_2O$ was used as the phosphate source, and $MgCl_2{\cdot}6H_2O$ was used for the magnesium source. $Na_2HPO_4{\cdot}12H_2O$, $MgCl_2{\cdot}6H_2O$, NaOH, $MgNH_4PO_4{\cdot}6H_2O$, and $Mg(OH)_2$ were purchased from Guangzhou Chemical Reagent Factory, P.R. China. All these reagents were of analytical grade and were applied directly.

To determine the best pH, screened swine wastewater (250 mL) was transferred into a 500-mL square beaker. Magnesium chloride and disodium hydrogen phosphate were added to the sample at a final Mg^{2+}/NH_4^+ molar ratio of 1.6 and a final PO_4^{3-}/NH_4^+ molar ratio of 1.2 (the ratios were based on previous orthogonal experiments). The solution pH was adjusted to 9.0, 9.5, 10.0, 10.5, and 11.0, respectively. Then, the solution was stirred with magnetic bars at a constant speed of 50 rpm for 20 min and quiescent settled for 30 min. In addition, at the optimum pH, the effects of Mg^{2+}/NH_4^+ molar ratio on the NH_4^+-N and PO_4^{3-} removal efficiencies were analyzed by adjusting the Mg^{2+}/NH_4^+ molar ratio to 1.4:1, 1.5:1, 1.6:1, 1.7:1, and 1.8:1, and reacting as above. Furthermore, at the optimum pH and Mg^{2+}/NH_4^+ molar ratio, the effects of PO_4^{3-}/NH_4^+ molar ratio on the NH_4^+-N and PO_4^{3-}-P removal efficiencies were also analyzed by adjusting the PO_4^{3-}/NH_4^+ molar ratio to 1.0:1, 1.1:1, 1.2:1, 1.3:1, and 1.4:1.

After the settling period, the solution supernatant was filtered through a 0.45-μm membrane filter for chemical analysis, and the removal efficiency (%) was calculated according to the analysis of the supernatant. Three replications of each test were carried out.

2.3. Crystallization process, morphology and composition

Under optimal conditions, the crystallization process was observed under inverted microscope (BDS200-PH, China). The composition of the precipitates, analytical grade struvite, and magnesium hydroxide were compared by XRD (Rigaku DMAXRB, Japan), and their morphologies were observed under SEM (KYKY-2800, China). Before characterization by XRD and SEM, the filtered precipitates were dried for 48 h in an oven at 35℃. To verify the effects of pH on the struvite formation, the morphology of strong alkali precipitates (pH 11.5, Mg^{2+}/NH_4^+ molar ratio 1.6:1, and PO_4^{3-}/NH_4^+ molar ratio 1.3:1) was also observed.

2.4. Chemical analysis

The concentrations of NH_4^+-N, TP, PO_4^{3-}-P and SS were measured using a spectrophotometer (752 N, China) with standard methods [22]. Ammonium

Table 1
Characteristics of swine wastewater used in experiments

Parameter	Mean	Std. deviation
pH	7.0	0.3
Chemical oxygen demand (COD_{Cr}, mg/L)	7,094	525
Total phosphorus (TP, mg/L)	187	56.8
PO_4^{3-}-P (mg/L)	89.5	36.4
NH_4^+-N (mg/L)	535	46.7
Mg^{2+} (mg/L)	131	22.3
Ca^{2+} (mg/L)	253	65.8
Suspended solid (SS, mg/L)	8.8	2.1

nitrogen was determined with Nessler's reagent colorimetric method. Total phosphorus was measured with ammonium molybdate spectrophotometric method, and the phosphate concentration was determined with persulfate digestion molybdate–ascorbic acid colorimetric method. Calcium ions and magnesium ions were measured according to the standard method [23]. The COD_{Cr} was determined by potassium dichromate using a spectrophotometer analyzer (Hach model DR2800, USA). The pH was measured by a pH meter (pHS-3C, Shanghai Precision & Science Instrument, China).

3. Results and discussion

3.1. Effects of pH on the NH_4^+-N and PO_4^{3-}-P removal efficiencies

Based on the previous literature [19], the experiments were performed at a pH range between 9.0 and 11.00. The NH_4^+-N and PO_4^{3-}-P removal efficiencies (with 1.6 of Mg^{2+}/NH_4^+ molar ratio and 1.2 of PO_4^{3-}/NH_4^+ molar ratio) at different pH conditions are presented in Fig. 1. These results showed that the NH_4^+-N and PO_4^{3-}-P removal efficiencies were greatly affected by pH value, and they reached the maximum at pH 10.0 and pH 10.5, respectively. When the pH was below the optimum range, the increase of OH^- in the solution helped the struvite crystallization, resulting in the increase of the NH_4^+-N and PO_4^{3-}-P removal ratio. In strong alkali conditions ($pH > 10.5$), $Mg(OH)_2$ was formed instead of struvite, so decreased the productivity of struvite crystallization, which was proved by SEM results. Finally, this brought a decrease in the NH_4^+-N and PO_4^{3-}-P removal ratios. The maximum $NH_4{}^+$-N and PO_4^{3-}-P removal ratio appeared in the range of 10.0–10.5, which was in agreement with other literature concerning struvite precipitation in synthetic swine wastewater [24].

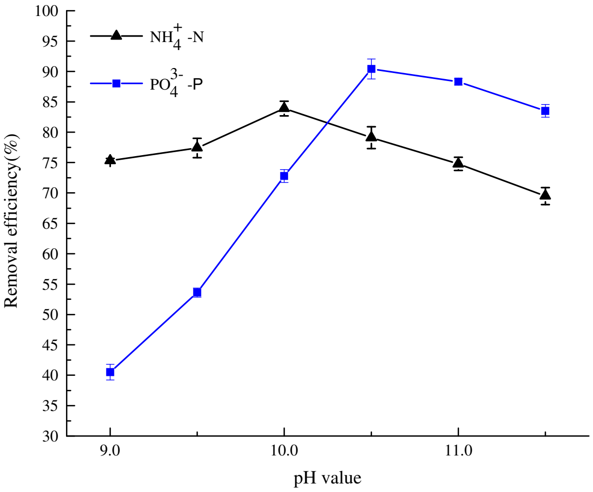

Fig. 1. Effects of pH on the NH_4^+-N and PO_4^{3-}-P removal efficiencies (Mg^{2+}/NH_4^+ molar ratio 1.6 and PO_4^{3-}/NH_4^+ molar ratio 1.2).

Fig. 1 showed an increase in PO_4^{3-}-P removal until pH 10.5; however, the max $NH_4{}^+$-N removal was obtained at pH 10.0. This suggested that other phosphorus compounds (i.e. not containing N) were formed at pH 10.5, it might well be calcium phosphate and magnesium phosphate [12,19], and the detailed mechanisms need further investigation.

3.2. Effects of Mg^{2+}/NH_4^+ molar ratio on the NH_4^+-N and PO_4^{3-}-P removal efficiencies

Fig. 2 shows that the NH_4^+-N and PO_4^{3-}-P removal efficiencies could be markedly affected by Mg^{2+}/NH_4^+ molar ratio when the pH value was set at 10.5. As the Mg^{2+}/NH_4^+ molar ratio increased from 1.4 to 1.6, the $NH_4{}^+$-N removal ratio increased rapidly, whereas excessive Mg^{2+}/NH_4^+ molar ratio(>1.6) could decrease

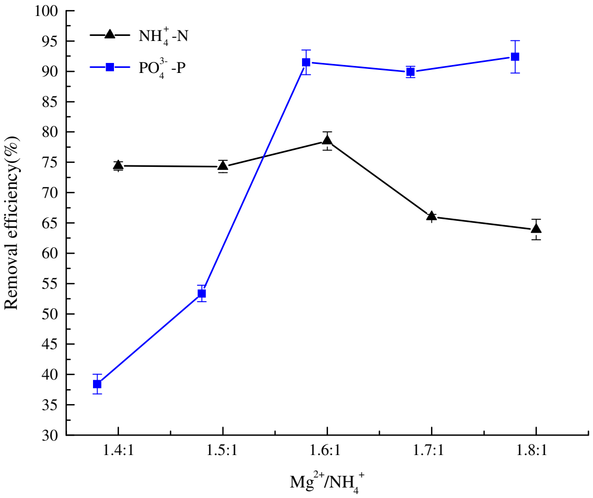

Fig. 2. Effects of Mg^{2+}/NH_4^+ molar ratio on the NH_4^+-N and PO_4^{3-}-P removal efficiencies (pH 10.0 and PO_4^{3-}/NH_4^+ molar ratio 1.2).

the NH_4^+-N removal ratio. At lower Mg^{2+}/NH_4^+ molar ratio, NH_4^+ could be combined together with Mg^{2+} and phosphate ions to form struvite, so it could be removed with struvite crystals. At higher Mg^{2+}/NH_4^+ molar ratio, NH_4^+-N was the limiting factor of struvite precipitates, and excessive Mg^{2+} could be combined together with OH^- and lowered the pH values, which was proved by the results that the experiments performed with Mg^{2+}/NH_4^+ molar ratio of 1.4, 1.6, and 1.8 had 0.58, 0.76, and 0.93 pH unit reduction after 50-min reaction period, respectively.

Generally speaking, the concentration of free ammonia in solution was a function of NH_4^+-N concentration, pH value, and temperature (Eqs. (2) and (3)) [25]. Therefore, the removal amount of NH_4^+-N decreased along with the decrease in the pH values.

$$[NH_3] = \frac{[NH_3] + [NH_4^+]}{(1 + [H^+])/K_a} \tag{2}$$

$$K_a = \frac{K_W}{K_b} = e^{-(6344/(273/T))} \tag{3}$$

As also shown in Fig. 2, when the Mg^{2+}/NH_4^+ molar ratio increased from 1.4 to 1.6, the PO_4^{3-}-P removal ratio rapidly increased, whereas further increases in the Mg^{2+}/NH_4^+ range of 1.6–1.8 caused a slow increase in the removal ratio of PO_4^{3-}-P. At higher Mg^{2+}/NH_4^+ molar ratio, the PO_4^{3-}-P could still be removed by being combined together with Mg^{2+} to form magnesium phosphate.

3.3. Effects of PO_4^{3-}/NH_4^+ molar ratio on the $NH_4{}^+$-N and PO_4^{3-}-P removal efficiencies

With the increasing PO_4^{3-}/NH_4^+ molar ratio, the NH_4^+-N removal ratio increased very rapidly and thereafter stayed at the plateau value, while the PO_4^{3-}-P removal efficiency decreased gradually (Fig. 3). It was explained that when the PO_4^{3-}/NH_4^+ molar ratio exceeded 1.3, the magnesium concentrations became limiting, thus the NH_4^+-N removal ratio achieved a relatively stable value. In addition, phosphates were also removed by forming magnesium phosphate and calcium phosphate, so the PO_4^{3-}/NH_4^+ molar ratio was more than 1.0.

Batch experiments showed that the optimal conditions were as follows: pH 10.0, Mg^{2+}/NH_4^+ molar ratio 1.6, and PO_4^{3-}/NH_4^+ molar ratio 1.3.

3.4. Crystallization process figuration

The crystal images under optimal conditions at different periods are presented in Fig. 4. Due to the abundance of foreign solid phases in the swine wastewater environment, the principal precipitation mechanism was likely to be heterogeneous. However, precipitation was still rapid, and a large number of crystals had been formed in 5 min. Then, crystals began to aggregate, and aggregation gradually gathered the smaller nuclei together to form larger particles with improved settling characteristics.

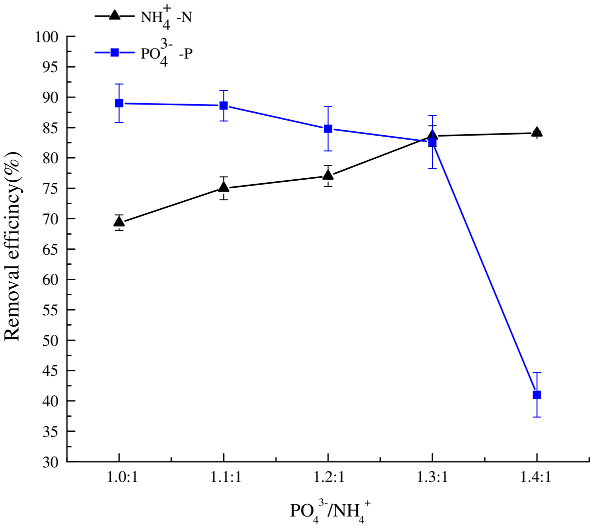

Fig. 3. Effects of PO_4^{3-}/NH_4^+ molar ratio on the NH_4^+-N and PO_4^{3-}-P removal efficiencies (pH 10.0 and Mg^{2+}/NH_4^+ molar ratio 1.6).

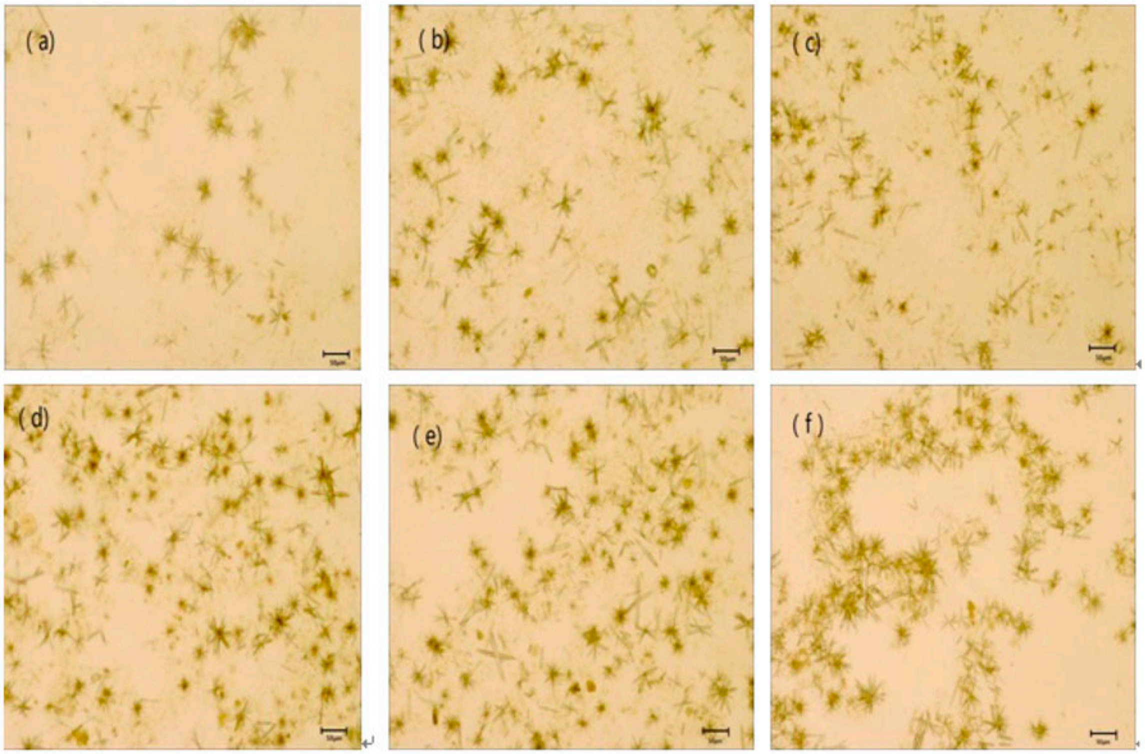

Fig. 4. Crystals figuration at pH 10.0, with 1.6 of Mg^{2+}/NH_4^+ molar ratio and 1.3 of PO_4^{3-}/NH_4^+ molar ratio. (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 25 min, and (f) 30 min.

3.5. Precipitate characterization

XRD was applied to characterize the composition of the formed crystals, as shown in Fig. 5. No apparent position differences could be observed by comparing the XRD patterns of the precipitates (Fig. 5(c)) with those of $MgNH_4PO_4$ (analytical grade) crystals (Fig. 5(b)). However, intensity of peaks was relatively higher, as compared to $MgNH_4PO_4$ (analytical grade) crystals, indicating higher crystallinity of these precipitates. It also agreed well with layered settlement during quiescent settling. The XRD patterns identified that these precipitates should be struvite.

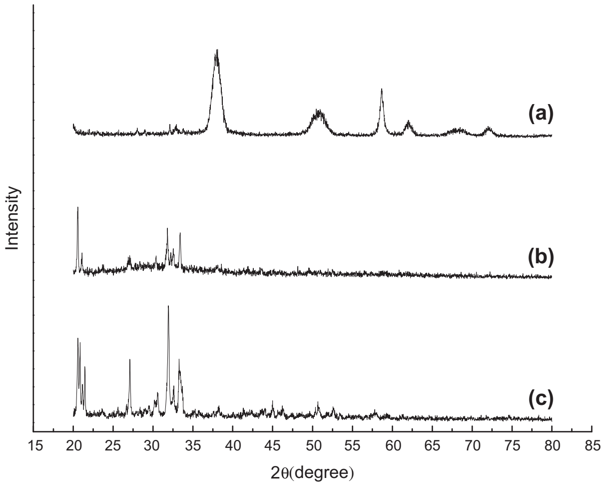

Fig. 5. XRD analysis of $Mg(OH)_2$ (a), $MgNH_4PO_4$ (b), and optimal precipitates (c).

3.6. SEM analysis

The SEM images of optimal precipitates, strong alkali precipitates, $MgNH_4PO_4$ (analytical grade) and $Mg(OH)_2$ (analytical grade) are illustrated in Fig. 6. Compared with $MgNH_4PO_4$ (Fig. 6(c)), though there were some other components, the orthorhombic shape crystals could still be distinguished in the optimal precipitates (Fig. 6(a)), and the length of these crystals was 10–20 μm. On the contrary, there were few crystals in the relatively strong alkali precipitates (Fig. 6(b)) and $Mg(OH)_2$ (Fig. 6(d)), and both of them had flake-like structure, which also proved $Mg(OH)_2$ was formed under strong alkali condition (pH 11.5). pH is a key factor in the struvite formation process, and the optimum pH for the formation of struvite in

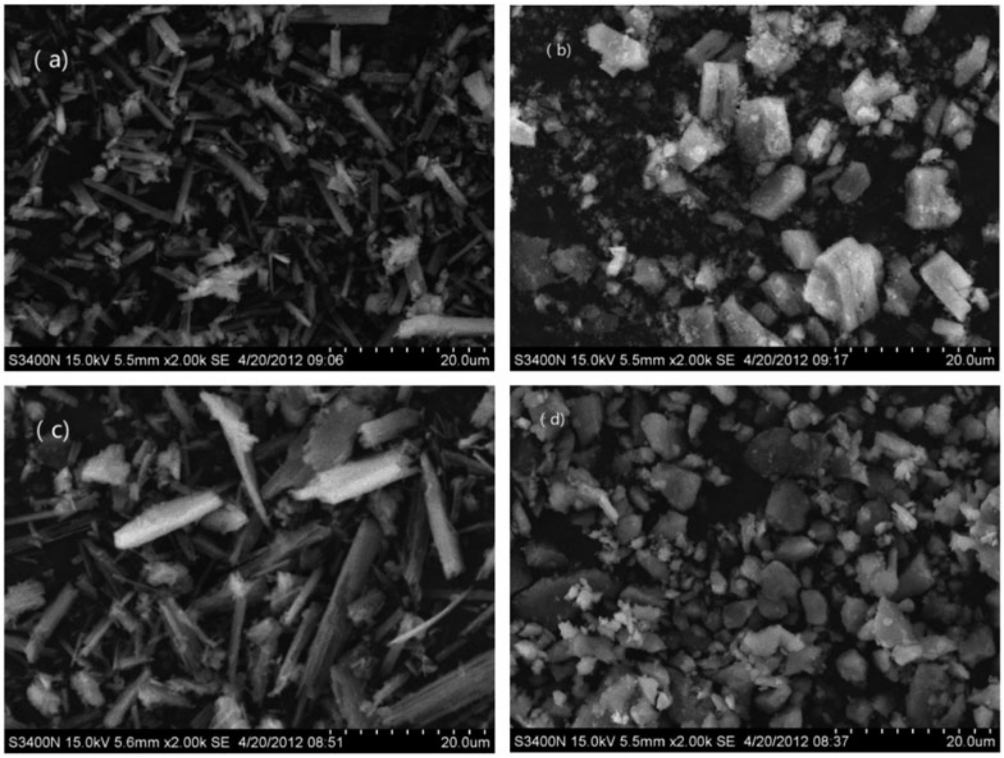

Fig. 6. SEM photos of optimal precipitates (a), strong alkali precipitates (b), $MgNH_4PO_4$ (c), and $Mg(OH)_2$ (d).

swine wastewater was about 10.0. SEM confirmed the results of the XRD analysis.

4. Conclusions

The chemical processes controlling the precipitation of struvite in raw swine wastewater were investigated, and the optimally operational parameters for max Mg^{2+}/NH_4^+ removal were as follows: Mg^{2+}/NH_4^+ molar ratio was 1.6:1, PO_4^{3-}/NH_4^+ molar ratio was 1.3:1, and pH was 10.0. Under optimal conditions, a large number of crystals had been formed in 5 min, and the precipitates were orthorhombic crystal systems with 10–20 μm in length, which were very similar to $MgNH_4PO_4$. The XRD and SEM analyses proved that these precipitates were struvite. However, when pH value reached 11.5, there were few crystals in the precipitates, and $Mg(OH)_2$ was formed instead of struvite.

The PO_4^{3-}-P removal and the max NH_4^+-N removal were obtained at pH 10.5 and 10.0, respectively. This suggested that other phosphorus compounds (i.e. not containing N) were formed at pH 10.5, it might well be some calcium phosphate, and the detailed mechanisms need further investigation.

From the above experimental studies, it can be concluded that struvite crystallization may be an effective way to remove and recover nutrients from raw swine wastewater.

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