



## Phosphorus recovery from swine wastewater by struvite precipitation: compositions and heavy metals in the precipitates

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Received 1 October 2014; Accepted 22 March 2015

### ABSTRACT

Recovering phosphate and ammonium as struvite from swine wastewater has gained importance as a means of relieving water eutrophication and the scarcity of phosphorous rock resources. Recently, it has been generally accepted that the quality of recovered products can facilitate the market development of nutrient recovery. In this work, the compositions and heavy metals in the recovered products of struvite recovered from swine wastewater were investigated by dosing industrial-grade (IG) MgO and Mg(OH)<sub>2</sub> as the low-cost magnesium sources. Results revealed that struvite (34.4–40.4% weight ratio) was the dominant mineral in the precipitates, mixing up with amorphous calcium phosphate (7.8–9.5%) and residual IG-MgO or IG-Mg(OH)<sub>2</sub> (9.0–19.3%). The inactive components of organic matter and refractory materials occupied significant parts of the precipitates, with their levels of 14.1–20.6% and 18.9–24.4%, respectively. It was noticeable that Cu and Zn in the collected solids were above the legal limits, suggesting that pretreatment methods were necessary to remove heavy metals from swine wastewater before struvite recovery.

*Keywords:* Struvite; Phosphorus recovery; Swine wastewater; Organic matter; Heavy metal

### 1. Introduction

Swine wastewater is characterized by high phosphate and ammonium contents, which has been regarded as an important source of nutrient recovery [1]. For instance, the discharge amounts of nitrogen and phosphorus from swine wastewater in China are more than 14 and 3 million tons per year, respectively [2], posing great potential for nutrient recovery. Recovering phosphorus from swine wastewater by struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O) crystallization has gained importance as a means of relieving water eutrophica-

tion and the scarcity of phosphorus rock resources [3]. The recovered product is preferred as a good fertilizer in agriculture for its slow release rate and much lower impurity level than other phosphate fertilizers [3].

Recently, stakeholders on nutrient recovery, including governments, researchers, and industrial communities, have agreed that constructing mature markets is important to sustain nutrient recovery, and the quality of recovered products can facilitate market development [4]. Although lots of works have been devoted on struvite recovery and achieved beneficial outcomes [5–7], most of the works focused on phosphate recovery efficiency and new recovering

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methods. Actually, swine wastewater is characterized by not only high concentrations of phosphate and ammonium but also high contents of organic matter, which may result in relatively high impurity in the recovered products. Besides, swine wastewater also contains various heavy metals, especially Cu and Zn, posing high risks to the final products. The presence of heavy metals in fertilizers is strictly regulated by governments [8,9] and excessive amounts can result in the recovered products banned for use in agriculture. Despite the benefits of struvite recovery from swine wastewater and the need to ensure a consistent product, it is necessary to conduct studies focusing on the quality evaluation of the recovered products, especially in terms of the organic matter and heavy metals.

Since  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  in swine wastewater are normally sufficient, an adequate amount of magnesium salts is required for effective struvite recovery. At present, there are four common industrial-grade (IG) magnesium salts on the markets, i.e.  $\text{MgSO}_4$ ,  $\text{MgCl}_2$ ,  $\text{MgO}$ , and  $\text{Mg(OH)}_2$ , which are suitable to be adopted as steady-supply and extensive magnesium sources. Although IG- $\text{MgSO}_4$  and IG- $\text{MgCl}_2$  are technically feasible for the treatment of high-strength wastewater [10,11], they are not adopted economically since they are six to nine times more expensive than IG- $\text{MgO}$  and IG- $\text{Mg(OH)}_2$ . Previous literature has reported that  $\text{MgO}$  and  $\text{Mg(OH)}_2$  can be successfully used in struvite precipitation [12,13] and can substitute sodium hydroxide to neutralize acids during the struvite precipitation reaction [14]. It should be noted that IG- $\text{MgO}$  or IG- $\text{Mg(OH)}_2$  contain a certain amount of refractory materials, which may give rise to the concern of recovered product purity and thereby reduce the recovering efficiency. Although some studies analyzed the compositions that might be formed in struvite precipitation when dosing pure  $\text{MgO}$  as a raw material, limited information is practical for the application of IG- $\text{MgO}$  and IG- $\text{Mg(OH)}_2$  since these studies only concerned the amount of struvite formed [7,13].

The objective of this study was therefore to investigate the compositions and heavy metals in the products of struvite recovered from swine wastewater, and IG- $\text{MgO}$  and IG- $\text{Mg(OH)}_2$  were applied as low-cost and sufficient magnesium sources for struvite crystallization. First, the compositions formed in the precipitates were analyzed and the effects of Mg/P molar ratio during both IG- $\text{MgO}$  and IG- $\text{Mg(OH)}_2$  additions were evaluated. Second, the effects of mixing time on the composition variation were examined. Finally, the assessment on heavy metals in the precipitates was conducted.

## 2. Materials and methods

### 2.1. Swine wastewater and magnesium sources

Swine wastewater was obtained from an anaerobic digester in an intensive pig farm operated by Yinxiang Group (Xiamen City, China). The supernatant was collected and screened by 0.5-mm mesh to remove large solids. The property of the anaerobically digested wastewater is presented in Table 1. The initial molar ratio of  $\text{PO}_4\text{-P}:\text{Mg}^{2+}:\text{NH}_4\text{-N}$  was 1.0:0.1:13.8, suggesting that magnesium sources were necessary for struvite precipitation.

IG- $\text{MgO}$  and IG- $\text{Mg(OH)}_2$  used as magnesium sources were produced by Laizhou Zhonghao Magnesium Co. Ltd. (Shandong Province, China). The initial prices of IG- $\text{MgO}$  and IG- $\text{Mg(OH)}_2$  were, respectively, 491 RMB/ton and 700 RMB/ton (1 US dollar equals to 6.23 RMB), much lower than the price of IG- $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (4,300 RMB/ton). The compositions in the solids and other physical parameters are presented in Table 2.

### 2.2. Experimental procedure

Batch experiments were performed in a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd, China) at the ambient temperature of 25°C. In each experiment, 400 mL of raw wastewater was firstly transferred into a 500-mL beaker with agitation at 400 rpm, and then a predetermined quantity of IG- $\text{MgO}$  or IG- $\text{Mg(OH)}_2$  was dosed into the beaker for struvite precipitation. The experiments concerning the influence of Mg/P on struvite precipitation were conducted for 6 h, by adding different amounts of IG- $\text{MgO}$  or IG- $\text{Mg(OH)}_2$  to keep the Mg/P molar ratio at 1.4, 1.9, 2.4, 2.8, 3.3, and 3.8, respectively. The investigation into the mixing time was carried out by fixing the Mg/P molar ratio

Table 1  
Initial compositions of swine wastewater

Parameter	Value
pH	7.87 ± 0.20
Total solids (mg/L)	2,481.20 ± 45.40
Suspended solids (mg/L)	1,757.10 ± 38.22
COD (mg/L)	994.50 ± 32.18
$\text{NH}_4^+\text{-N}$ (mg/L)	539.60 ± 4.35
$\text{Mg}^{2+}$ (mg/L)	8.41 ± 0.17
$\text{Ca}^{2+}$ (mg/L)	12.85 ± 0.03
$\text{PO}_4^{3-}\text{-P}$ (mg/L)	86.33 ± 0.81
$\text{NO}_3^-\text{-N}$ (mg/L)	6.31 ± 0.11
$\text{SO}_4^{2-}$ (mg/L)	142.42 ± 2.89
$\text{Cl}^-$ (mg/L)	82.43 ± 1.02

Table 2  
Property of IG-Mg and IG-Mg(OH)<sub>2</sub>

Parameter	IG-MgO	IG-Mg(OH) <sub>2</sub>
Mg-MgO (%)	77.6	52.2
Ca-CaO (%)	1.2	2.1
Al-Al <sub>2</sub> O <sub>3</sub> (%)	1.4	1.6
Fe-Fe <sub>2</sub> O <sub>3</sub> (%)	1.1	1.0
SiO <sub>2</sub> (%)	3.3	3.3
LOI* (%)	15.4	39.8
<i>d</i> <sub>100</sub> ** (μm)	440	611
<i>d</i> <sub>50</sub> (μm)	18	154
<i>d</i> <sub>10</sub> (μm)	3	5

\*LOI: Loss of ignition at 1,100°C.

\*\**d*<sub>x</sub>: accumulated fraction lower than particle size.

at 2.4, and the sampling time was set at 0.5, 0.75, 1, 1.5, 2, 3, 4, 6, 8, and 12 h, respectively. After the experiments, samples were withdrawn through 0.45-μm pore size membranes. The supernatant was used for chemical analysis and the precipitates were collected to dry at 40°C for solid phase assay.

### 2.3. Analytical methods

Wastewater analyses were performed according to standard methods [15]. Metal concentrations were analyzed by inductively coupled plasma mass spectrometry (7500 Cx ICP-MS, Agilent, USA). As to the precipitated solids, they were firstly examined with X-ray diffraction (X'Pert PROMPD, Holland) for crystalline analysis, and the diffractograms were analyzed by Crystallographica Search-Match version 2.1.0.2 (Oxford Cryosystems Ltd, UK). Afterwards, the samples were dissolved by 0.5% HNO<sub>3</sub>, following 0.45-μm membrane filtration. The supernatants were collected for PO<sub>4</sub>-P, NH<sub>4</sub>-N, Mg, and Ca determination, while the residual solids were collected and dried at 105°C for dry weight assay, and ignited at 600°C for refractory material determination. Organic matter in the solids was determined by dry weight minus refractory materials. To analyze heavy metals in the precipitates, solid samples were firstly digested at 120°C using H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> [16] and then the supernatants were subjected to 0.45-μm membrane filtration for ICP-MS assay.

## 3. Results and discussion

### 3.1. Effect of Mg/P molar ratio

Fig. 1 shows the relationship between PO<sub>4</sub><sup>3-</sup>-P removal efficiencies and Mg/P molar ratios in the experiments. A similar phosphate precipitation rate was observed when IG-MgO and IG-Mg(OH)<sub>2</sub> were

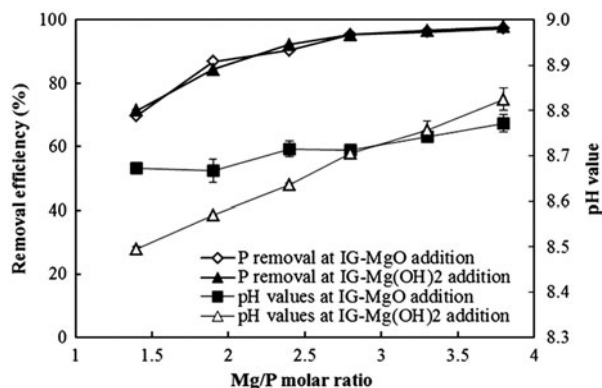


Fig. 1. Phosphorus removal efficiencies and pH variation at different Mg/P molar ratios under respective IG-MgO and IG-Mg(OH)<sub>2</sub> additions.

used. When adding IG-MgO or IG-Mg(OH)<sub>2</sub>, a Mg/P molar ratio of 1.4, 1.9, or 2.4 was corresponding to a recovery P efficiency of 70, 85, or 90%, respectively. A relatively stable PO<sub>4</sub><sup>3-</sup>-P removal of 95% was observed when Mg/P was above 2.8. The function between the Mg/P ratio and pH values was also depicted. It could be seen that pH values greater than 8 could be easily achieved. Otherwise, pH less than 9.0 was observed throughout the experimental runs. Considering the equilibrium solubility of Mg(OH)<sub>2</sub> at 10<sup>-11.1</sup> [14], the results indicated that excess Mg ions generated from struvite precipitation and thereafter inhibited the dissolution of MgO or Mg(OH)<sub>2</sub>.

The collected solid samples were subjected to X-ray diffraction to assay the minerals in the precipitates, and the diffractograms were analyzed by Crystallographica Search-Match version 2.1.0.2 (Oxford Cryosystems Ltd, UK). As presented in Fig. 2, struvite (standard card: PDF#15-0762) was identified as the main crystalline phase, as well as periclase (MgO) (standard card: PDF#01-087-0651). Quartz (SiO<sub>2</sub>) (standard card: PDF#01-087-2096) was also identified as minor phase present in the solids. The existence of MgO suggested that the initial IG-MgO or IG-Mg(OH)<sub>2</sub> was not totally dissolved, and the residual IG-MgO or IG-Mg(OH)<sub>2</sub> settled down and mixed with other precipitated components.

Table 3 presented the solid yields and contents of different compositions under different Mg/P molar ratios. Increasing Mg/P molar ratio resulted in the increase in the solid yield. Under similar Mg/P levels, a higher solid yield of 2.474–2.979 g/L during IG-Mg(OH)<sub>2</sub> addition was observed, while 2.420–2.840 g/L solids were produced during IG-MgO addition. In order to clarify the compositions formed and their corresponding concentrations in the collected precipi-

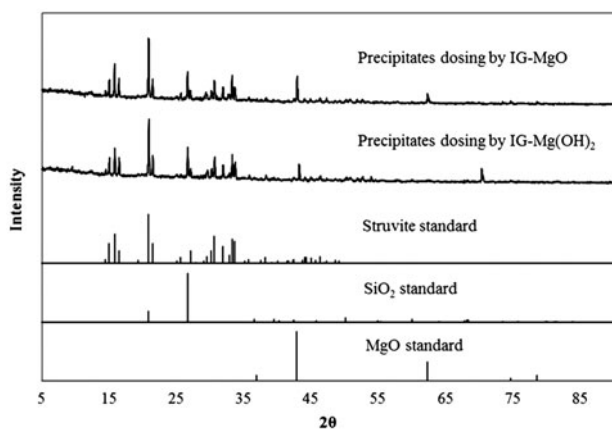


Fig. 2. X-ray diffractogram of the precipitates obtained under respective IG-MgO and IG-Mg(OH)<sub>2</sub> additions.

tates, mass balance analysis under various Mg/P molar ratios were carried out. The precipitated samples were firstly dissolved by 0.5% nitric acid and the mmol/L of ions in the solids and their corresponding molar ratios were calculated by the solution concentrations of Mg, N, P, and Ca, respectively. Besides minerals, other components, including organic matter and refractory materials, were determined by gravimetric analyses.

It should be noted that the precipitates contained high proportions of organic matter and refractory materials with their values of 14.1–20.6% and 18.9–24.4%, respectively, which consequently resulted in dramatic reductions in P and N contents in the precipitates. These inactive components were derived from magnesium sources and wastewater, including suspended solids (Table 1), SiO<sub>2</sub>, and LOI (Table 2), and they failed to dissolve and thus gave rise to impurities in the final precipitates. Through calculations, the available nutrient contents (N + P<sub>2</sub>O<sub>5</sub>) in the precipitates were approximately 17.2%, lower than the legal requirement of compound fertilizer (25.0%) [9]. From the results, pretreatment methods, such as flocculation or parameter optimization, are suggested to remove high suspended solids from wastewater before struvite recovery.

According to Çelen et al. [17] and Pastor et al. [18], the possible minerals precipitated in struvite recovery from swine wastewater are struvite, amorphous calcium phosphate (ACP, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O), and brucite (Mg(OH)<sub>2</sub>), which were also confirmed by our previous works [2]. As to brucite, it forms under highly alkaline conditions at pH above 10, indicating that the precipitated magnesium compounds in the present study were struvite and residual IG-Mg(OH)<sub>2</sub> or IG-MgO. Hence, the yields of struvite and ACP were

calculated by the molar masses of N and Ca in the solids and their contents in precipitated minerals were determined by the molar ratio of Mg:N:P:Ca, as per methods described by [2]. As shown in Table 3, the precipitant molar ratios of N:P:Ca were kept approximately at 1:1.3:0.5 in all runs, matching to relatively stable struvite and ACP percentages of 34.4–40.4% and 7.8–9.5%, respectively. A stable increase in Mg molar ratios from 1.5 to 2.4 implied that excessive Mg contents were contributed by residual IG-MgO or IG-Mg(OH)<sub>2</sub>.

Based on the above statement and experimental results originated from the composition analyses, struvite was the dominant mineral in the precipitates, mixing up with ACP and residual IG-MgO or IG-Mg(OH)<sub>2</sub>. The inactive components of organic matter and refractory materials occupied significant parts of the precipitates. In order to recover more than 90% phosphate from wastewater, the amount of Mg greater than Mg/P = 2.4 should be supplied by IG-MgO or IG-Mg(OH)<sub>2</sub>. As shown in Fig. 1 and Table 3, IG-MgO displayed a behavior similar to that of IG-Mg(OH)<sub>2</sub> in the struvite recovery process. Nevertheless, relatively high IG-Mg(OH)<sub>2</sub> residue and refractory materials were detected in the precipitates, compared to those provided by IG-MgO. This was due to low Mg contents and much more refractory components (Table 2); more IG-Mg(OH)<sub>2</sub> addition was necessary to ensure similar Mg/P levels, and therefore resulted in the increase in residual IG-Mg(OH)<sub>2</sub> and refractory materials in the collected solids.

### 3.2. Effect of mixing time

The effects of mixing time on composition variation in the collected solids were examined. Fig. 3 shows that dosing IG-MgO to remove 90% phosphate took 6 h, compared to 45 min during IG-Mg(OH)<sub>2</sub> addition. pH profiles revealed that IG-MgO had a buffer capacity so slower than that of IG-Mg(OH)<sub>2</sub> that it could not quickly enhance solution pH values for sufficient struvite precipitation. This was because the presence of MgO in struvite precipitation played a dual function, that is, hydrolyzing in solution to form Mg(OH)<sub>2</sub> and neutralizing H<sup>+</sup> to release Mg<sup>2+</sup> as magnesium source for struvite precipitation [19]. Due to the formation of struvite on the surface of IG-MgO particle instead of bulk solution [14,19], the dissolution of MgO was inhibited and thereby it displayed a slow reaction rate. For adding IG-Mg(OH)<sub>2</sub> runs, further increases in P removal efficiency was restricted in one hour, following a steady state till the end of the experiments. These results suggested that compared to

Table 3  
Minerals and compositions in the precipitates under different Mg/P molar ratios

Term	Main ions in the precipitates				Solid yield g/L wastewater	Minerals		Residual IG- MgO/Mg (OH) <sub>2</sub> (%)	Organic matters (%)	Refractory materials (%)				
	Molar ratio	mmol/g precipitated PO <sub>4</sub> -P	NH <sub>4</sub> -N	Mg Ca		molar ratio Mg:N:P:Ca	Precipitated minerals (%)				Struvite (%)	ACP* (%)		
IG-MgO	1.4	2.0	1.5	2.3	0.7	1.5:1:1.3:0.5	2.420 ± 0.033	58.9 ± 0.3	38.0 ± 0.0	8.2 ± 0.3	9.0 ± 0.9	19.3 ± 1.2	21.9 ± 1.5	
	1.9	2.1	1.6	2.5	0.7	1.6:1:1.3:0.4	2.610 ± 0.19	60.5 ± 0.5	38.6 ± 0.3	8.0 ± 0.2	10.0 ± 1.0	20.6 ± 0.0	18.9 ± 0.0	
	2.4	2.1	1.6	2.7	0.7	1.7:1:1.3:0.4	2.597 ± 0.033	61.5 ± 0.8	40.4 ± 1.3	7.8 ± 0.8	10.9 ± 0.5	18.2 ± 1.7	20.1 ± 1.9	
	2.8	2.1	1.6	2.9	0.7	1.8:1:1.3:0.4	2.668 ± 0.043	61.3 ± 0.1	39.5 ± 0.1	8.2 ± 0.6	11.5 ± 0.7	18.2 ± 0.0	20.6 ± 0.0	
	3.3	2.1	1.6	3.1	0.7	2.0:1:1.3:0.5	2.698 ± 0.024	61.4 ± 0.3	38.8 ± 0.1	8.2 ± 0.4	12.6 ± 0.8	18.6 ± 0.5	19.9 ± 0.6	
	3.8	2.0	1.5	3.4	0.7	2.2:1:1.3:0.4	2.840 ± 0.021	61.4 ± 0.5	37.7 ± 0.5	7.9 ± 0.7	13.7 ± 0.9	17.2 ± 0.7	21.3 ± 0.7	
	IG-Mg (OH) <sub>2</sub>	1.4	2.0	1.5	2.2	0.8	1.5:1:1.3:0.5	2.474 ± 0.019	58.8 ± 0.3	36.9 ± 0.5	9.5 ± 0.3	12.8 ± 1.1	17.2 ± 0.1	23.9 ± 0.1
		1.9	2.1	1.5	2.5	0.8	1.6:1:1.3:0.5	2.578 ± 0.017	60.5 ± 0.6	38.0 ± 1.1	9.5 ± 0.6	14.4 ± 1.2	17.5 ± 0.3	22.0 ± 0.5
2.4		2.1	1.5	2.7	0.8	1.8:1:1.3:0.5	2.647 ± 0.060	61.5 ± 0.4	39.0 ± 0.9	9.2 ± 0.9	15.7 ± 1.3	17.1 ± 0.6	21.4 ± 0.7	
2.8		2.0	1.5	3.0	0.8	2.0:1:1.4:0.5	2.790 ± 0.003	60.9 ± 0.9	36.5 ± 0.1	8.9 ± 0.9	17.4 ± 0.7	16.3 ± 1.0	22.8 ± 1.1	
3.3	2.0	1.5	3.2	0.8	2.2:1:1.4:0.5	2.854 ± 0.029	61.5 ± 0.7	35.9 ± 0.4	9.2 ± 0.8	18.6 ± 0.6	14.1 ± 0.6	24.4 ± 0.7		
3.8	1.9	1.4	3.3	0.8	2.4:1:1.4:0.5	2.979 ± 0.006	61.4 ± 0.3	34.4 ± 0.3	8.9 ± 0.7	19.3 ± 1.0	14.6 ± 0.7	24.0 ± 0.7		

\*ACP: Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O.

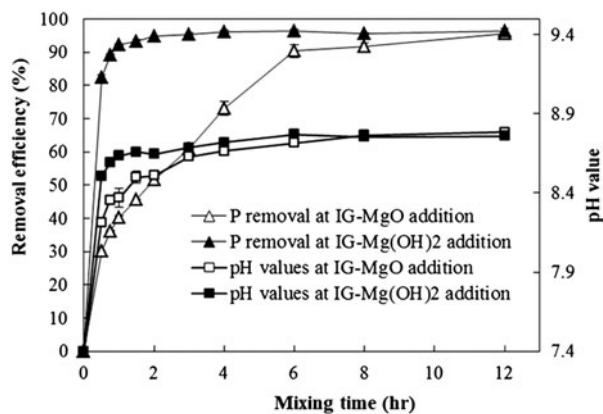


Fig. 3. Phosphorus removal efficiency and pH variation according to mixing time under respective IG-MgO and IG-Mg(OH)<sub>2</sub> additions.

IG-Mg(OH)<sub>2</sub>, IG-MgO displayed a more slower capability for struvite recovery from wastewater.

Since the solids precipitated were mainly struvite, ACP, residual IG-MgO/IG-Mg(OH)<sub>2</sub>, organic matter, and refractory materials, the variations of their contents in the experiments were examined, as shown in Figs. 4 and 5. It was observed that the presence of IG-MgO and IG-Mg(OH)<sub>2</sub> gave rise to the formation of struvite and ACP, and the aggregation of organic matter. All the components except struvite increased quickly to a significant extent (within 30 min), and stayed steady till the end of the experiments. As to struvite, dosing MgO into the wastewater resulted in a quick increase to 30% in less than 30 min, following a steady increase to 43.5% till the end of the experiment (Fig. 4). The sluggish behavior of struvite formation, similar to the profiles of P removal efficiency and

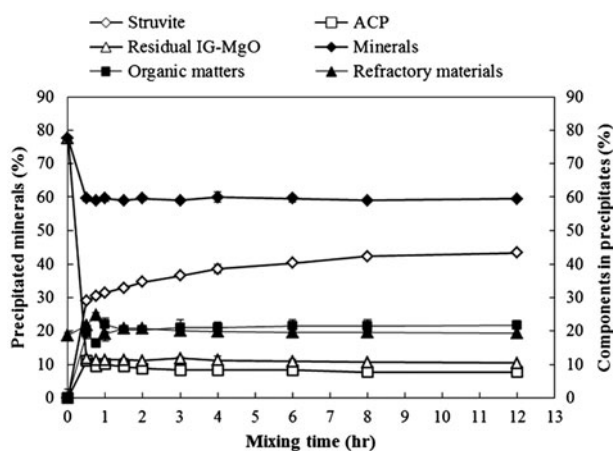


Fig. 4. Compositions in the collected precipitates under IG-MgO addition.

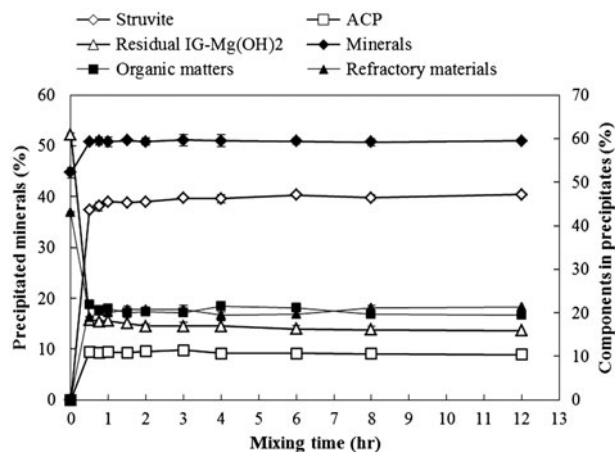


Fig. 5. Compositions in the collected precipitates under IG-Mg(OH)<sub>2</sub> addition.

pH variation (Fig. 3), was due to struvite precipitating on MgO particles and thereby inhibiting MgO dissolution [19,20]. In contrast, struvite contents in dosing IG-Mg(OH)<sub>2</sub> runs rose quickly to 37.3% in 30 min (Fig. 5) and kept unchanged till the end of the experiments. These results revealed that mixing time had insignificant impacts on struvite formation in the course of IG-Mg(OH)<sub>2</sub> addition, while sufficient mixing time was required when using IG-MgO as magnesium source.

### 3.3. Heavy metals

Heavy metals are a concern in struvite recovery and are thus seen as a potential hazard. Heavy metal contents in wastewater and the precipitated products during the experiments are displayed in Table 4, with a comparison to those levels required by the Chinese discharge standards. In all the observations, high levels of Fe in wastewater and magnesium sources were detected. Since the presence of Fe was able to form insoluble phosphate compounds [14,21], this could be the main reason for the presence of solids containing relatively high levels of Fe with the concentration of approximately 7.0 mg/g. Cu and Zn in the precipitates were significantly high on the basis of the present ruling standard, with their concentrations of approximately 800 µg/g and 5,000 µg/g, respectively. Other heavy metals in the collected precipitates were regularly controlled, with their contents lower or substantially lower than the ruling standards of chemical fertilizer in China.

Zinc oxide (ZnO) and copper sulfate (CuSO<sub>4</sub>) are commonly used as growth promoters in intensive swine farming [22]. However, the high rate of their

Table 4  
Concentrations of heavy metals in wastewater, raw IG-MgO and IG-Mg(OH)<sub>2</sub>, and the precipitates produced at a Mg/P molar ratio of 2.4

Item	Wastewater (μg/mL)	IG-MgO (μg/g)	Precipitates produced by IG-MgO addition		Precipitates produced by IG-Mg(OH) <sub>2</sub> addition		Standard on chemical fertilizer <sup>a</sup> (μg/g)
			(μg/g)	(μg/g)	(μg/g)	(μg/g)	
Cr	0.038 ± 0.003	11.60 ± 0.46	10.45 ± 2.49	11.56 ± 0.32	5.45 ± 0.28	500	
As	0.0111 ± 0.0004	N.D.	2.45 ± 0.02	N.D.	2.02 ± 0.07	50	
Cd	0.0020 ± 0.0003	0.01 ± 0.00	0.35 ± 0.01	N.D.	0.33 ± 0.01	10	
Pb	0.021 ± 0.002	0.35 ± 0.04	7.16 ± 0.51	0.53 ± 0.01	7.66 ± 0.09	200	
Co	0.017 ± 0.001	0.84 ± 0.02	2.86 ± 0.11	1.19 ± 0.18	2.67 ± 0.05	N.R.	
Ni	N.D. <sup>a</sup>	6.50 ± 0.21	10.68 ± 0.52	12.76 ± 3.40	9.10 ± 0.21	N.R.	
V	0.044 ± 0.002	7.61 ± 0.14	10.13 ± 0.00	7.00 ± 0.08	9.88 ± 1.03	40	
Fe	20.86 ± 0.16	7,440 ± 90	7,005 ± 0	6,950 ± 10	6,922 ± 608	N.R.	
Cu	2.36 ± 0.09	N.D.	804 ± 15	N.D.	780 ± 1	35	
Zn	11.93 ± 0.42	N.D.	5,039 ± 60	N.D.	4,936 ± 127	100	

Notes: N.D.— undetected; N.R.— not required.

<sup>a</sup>The standard levels are required on the basis of Chinese national standard of "Ecological index of arsenic, cadmium, lead, chromium and mercury for fertilizers (GB/T 23349-2009)".

excretion through feces and urine has led to interest in the potential of organic minerals and gives rise to environmental problems and public concerns [23]. Previous research has confirmed that struvite crystals retrieved from swine wastewater contained very low levels of heavy metals that were far below the legal limits [24–26]. Nevertheless, in this study, the contents of Cu and Zn were significantly high in the collected solids. Considering the absence of Cu and Zn in IG-MgO and IG-Mg(OH)<sub>2</sub> but its presence in sufficient quantities in swine wastewater (Table 4), it was conclusive that the presence of Cu and Zn in the collected solids originated from swine wastewater. It has been reported that the major fraction of Cu and Zn in wastewater is easily complex to organic colloids and can be removed as sludge by precipitation [27], which may be coupled with struvite precipitation in wastewater. These results indicated that Cu and Zn contamination in recovered products is of concern if wastewater contained high concentrations of organic compounds. Therefore, there is a need to develop pretreatment methods, such as coagulation and flotation, to remove organic compounds before struvite recovery. Such pretreatment methods could not only remove organic compounds, Cu and Zn effectively, but also enhance struvite contents in the final products.

#### 4. Conclusions

In this study, struvite recovery from swine wastewater was investigated by dosing IG-MgO and IG-Mg(OH)<sub>2</sub> as the low-cost magnesium sources, and the compositions and heavy metals in the recovered products were analyzed. Experimental results revealed that struvite was the dominant mineral in the precipitates, mixing up with ACP and residual IG-MgO or IG-Mg(OH)<sub>2</sub>. The inactive components of organic matter and refractory materials occupied a significant portion of the precipitates, with their levels of 14.1–20.6% and 18.9–24.4%, respectively. Mixing time had insignificant effects on struvite formation during IG-Mg(OH)<sub>2</sub> addition, while sufficient mixing time was required when using IG-MgO as the magnesium source. Cu and Zn contamination in the recovered products is of concern if swine wastewater contained high concentrations of organic compounds. Pretreatment methods to remove organic compounds from wastewater were suggested so as to avoid Cu and Zn contamination and enhance struvite contents in the final products.

#### Acknowledgements

The work was supported by the Chinese Hi-Tech Research and Development Program (863) (No.

2011AA060902), the Xiamen Science and Technology Planning Project (No. 3502Z20132016) and the Chinese National Key Technology Support Program (No. 2012BAJ21B07).

#### References

- [1] Y. Song, Y. Dai, Q. Hu, X. Yu, F. Qian, Effects of three kinds of organic acids on phosphorus recovery by magnesium ammonium phosphate (MAP) crystallization from synthetic swine wastewater, *Chemosphere* 101 (2014) 41–48.
- [2] Z. Ye, S. Chen, M. Lu, J. Shi, L. Lin, S. Wang, Recovering phosphorus as struvite from the digested swine wastewater with bitter as a magnesium source, *Water Sci. Technol.* 64 (2011) 334–340.
- [3] Z. Ye, Y. Shen, X. Ye, Z. Zhang, S. Chen, J. Shi, Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates, *J. Environ. Sci.* 26 (2014) 991–1000.
- [4] European Sustainable Phosphorus Platform (ESPP), *Scope Newsletter* 104, 2014.
- [5] L. Qiu, G. Wang, S. Zhang, K. Huang, Phosphate removal through crystallization using hydrothermal modified steel slag-based material as seed crystal, *Desalin. Water Treat.* 52 (2014) 384–389.
- [6] L. Ouchah, L. Mandi, F. Berrekhis, N. Ouazzani, Essays of phosphorus recovery into struvite from fertilizer industry effluents, *Desalin. Water Treat.* 52 (2014) 2886–2892.
- [7] J. Bohdziewicz, M. Kuglarz, Treatment of post-digestion liquors with the application of struvite precipitation and reverse osmosis, *Desalin. Water Treat.* 51 (2013) 366–373.
- [8] European Parliament and European Council, Regulation (EC) No 2003/2003 of the European Parliament and of the Council, 2003. Available from: <<http://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:02003R2003-20140607&rid=1>>.
- [9] General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (GAQSIQ), Standardization Administration of the People's Republic of China (SAPRC), Compound fertilizer (Complex fertilizer)(GB 15063-2009), 2009.
- [10] A.L. Forrest, K.P. Fattah, D.S. Mavinic, F.A. Koch, Optimizing struvite production for phosphate recovery in WWTP, *J. Environ. Eng.* 134 (2008) 395–402.
- [11] Y. Liu, S. Kumar, J. Kwag, C. Ra, Magnesium ammonium phosphate formation, recovery and its application as valuable resources: A review, *J. Chem. Technol. Biotechnol.* 88 (2013) 181–189.
- [12] M. Carballa, W. Moerman, W. De Windt, H. Grootaerd, W. Verstraete, Strategies to optimize phosphate removal from industrial anaerobic effluents by magnesium ammonium phosphate (MAP) production, *J. Chem. Technol. Biotechnol.* 84 (2009) 63–68.
- [13] C. Di Iaconi, M. Pagano, R. Ramadori, A. Lopez, Nitrogen recovery from a stabilized municipal landfill leachate, *Bioresour. Technol.* 101 (2010) 1732–1736.
- [14] J.M. Chimenos, A.I. Fernández, G. Villalba, M. Segarra, A. Urruticoechea, B. Artaza, F. Espiell, Removal of ammonium and phosphates from



- wastewater resulting from the process of cochineal extraction using MgO-containing by-product, *Water Res.* 37 (2003) 1601–1607.
- [15] American Public Health Association (APHA), *Standard Methods for the Examination of Water and Wastewater*, twentieth ed., American Public Health Association/Water Pollution Control Federation, Washington, DC, 1998.
- [16] P.N. Williams, M. Lei, G.X. Sun, Q. Huang, Y. Lu, C. Deacon, A.A. Meharg, Y.G. Zhu, Occurrence and partitioning of cadmium, arsenic and lead in mine impacted paddy rice: Hunan, China, *Environ. Sci. Technol.* 43 (2009) 637–642.
- [17] I. Çelen, J.R. Buchanan, R.T. Burns, R.B. Robinson, D.R. Raman, Using a chemical equilibrium model to predict amendments required to precipitate phosphorous as struvite in liquid swine manure, *Water Res.* 41 (2007) 1689–1696.
- [18] L. Pastor, D. Mangin, J. Ferrer, A. Seco, Struvite formation from the supernatants of an anaerobic digestion pilot plant, *Bioresour. Technol.* 101 (2010) 118–125.
- [19] H. Huang, C. Xu, W. Zhang, Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology, *Bioresour. Technol.* 102 (2011) 2523–2528.
- [20] T. Chen, X. Huang, M. Pan, S. Jin, S. Peng, P. Fallgren, Treatment of coking wastewater by using manganese and magnesium ores, *J. Hazard. Mater.* 168 (2009) 843–847.
- [21] A. Uysal, B. Kuru, Magnesium ammonium phosphate production from wastewater through Box-Behnken design and its effect on nutrient element uptake in plants, *CLEAN– Soil Air Water* 41 (2013) 447–454.
- [22] G.B. Salyer, M.L. Galyean, P.J. Defoor, G.A. Nunnery, C.H. Parsons, J.D. Rivera, Effects of copper and zinc source on performance and humoral immune response of newly received, lightweight beef heifers, *J. Anim. Sci.* 82 (2004) 2467–2473.
- [23] P. Tulayakul, A. Boonsoongnern, S. Kasemsuwan, S. Wiriyarampa, J. Pankumnoed, S. Tippayaluck, H. Hananantachai, R. Mingkhwan, R. Netvichian, S. Khaodhiar, Comparative study of heavy metal and pathogenic bacterial contamination in sludge and manure in biogas and non-biogas swine farms, *J. Environ. Sci.* 23 (2011) 991–997.
- [24] Y.H. Liu, J.H. Kwag, J.H. Kim, C.S. Ra, Recovery of nitrogen and phosphorus by struvite crystallization from swine wastewater, *Desalination* 277 (2011) 364–369.
- [25] K. Guney, A. Weideler, J. Krampe, Phosphorus recovery from digested sewage sludge as MAP by the help of metal ion separation, *Water Res.* 42 (2008) 4692–4698.
- [26] M.M. Rahman, M.A.M. Salleh, A. Ahsan, U. Rashid, M.M. Hossain, C.S. Ra, Production of slow release crystal fertilizer from wastewaters through struvite crystallization—A review, *Arab. J. Chem.* 7 (2014) 139–155.
- [27] M. Baalousha, B. Stolpe, J.R. Lead, Flow field-flow fractionation for the analysis and characterization of natural colloids and manufactured nanoparticles in environmental systems: A critical review, *J. Chromatogr. A* 1218 (2011) 4078–4103.