Study on the mechanism of copper–ammonia complex decomposition in struvite formation process and enhanced ammonia and copper removal

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Abstract
Heavy metals and ammonia are difficult to remove from wastewater, as they easily combine into refractory complexes. The struvite formation method (SFM) was applied for the complex decomposition and simultaneous removal of heavy metal and ammonia. The results indicated that ammonia deprivation by SFM was the key factor leading to the decomposition of the copper–ammonia complex ion. Ammonia was separated from solution as crystalline struvite, and the copper mainly co-precipitated as copper hydroxide together with struvite. Hydrogen bonding and electrostatic attraction were considered to be the main surface interactions between struvite and copper hydroxide. Hydrogen bonding was concluded to be the key factor leading to the co-precipitation. In addition, incorporation of copper ions into the struvite crystal also occurred during the treatment process.

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Introduction
Large discharges of heavy metal-ammonia complexes may occur from many sources including landfill leachate, hydrometallurgy, mining, electroplating, and printed circuit board (PCB) manufacturing (Kim et al., 2011; Sun et al., 2015; Xie et al., 2015; Xiao et al., 2015b). For example, NH3-N and heavy metals can be widely found in different landfill leachates (Battistoni et al., 2006; Primo et al., 2015; Xiao et al., 2015b). In the hydrometallurgy field, copper can be effectively extracted by ammonia solution (Xiao et al., 2013), thus generating effluent containing copper–ammonia complexes. Ammonium oxalate ([NH4]2C2O4) solution is frequently used to precipitate cobalt ions as CoC2O4·2H2O (Chen et al., 2015), which also leads to production of a cobalt–ammonia complex solution. For the treatment of industrial effluent containing heavy metals, some traditional methods such as hydroxide precipitation (Chen et al., 2009), sulfide precipitation (Qin et al., 2012; Su et al., 2015) and electrolytic methods are utilized (Qian et al., 2014). These methods are feasible in removal of heavy metals from wastewater, but they are not effective for heavy metal-ammonia complexes, since the complex ions are quite stable in solution and are hard to decompose (Fu et al., 2015; Kawahara et al., 2010; Orabi and Lamoureux, 2013; Xiao et al., 2015a). Neither the heavy metal nor the ammonia can be removed by the conventional hydroxide precipitation method. For sulfide precipitation, the ammonia removal is not satisfactory, although heavy metal removal is efficient (Peng et al., 2016). Then the need for an
additional nitrogen removal process is inevitable, which leads to high cost. Furthermore, the electrolytic method is also not very effective for ammonia removal, and requires a long time and high energy cost. Thus the traditional methods for the removal of heavy metals are not feasible for heavy metal-ammonia complex wastewater. Although biological methods have been widely used for removal of ammonia nitrogen, they are not feasible for heavy metal-ammonia wastewater treatment since heavy metals can cause severe inhibition of bacteria (Feng et al., 2013). For example, Sarker et al. reported that the activities of ammonia-oxidizing bacteria and anaerobic ammonia-oxidizing bacteria were severely inhibited when the copper concentration reached 0.25 mg/L (Sarker et al., 2015). Therefore, it is a great challenge for the traditional processes to treat heavy metal-ammonia complexes. The development of novel and efficient technologies for simultaneous removal of heavy metals and ammonia from wastewater is urgently required.

The struvite formation method (SFM) has been widely used for treatment of ammonia-rich wastewater (Stolzenburg et al., 2015; Triger et al., 2012), and for the recovery of phosphorus from solutions (Hartke et al., 2015; Hao et al., 2013; Zhang et al., 2013). As a source of plentiful Mg, N and P, struvite has been considered as a potential fertilizer that could be further used in agricultural activities (Desmidt et al., 2013). These studies and practical cases provide clues for the treatment of heavy metal-ammonia complexes. First of all, the SFM might be able to deprive the heavy metal-ammonia complex ions of ammonia, and to form crystalline struvite with extremely low solubility ($K_{sp} = 10^{-13.26}$). Moreover, the heavy metal might be dissociated from the complex ions after being deprived of ammonia. So the SFM could use the ammonia to form struvite, thus decomposing the heavy metal-ammonia complex ions. Once decomposition occurs, the free metal ions can be released. As reported, struvite has the potential to interact with heavy metal ions including zinc, chromium and arsenic, resulting in favorable heavy metal removal efficiencies (Rouff, 2012; Rouff and Juarez, 2014). These works introduced the possibility of removing ammonia and heavy metal from complex wastewater by SFM. The ammonia can be initially removed from the solution by forming struvite precipitate, and then the heavy metal could be precipitated simultaneously by interacting with the newly-generated struvite.

In order to clarify the feasibility of the SFM process for separation of heavy metals and ammonia from solution, decomposition of the metal-ammonia complex and co-precipitation of struvite and heavy metal are two main aspects that need to be investigated intensively. So far there is no analysis relevant to the decomposition of heavy metal-ammonia complex ions by SFM, and also no report on the specific surface interaction between heavy metal hydroxides and struvite, which might provide powerful insight into the co-precipitation of struvite and heavy metals.

Accordingly, four groups of experiments with different copper contents were implemented in the present study to investigate the mechanisms related to SFM. Changes in the solid and solution before and after SFM treatment were carefully compared and analyzed. A possible explanation for co-precipitation during the SFM process was proposed, which could be used as guidance for the application of this novel technology in metal recovery and ammonia removal from polluted water.

1. Materials and methods

1.1. Materials

The copper-ammonia complex, which is frequently generated in real industrial effluent, was selected as a representative of heavy metal-ammonia complex ions.

All the reagents were of analytical grade and were used without further purification. Ultrapure water (18 MΩ resistance) was used in all experiments. Concentrated sulfuric acid (H2SO4), ammonium sulfate ((NH4)2SO4), magnesium chloride hexahydrate (MgCl2·6H2O), disodium hydrogen phosphate (Na2HPO4), copper sulfate (CuSO4), and sodium hydroxide (NaOH) were purchased from the Sinopharm Group Chemical Reagent Co., Ltd.

The copper-ammonia complex solution was prepared by mixing copper sulfate and ammonium sulfate. The concentrations of ammonia and copper selected in this study are widely seen in PCB manufacturing enterprises and in industrial parks in China. The ammonia concentration was maintained at 1000 mg/L for each sample, and the copper content of the four samples was controlled at 200, 400, 600, and 800 mg/L, respectively (referred to hereafter as copper1, copper2, copper3 and copper4, respectively).

1.2. Analyzing methods

The concentration of ammonium nitrogen was measured according to the Phenol Method in Standard Methods (APHA, 1998). The concentration of copper was measured by inductively coupled plasma spectroscopy (ICP-AES, IRIS Intrepid II XSP). The pH value was measured by a Mettler FE20K pH meter.

The Ultraviolet-visible spectroscopy (UV–vis) spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fourier transform infrared spectroscopy (FT-IR) of the precipitate samples was collected via Nicolet IS10 infrared spectrometer in the range of 4000–400 cm⁻¹ with resolution of 4 cm⁻¹. X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max-RB diffractometer with Cu-Kα radiation (40 kV, 40 mA), from 10° to 60° (2θ). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Fisher Scientific K-Alpha 1063 using Al-Kα radiation as the excitation source, with the analysis chamber ≤10⁻¹⁰ Torr. A FEI Quanta 650 FEG Scanning electron microscope (SEM) was used to characterize the morphology of the precipitates, with accelerating voltage of 20 kV. Energy-dispersive spectrum (EDS) spectra were also collected on the FEI Quanta 650 FEG Scanning electron microscope equipped with an energy-dispersive X-ray spectrometer. The particle size distribution (PSD) of all samples was determined using a Mastersizer 2000 laser particle analyzer (Malvern Instruments Ltd., UK). Photo images were collected using a camera (Canon EOS 600D). Zeta potential measurements were performed with a Malvern Zetasizer Nano ZS90 instrument using graphite electrodes. The turbidity was measured by a Universal TU100 + SS90-100 Turbidity...
1.3. Experimental procedures

1.3.1. Performance evaluation under different pH and Cu/N ratios

In the performance investigations, the MgCl₂ and Na₂HPO₄ agents were introduced into copper–ammonia wastewater by a peristaltic pump, with flow rate of 10 mL/min. The whole experiment was conducted at 25°C. The pH value was controlled in real time through addition of NaOH or H₂SO₄ solution. Different pH values from 6.0 to 11.0 were adopted to investigate the effect of pH on the removal efficiency. The system was stirred by a magnetic stirrer with a speed of 300 r/min. In these experiments, the addition of Mg and P sources for each sample was controlled according to the molar ratio of n(Mg):n(N):n(P) = 1:2:1.2:1. The reaction time was controlled at 20 min for each experiment. Then, the samples were filtered with 3 μm pore size filter paper and the solution was stored in a sample vial. The solids were washed by ion-free water several times to remove residual solution, and then were dried in a vacuum freeze drier (LGJ-10F, Beijing Songyuan Technology, China) for 6 hr. Finally, the copper and ammonia concentrations in the solutions were measured. The solids collected from copper1 to copper4 at pH 9.0 (the best pH value for struvite formation) were analyzed by FT-IR, SEM, XRD, and EDS.

For UV–vis comparison, copper–ammonia complex sample copper1, as a representative, was adopted for UV–vis measurements. It was adjusted to different pH values from 5.0 to 10.0 for comparison of UV–vis spectra, in order to identify the copper–ammonia species present under different pH conditions. After treatment by SFM, the solution of copper1 was also measured by UV–vis.

1.3.2. Assessment of sole addition of Mg²⁺ and PO₄³⁻

In order to clarify the reason for the decomposition of copper–ammonia complex ions, additions of Mg²⁺ and PO₄³⁻ alone were also considered. The separate effects of Mg and P sources on copper and ammonia removal were compared by addition of only MgCl₂ or Na₂HPO₄ into the sample copper1 respectively. The addition of Mg or P sources was in accordance with molar ratios of n(Mg):n(N) or n(P): n(N) ranging from 1:1 to 5:1.

After treatment, the precipitates were also filtered with a 3-μm pore size filter paper, and then were collected and washed with deionized water at least 3 times to remove ions possibly remaining in the solids. The supernatant was collected for subsequent UV–vis measurements. The precipitates were dried in freeze-dryer for 6 hr, and kept for further analysis (XRD, XPS, SEM, EDS, FT-IR, and PSD).

1.3.3. Electrostatic attraction evaluation

In order to obtain the electrostatic properties of struvite and copper hydroxide during the SFM process, Zeta potential (ζ) was determined by the dynamic light scattering technique, where the electrophoretic mobility of the particles gives ζ values using the Smoluchowski equation. The zeta potential measurements were carried out on struvite, struvite & copper hydroxide particles obtained during the SFM process, and copper hydroxide. The MgCl₂ and Na₂HPO₄ were added simultaneously, and ζ values were measured 2 min after addition. For the zeta potential measurement of copper hydroxide, the value was recorded at pH ranging from 7.0 to 12.0. The zeta potential of struvite corresponding to n(N):n(Mg):n(P) = 1:1.2:1.2 (ratio selected for copper and ammonia removal in this study) was negative, so it had an electrostatic attraction with the positively charged copper hydroxide. But if a large quantity of residual Mg²⁺ ions existed in the solution, ζ for struvite might reach positive values. Because struvite consists of Mg²⁺ and PO₄³⁻ ions, surplus Mg²⁺ or PO₄³⁻ would be spread over surface of struvite and render it positively charged or negatively charged, respectively. So it is essential to take surplus Mg²⁺ into consideration, because its presence can turn electrostatic attraction into electrostatic repulsion. Thus, zeta potential measurements of struvite were carried out considering different additions of MgCl₂ under fixed Na₂HPO₄ addition. The molar ratio of Mg/N was varied from 1.0 to 1.6. The zeta potential measurement of copper hydroxide was conducted by adding NaOH into copper sulfate solutions (without ammonia) with copper concentrations of 200, 400, 600 and 800 mg/L respectively. In addition, an experiment was carried out by adding Na₂HPO₄ into the copper hydroxide system (copper concentration 400 mg/L), considering that phosphate might be able to weaken the double layer of copper hydroxide colloids. The phosphate additions were 50, 100, 150, and 200 mg/L, respectively. The solutions were added into copper sulfate solution (copper 400 mg/L) and pH was adjusted to 9.0 in all cases, and afterwards the samples were used for zeta potential measurements.

In order to characterize the removal performance of co-precipitation of struvite and copper hydroxide, turbidity was measured for the samples from copper1 to copper4 after treatment by SFM under different Mg/N ratios from 1.0 to 1.6, and turbidity was also measured for the precipitation of copper hydroxide alone. The samples were left to stand for 10 min after reaction, and the supernatants (without any filtration) were collected for the turbidity measurements.

2. Results

2.1. Performance at different pH and Cu/N ratios

Fig. 1 shows the performance of SFM in removal of copper and ammonia over the pH range of 6–11. pH had a great impact on the removal efficiency of ammonia and copper. For copper concentrations from 200 to 800 mg/L (copper1 to copper4), the residual contents of both copper and ammonia decreased as pH increased from 6.0 to 9.0, and afterwards increased as pH further increased. It can be deduced that alkaline conditions were favorable for the removal of copper and ammonia compared to acidic conditions. For example, the ammonia concentrations at pH 6.0 were 200.9, 205.3, 198.2 and 194.0 mg/L for samples from copper1 to copper4 respectively, but they were 39.1, 38.3, 36.2 and 33.7 mg/L respectively, at pH 11.0 (Fig. 1b). The best pH value for all samples investigated was 9.0. For example, the residual copper concentration was reduced to 0.08 mg/L, and the ammonia...
content was merely 4.8 mg/L, for copper1 (Fig. 1a). The residual copper increased from copper1 to copper4, where the molar ratio of Cu/N increased from 1.0:22.7 to 4.0:22.7. In particular, at the optimal pH value (9.0), the residual copper contents were 0.08 mg/L, 0.6 mg/L, 1.9 mg/L, and 7.3 mg/L for copper1 to copper4, respectively. However, the residual ammonia at pH 9.0 showed no significant difference from copper1 to copper4. It is interesting to see that the residual copper for sample copper4 was markedly higher than for the other three samples. The copper content was much higher than the level regulated in the discharge standard. Thus further increasing the copper content was not applied in this study.

2.2. UV–vis comparison before and after treatment

The UV–vis spectra of solutions before and after treatment by SFM are compared in Fig. 2. For the untreated solution (copper1) with copper and ammonia concentrations of 200 and 1000 mg/L, respectively, the UV–vis spectra at different pH values from 5.0 to 10.0 were measured. The synthetic wastewater showed a peak at 620 nm for pH varying from 7.0 to 10.0, which was attributed to the complex ion [Cu(NH$_3$)$_4$]$^{2+}$ in the solution (Haram et al., 1996); whereas, at pH values from 5.0 to 6.0, a peak appeared at 660 nm, which was assigned to the complex ion [Cu(NH$_3$)$_3$]$^{2+}$ (Haram et al., 1996; Arenas et al., 2007). The results were in accordance with the fact that copper–ammonia complex ions tend to form under alkaline conditions, and the coordination number (x) in the copper–ammonia ions [Cu(NH$_3$)$_x$]$^{2+}$ increases as pH increases, where the complex ions would be more stable. The transformation of copper1, copper2, copper3, and copper4 solutions before and after treatment is shown in Fig. 2b. The solution became darker blue as the copper concentration increased. It was also obvious that the dark blue copper–ammonia complex solution turned clear and colorless after SFM, which was in accordance with the UV–vis spectra, where no significant peak appeared. This was the direct proof of the decomposition of copper–ammonia complexes by SFM.

Fig. 1 – Performance of struvite formation process under different conditions. (a) residual copper concentration; (b) residual ammonia concentration.

Fig. 2 – The solution characteristics before and after struvite formation method (SFM). (a) Ultraviolet-visible spectroscopy (UV–vis) spectra of copper1 at different pH, (b) pictures of SFM treatment with different copper concentrations.
2.3. Precipitate characterization

2.3.1. SEM observation
After SFM treatment, the surface morphologies of the precipitates from the four solution samples with different Cu/N ratios (copper1 to copper4) could be clearly observed by SEM (Figs. 3 and 4). As seen in Fig. 4, there were prism-shaped particles surrounded by small irregular particles. By virtue of EDS measurements, it was clear that the regular prism-shaped particles had quite low content of Cu but high content of Mg and P, while the small particles attached on surface of the prism-shaped particles had a prominent peak attributed to copper. Therefore it can be deduced that the big prism-shaped particles were probably struvite, while the small particles on the surface were from a copper compound, probably the copper hydroxide, given the alkaline conditions of the experiment, which was further confirmed by subsequent XPS and XRD analysis.

It is interesting that the copper precipitates (most probably copper hydroxide) were closely attached to the surface of struvite. Moreover, more copper precipitate particles were found on the surface of struvite as the Cu/N ratio increased. It seemed that the copper precipitates had adhered to struvite. Actually, the quantity of struvite formed was relatively equivalent for the 4 samples, as the ammonia concentration and the addition of Mg and P remained the same for all experiments. But the newly-generated fine copper precipitates increased as Cu/N increased, which was also confirmed by the increase in the amount of precipitates at higher copper content (Fig. 2b). Correspondingly, the bare surface of struvite might tend to be reduced or even saturated when the number of fine copper precipitates increased, which might reduce the ability of struvite to adhere to copper particles. This could be confirmed by the relatively lower copper removal of copper4 with the high Cu/N ratio of 4:22.7, as aforementioned (Fig. 1a).

2.3.2. XPS analysis
The XPS spectra taken from the precipitates of the SFM process are shown in Fig. 5. It is clear that the samples from precipitates of copper1 to copper4 had clear peaks due to copper between 930 and 965 eV (Fig. 5a). The Cu 2p spectra (Fig. 5c) showed typical peaks of divalent copper (Godoi et al., 2013; Lv et al., 2013). Based on analysis of the Cu 2p spectra, all precipitate samples showed typical Cu 2p3/2 and Cu 2p1/2 peaks with measured binding energy of 935.1 and 955.1 eV, respectively, as well as their associated shake-up lines at 944.1 and 963.1 eV, which confirmed that Cu(OH)₂ is the main copper compound in the precipitate (Biesinger et al., 2010; Yu and Ran, 2011). Based on the peak fitting of the Cu 2p3/2 peak (935.1 eV), the proportion of Cu(OH)₂ was estimated to be 88.7%, 90.5%, 94.5%, and 89.9% for copper1, copper2, copper3 and copper4 precipitate samples, respectively. Less than about 10% of the copper was in another copper compound giving a Cu 2p3/2 peak around 932.5 eV, which will be discussed in detail below. For further confirmation, Cu Auger spectra were also measured (Fig. 5b). The Auger peak at 571.2 eV was also attributed to Cu(OH)₂ (Chawla et al., 1992).

2.3.3. XRD analysis
The precipitate samples of copper1, copper2, copper3, and copper4 collected from the SFM process were analyzed by XRD (Fig. 6). Fig. 6a shows a comparison of the XRD pattern of the
precipitate from SFM and that of MgNH₄PO₄·6H₂O (struvite) powder from the Joint Committee on Powder Diffraction Standards (JCPDS) card (No. 15-0762). Based on comparison with the standard pattern, all of the diffraction peaks were consistent with that of MgNH₄PO₄·6H₂O. This result was in accordance with the aforementioned EDS results (Bhuiyan et al., 2008). The XPS and XRD results clearly agree with the SEM observations, which confirmed the fact that Cu(OH)₂ coexisted with struvite in the precipitates. In other words, co-precipitation of struvite and copper hydroxide occurred in the copper–ammonia complex system after introducing Mg²⁺ and PO₄³⁻.

The high simultaneous removal of copper and ammonia from the complex wastewater and the co-precipitation of copper hydroxide with struvite by external addition of Mg²⁺ and PO₄³⁻ have not been reported previously.

3. Discussion

3.1. Decomposition of copper–ammonia complexes by struvite formation

As demonstrated by the UV–vis results, copper–ammonia complex ions can be decomposed by adding Mg²⁺ and PO₄³⁻ into the solution. The SEM, XRD and XPS results confirmed that Cu and NH₃ in the complex ions entered into precipitates mainly in the form of Cu(OH)₂ and struvite, respectively. The introduction of Mg²⁺ and PO₄³⁻ was considered to be the key reason for the decomposition of the copper–ammonia complex ions.

In order to better understand the decomposition mechanism and specific effect of SFM on the complex ions, additional investigations on separate addition of Mg²⁺ and PO₄³⁻ into the copper–ammonia complex system were carried out. As illustrated in Fig. 7, there was no observable removal of copper or ammonia in the solution on addition of MgCl₂ alone. The UV–vis spectrum measured after adding MgCl₂ had no obvious difference from that of untreated solution. As to addition of Na₂HPO₄ alone, slight copper removal and no significant ammonia removal were observed. With increasing addition of Na₂HPO₄, the copper content decreased slightly, and the maximum copper removal efficiency was only 13.2%, when the addition of molar PO₄³⁻/Cu reached 5:1. Moreover, the UV–vis spectra after addition of Na₂HPO₄ also showed no obvious difference, indicating that the complex ions were not decomposed. The precipitate sample obtained after addition of the P source alone was subjected to XPS analysis. Appendix A Fig. S1 shows a comparison of the XPS spectra of Cu₃(PO₄)₂ (AR) and the precipitate sample. The spectrum of the precipitate sample was the same as that of Cu₃(PO₄)₂ (AR), which confirmed that the precipitate was mainly consisted of copper phosphate. So the formation of copper phosphate after adding PO₄³⁻ was the reason for the slight copper removal. Therefore, it could be concluded that the addition of either
PO₄³⁻ or Mg²⁺ separately fails to achieve the high efficient decomposition of copper-ammonia complex ions. After these analyses and comparisons, it is easy to deduce the mechanism for the decomposition of copper-ammonia complexes by the SFM method. The simultaneous introduction of Mg²⁺ and PO₄³⁻ would lead to deprivation of ammonia from copper-ammonia complexes [Cu(NH₃)₄]²⁺, to form struvite (MgNH₄PO₄·6H₂O) with magnesium and phosphate. The struvite is a quite stable mineral in solution, with low solubility. The tendency for ammonia to participate in struvite formation is stronger than the formation of the copper-ammonia complex. Therefore, the coordination bonding between copper and ammonia would be increasingly broken. The decomposition of the copper-ammonia complex would result in release of copper ions, which function as the central atom in the complex. As the addition of Mg and P sources proceeded, more copper-ammonia complex ions were decomposed.

This decomposition mechanism explains the concomitant phenomenon that the dark blue color of the system gradually disappeared (Fig. 2b), and the UV–vis adsorption peak finally disappeared (Fig. 2a), since the complex ion content was too low to be detected.

3.2. Mechanism of co-precipitation of struvite and copper

According to the results described above, the removal of copper and ammonia in the solution reached an extremely high degree, with removal efficiency of 99.5% and 99.9% respectively. As reported, the removal of ammonia by SFM can only reach about 90% under similar ammonia concentrations (Huang et al., 2011); while for the copper hydroxide precipitation system, the copper removal from solution was still less than 90% for copper content from 200 to 800 mg/L. So the high removal of copper and ammonia by the tested SFM was quite an interesting phenomenon that deserves further investigation. Moreover, it is widely accepted that copper hydroxide is a flocculent precipitate with poor settling properties. As seen in Appendix A Fig. S2, pure copper hydroxide formed in alkaline conditions (pH = 9.0) had great difficulty in settling, and the system was still in a turbid state after twenty minutes’ settlement. In comparison, the copper-ammonia complex system had great settleability after the SFM process (Fig. 1c). The precipitates settled rapidly after reaction and the precipitation process lasted no more than 20 min. The supernatant was quite clear and transparent. These apparent differences with pure copper hydroxide precipitation further confirm

Fig. 5 – Full range (a), copper auger (b), and copper 2p (c) X-ray photoelectron spectroscopy (XPS) spectra of samples with different Cu/N ratios.

Fig. 6 – X-ray diffraction (XRD) patterns of the precipitates with different Cu/N ratios. (a) XRD patterns of samples from 10° to 60°, (b) XRD patterns of the samples from 20° to 22°.
that copper hydroxide generated in the SFM process co-precipitated with struvite. It suggests there may be some kinds of interaction forces between struvite and copper hydroxide. The generated fine copper hydroxide particles may be captured by the initially formed struvite. The co-precipitation then occurred, which contributed to the high removal of copper and ammonia as well as the better settling property of the precipitates. Therefore, the surface and interior interactions between the newly-generated struvite and copper hydroxide were investigated in more detail.

3.2.1. Surface adhesion
As discussed above, SEM photos showed that the copper hydroxide was attached closely to the struvite particles, so surface interaction between copper hydroxide and struvite might occur during the process. Struvite has six waters of crystallization and an ammonium group, indicating that it is a highly hydrophilic material. Thus it is filled with adhesion sites on the surface and even in the interior part. The copper hydroxide generated after hydrolysis of hydrated copper ions has two equivalent hydroxyl groups (–OH), which are prone to form hydrogen bonds of H–O with the hydroxyl groups of the adsorbed water, and to form hydrogen bonds of N–H with the ammonium group in struvite. FT-IR measurements were conducted because ammonium groups and H–O bonds can be detected by FT-IR spectra. The functional groups of precipitate samples with different Cu/P ratios and pure struvite were characterized by FT-IR in the wavenumber range from 1300 to 2500/cm, with spectra shown in Fig. 8 and Appendix A Fig. S3. For the pure struvite sample, there were two weak peaks at 1630 and 1685/cm, which were attributed to the bending vibrations of O–H in adsorbed water and O–H in crystal water, respectively (Rubasinghege and Grassian, 2013). The strong double peak at ~1436/cm was assigned to the N–H vibration in the ammonium group (Liu et al., 2013). As to copper1, with Cu/N of 1:22.7, the peak attributed to O–H in adsorbed water red-shifted. Specifically, it shifted to lower wavenumbers at ~1603/cm. Moreover, the adsorption peak of O–H in adsorbed water became widened, as did the peak attributed to N–H. This phenomenon indicated that the copper hydroxide and struvite had a certain degree of interaction. The FT-IR spectra of the copper2 sample also showed a similar trend as seen with copper1, compared with that of pure struvite, and the peaks for O–H and N–H were even wider than those of copper1. Interestingly, as to copper3 and copper4 precipitate samples, the peaks indexed to O–H and N–H had relatively significant changes compared with those in the pure struvite, copper1 and copper2 precipitates. The peak for O–H in adsorbed water disappeared, leaving only the crystal water O–H peak. The peak for O–H (in crystal water) of the copper4 precipitate also red-shifted compared with that of the copper3 precipitate. The peak for N–H of the copper4 precipitate became widened compared with that of the copper3 precipitate. These kinds of variations in FT-IR spectra of the samples indicated that there were probably hydrogen bonding interactions between struvite and copper hydroxide. The existence of hydrogen bonding would lead to red-shifting and peak widening (Gu et al., 2012; Okur et al., 2013; Wang et al., 2015), which explains the red-shift and widening of the O–H (in adsorbed water) peak of the copper1 and copper2 precipitates. Moreover, for copper3 and copper4, with relatively high Cu/N ratios, the adsorbed water was largely displaced by the fine copper hydroxide particles, since the increase of Cu/N ratio with fixed ammonia content would lead to an increase of fine copper hydroxide particles on the struvite surface. Thus the amount of adsorbed water on the crystal surface significantly decreased, resulting in disappearance of the adsorbed water peak, leaving only the peak of crystal water (as confirmed above). The copper hydroxide can form hydrogen bonds with hydrophilic groups (OH and NH3) of struvite, which explains the red-shift of the O–H peak (crystal water) between copper4 and copper3, and the progressive widening of the N–H peak in the copper1 to copper4 samples when compared with the pure struvite sample.

Thus, during the decomposition of copper-ammonia complexes, the struvite was simultaneously formed, followed by the gradual formation of copper hydroxide under alkaline conditions. The struvite crystal provided adhesion sites to adsorb the newly-generated copper hydroxides after the hydrolysis process. The hydrogen bonding between the struvite and copper hydroxide promoted the adhesion. The adhesion of copper hydroxide on the surface of struvite leads to the co-precipitation of struvite and copper hydroxide. This co-precipitation is likely the key reason for the thorough decomposition of...
the copper-ammonia complex and the high simultaneous removal of copper and ammonia.

3.2.2. Electrostatic attraction

In order to further investigate the surface interactions between struvite crystal and the copper hydroxide colloids, zeta potential (ζ) measurements were conducted. Fig. 9a shows the zeta potential of struvite for different Mg\(^{2+}/N\) ratios. ζ was negative when the molar ratio of Mg/N was no more than 1.4, while it became positive after the molar ratio exceeded 1.4. Fig. 9b shows ζ of copper hydroxide colloids at different pH. Considering that the phosphate in the solution might weaken the double layer of copper hydroxide colloids, we added phosphate into the copper hydroxide system (Appendix A Table S1), to investigate the effect of phosphate on the zeta potential of copper hydroxide. The introduction of phosphate slightly reduced the ζ of copper hydroxide, but all the copper hydroxide precipitates at different phosphate concentrations had positive and relatively high ζ, suggesting that the copper hydroxide colloids were positively charged and were relatively stable in the solution. Thus, the positively charged copper hydroxide can be attracted by negatively charged struvite by electrostatic attraction forces. This was another interaction between struvite particles and copper hydroxide colloids during the SFM process, apart from the hydrogen bonding interaction. Fig. 9c shows ζ of the struvite & copper hydroxide colloids during the SFM process for the 4 samples with different Cu/N ratios. The ζ variations were similar to that of struvite, but the absolute values of ζ were lower in negatively charged conditions (Mg/N from 1.0 to 1.3), and higher in positively charged conditions (Mg/N from 1.4 to 1.6). The results in negatively charged conditions can be easily explained by electrostatic attraction of struvite to the copper hydroxide. Interestingly, ζ of the system was still much lower than that of copper hydroxide (Fig. 9c and e) under the positively charged conditions, where electrostatic repulsion would occur. This suggested that the copper hydroxide still adhered to struvite under electrostatic repulsion conditions.

Thus this indicates that electrostatic attraction forces might not be the dominant reason for the adhesion of copper hydroxide to struvite.

To further clarify the main interaction force during the SFM process, measurements of turbidity after the SFM process were conducted. Turbidity was measured for the samples from copper1 to copper4 after SFM under different Mg/N. The turbidity of the samples was obviously much lower than that of copper hydroxide alone (Fig. 9d). It rose with increasing addition of Mg\(^{2+}\), which resulted from more copper hydroxide being present in the solution, suggesting the weakening of struvite’s adhesion to copper hydroxide. As the zeta potential of struvite gradually transformed to positive values, electrostatic repulsion occurred, leading to a negative effect on struvite’s adsorption of copper hydroxide. Thus the turbidity of the solution slightly increased. But it is noteworthy that although electrostatic repulsion occurred when Mg/N was higher than 1.3, the turbidity of struvite & copper hydroxide was still much lower than that of copper hydroxide alone, and the highest turbidity obtained with copper2 for the Mg/N ratio of 1.6 was merely 14.1. The high turbidity in the supernatant of the copper hydroxide precipitation system arises from the presence of small Cu(OH)\(_2\) particles with low settleability, and thus the adhesion of the fine Cu(OH)\(_2\) on struvite would greatly decrease the turbidity. So this suggests that electrostatic force has a much lower effect on the adhesion of Cu(OH)\(_2\) on struvite, compared with hydrogen bonding.

In conclusion, electrostatic attraction could occur during the SFM process, provided that Mg\(^{2+}\) was not in extreme excess in solution. However, the electrostatic attraction was not the main interaction force that promoted the adhesion of struvite and copper hydroxide, based on the analysis above. Hydrogen bonding should still be the main interaction force between struvite and copper hydroxide.

3.2.3. Copper doping in struvite with ion exchange

Since the radius of Cu\(^{2+}\)(0.073 nm) is just slightly larger than Mg\(^{2+}\)(0.072 nm), the Cu\(^{2+}\) ions can enter into the crystal structure of struvite and be located at interstices or occupy some of the lattice sites of Mg\(^{2+}\). For further confirmation, samples of struvite, copper1, copper2, copper3, and copper4 precipitates were investigated by XRD, with scanning speed controlled at 1°/min from 10° to 60°. As shown in Fig. 6b, the diffraction peaks at 20.9° (111 plane) and 21.5° (021 plane) of all samples slightly shifted. As the copper concentration increased, the shift values became larger. For the peak at 20.9°, the shift value of sample copper4 was 0.15°. This phenomenon demonstrates that the copper can interact chemically with the struvite crystal. As copper content in the solution increased, there were more copper ions entering into the crystal structure of struvite and exchanging with Mg\(^{2+}\) ions, thus occupying the lattice sites of Mg\(^{2+}\). Copper ions in interstitial sites or substituting for Mg\(^{2+}\) would lead to swelling of the crystal lattice, since the radius of copper ion is slightly larger than that of magnesium ion. The increase in the interatomic spacing would cause a slight shift in the diffraction peaks. According to the Bragg equation (Eq. (1)), when d increases, the value of sinθ decreases; namely the value of θ decreases, which would cause a shift of diffraction peaks to lower angles (Aksoy et al., 2012; Abbad et al., 2013).
This explains the diffraction peak shift observed in Fig. 6a. This phenomenon was enhanced as copper content increased in the solution.

\[ n\lambda = 2d\sin\theta \]  \hspace{1cm} (1)

where, \( n \) is an integer, \( \lambda \) is the wavelength, \( d \) is the inner spacing, and \( \theta \) is the diffraction angle.

As can be further confirmed by Fig. 6a, the XRD patterns of the samples scanned from 10° to 60° showed differences in peak intensities and widths. As copper concentration increased from 200 to 800 mg/L, the peak intensity gradually decreased, e.g., the diffraction peak for plane 001 (2\(\theta = 14.4^\circ\)) was intense and prominent, but it was weakened and broadened as the copper content increased, and was even hard to discern for the copper4 sample. These differences further confirm the increase in the amount of copper doping. Copper ions entering into the crystal structure of struvite explained the occurrence of the peak related to another copper compound besides copper hydroxide in the XPS pattern (Fig. 5c). It can be inferred that the other copper compound shown in XPS spectra might be CuNH\(_4\)PO\(_4\)·6H\(_2\)O, formed after Cu\(^{2+}\) exchange with Mg\(^{2+}\).

With increasing copper concentration, the microstructure of struvite showed slight changes and its crystallinity decreased (Fig. 6). Moreover, Appendix A Fig. S4 shows that the mean particle size showed a gradual decrease in the sequence struvite, copper1, copper2, copper3, and copper4. The corresponding surface area of the samples increased from struvite to copper4. It can be deduced that the copper substitution and doping might not only lower the crystallinity of struvite but also to some extent restrain the growth of struvite crystallites, leading to smaller particle sizes. The smaller particle size can provide larger surface area for surface adhesion of copper hydroxide, which can also contribute to the high ammonia and copper removal from the complex wastewater.

From all the results discussed above, the mechanism for co-precipitation of struvite and copper can be concluded. During the SFM treatment process, struvite was formed and the copper ions were released from their complexes. The fate of the copper ions can be divided into two parts: the main part formed Cu(OH)\(_2\) under alkaline conditions, and another small part entered into the crystal structure of struvite. The newly formed Cu(OH)\(_2\) would adhere to the struvite surface by hydrogen bonding and electrostatic attraction. The hydrogen bonding was the main factor in the adhesion. The adhesion of Cu(OH)\(_2\) to struvite and the copper ion doping in the struvite crystal led to the co-precipitation of copper and struvite.

4. Conclusions

The SFM was confirmed to be feasible for decomposing copper-ammonia complexes and removing copper and ammonia from solution, with copper and ammonia removal efficiency of 99.0%–99.95% and 99.5% for copper and ammonium concentrations of 200–800 mg/L and 1000 mg/L, respectively. It was found the deprivation of ammonia from the complex ions by SFM is the key factor in complex ion decomposition. During the SFM process, it was found that the newly-generated copper hydroxide could adhere to struvite, and a small part of the copper was
doped into struvite by ion exchange, which resulted in the co-precipitation and subsequent simultaneous removal of copper and ammonia. Hydrogen bonding and electrostatic attraction were found to be the two main surface interactions between struvite and copper hydroxide. Hydrogen bonding was the main mechanism for surface adhesion, while electrostatic attraction was a secondary mechanism. Copper ions can enter into the crystal structure of the struvite, which might diminish the crystallinity of struvite and limit its particle size, thus increasing the surface area of struvite and further enhancing the removal effect for copper.

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Appendix A. Supplementary data
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References


