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

Cong Peng, Liyuan Chai, Chongjian Tang*, Xiaobo Min, Yuxia Song, Chengshan Duan, Cheng Yu

Department of Environmental Engineering, School of Metallurgy and Environment, Central South University, Changsha 410083, China
Chinese National Engineering Research Centre for Control and Treatment of Heavy Metal Pollution, Changsha 410083, China

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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, NH_3-N and heavy metals can be widely found in different landfill leachates (Battistoni et al., 2006; Primo et al., 2008). 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 (($NH_4)_2C_2O_4$) solution is frequently used to precipitate cobalt ions as $CoC_2O_4 \cdot 2H_2O$ (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

* Corresponding author. E-mail: chjtang@csu.edu.cn (Chongjian Tang).

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 (H_2SO_4), ammonium sulfate ((NH_4)$_2SO_4$), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), disodium hydrogen phosphate (Na_2HPO_4), copper sulfate ($CuSO_4$), 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 (APHE, 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 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 with resolution of 4/cm. X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max-RB diffractometer with Cu-Ka 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-Ka 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. 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 + SS30-100