Struvite as seed materials for treatment of heavy metals in wastewater

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Abstract: Heavy metals (HMs) in the pollutants once discharge into nature without treatment, will easy to destroy the ecological balance. Crystallization is used as a feasible technology for treatment of HMs from wastewater owing to the advantage of obtaining the high purity struvite product, which used as a slow-release fertilizer. After experiments, the results revealed that struvite has a certain feasibility as a seed material to minimize HMs from wastewater. When the condition of pH was 9.5, usage of 2.5g struvite could achieve the removal efficiency of about 95%. The XRD pattern and SEM image analyzed that struvite removes HMs mainly through surface collapse as the adsorption or nucleation growth site for HMs adhering, thereby achieving the aim of removing HMs. This experiment can provide a new channel for the removal of HMs from real wastewater in the future application.

1. Introduction
Heavy metals are essential substances in production and life, but heavy metal ions are generally toxic and non-biodegradable. If excessive HMs discharge into the ecosystem, these will cause various health hazards and ecological imbalances[1]. With the rapid development of modern agriculture and population growth, HMs will accumulate easily in the environment and the composition of wastewater will become more complex[2]. In the past few decades, due to excessive HMs in the animal feed of...
animal husbandry, the content of some HMs or metalloids in animal manure and digestion tanks had increased[3]. Moreover, the routine of treatment of the pollutants was struvite crystallization technology, because the use of this struvite crystallization could not only recover the nutrients in the pollutants, but the obtained struvite (magnesium ammonium phosphate, MAP, MgNH₄PO₄) could be used as a slow-release fertilizer. However, if struvite crystallization is applied to deal with such pollutants, heavy metals (Zn, Cr, etc.) will enter the final struvite precipitates through adsorption or co-precipitation process[4]. This consequence will be reused in agricultural production and caused soil pollution, and finally affected the human body health along with the food chain.

Struvite crystals are rich in amino, hydroxyl and phosphate groups, which may coordinate or adsorb through the hydrophilic interaction with heavy metal hydroxides[5]. Previous literature also found that the hydrogen bonds and electrostatic forces between the HMs-OH fine particles and struvite were presence, which will also improve the removal process of HMs adsorption [6]. This paper aimed to explore the relationship between the removal of heavy metals by struvite crystallization approach and the interaction between struvite and heavy metals, so as to provide a novel insight of efficient removal strategy of heavy metal ions in heavy metal-containing wastewater.

2. Materials and Method

2.1. Experimental apparatus
The jacket crystallization system used in the experiment was independently self-designed by the research group in the early stage [7]. The reaction device is composed of three parts: a 1000 mL jacketed crystallizer, a constant temperature system and a stirring device.

![Figure 1 The experiment apparatus](image)

2.2. Materials
The heavy metal-containing wastewater required for this experiment was configured by ferric chloride (FeCl₃, AR), copper sulfate (CuSO₄, AR), zinc sulfate (ZnSO₄, AR). The concentration of Fe³⁺, Cu²⁺ and Zn²⁺ was controlled at 5mg/L. 0.5 mol/L sodium hydroxide (NaOH, AR) and hydrochloric acid (HCl, AR) were used for adjustment the pH during the experiment. All reagents were purchased from Shanghai Aladdin Company.

2.3. Experiment methods
First, in this experiment, the temperature was set at 298.15K and the stirring speed was 300 rpm. Based on this condition, the removal of Cu, Fe, and Zn ions under the conditions of pH 8.5-10 for 150 min were investigated. Then, under certain pH conditions, the influence of 0.5-3.0 g struvite as seed materials on the removal of three heavy metal ions (Cu, Fe, and Zn) was further investigated. Struvite seed materials were prepared with magnesium chloride (MgCl₂), ammonium dihydrogen phosphate (NH₄H₂PO₄) by reaction at the molar ratio of Mg: NH₄⁺: PO₄³⁻ 1:1:1 for 150 minutes. After the supernatant was poured, the remaining solution was suction filtered, and the obtained product was
dried in the oven of 50°C for 18h.

2.4. Analytical methods
After the reaction, 1 mL of the supernatant was diluted into a 50 mL colourimetric tube, and the remaining solution was separated into solid and liquid by suction filtration. The obtained precipitate was placed in an oven at 80°C for 18 hours. Meanwhile, the Inductively Coupled Plasma Massspectrometer (ICP-MS, iCAP RQ, Thermo Fisher Scientific, the U.S.A) was used to determine the concentration of heavy metals (Cu²⁺ and Fe³⁺). X-ray Diffraction (XRD, Rigaku, Japan) and Scanning Electron Microscope (SEM, INCA 250 X-Max 50, UK) were used to characterize the structure and morphology of the obtained product. The calculation process of the HMs content in struvite as follows: take 0.5 g obtained precipitate and use 1 mL of dilute nitric acid to dissolve then dilute it. Using equation 1 to determine the content of each HMs.

\[ m_{HMs} = \frac{C_{HMs} \times V}{m_{precipitate}} \]  

Where, \( C_{HMs} \) was the concentration of heavy metals; \( m_{precipitate} \) was the mass of product.

3. Results and Discussion

3.1. Effect of pH on heavy metals removal
The pH of the solution plays an extremely important role in the process of removing heavy metal from the wastewater. The results were shown in Figure 2. From figure 2, with the pH increases from 8.5 to 10.0, the removal efficiency of Fe, Cu, and Zn in the solution gradually increases. This process was owing HMs mainly react with OH⁻ to form hydroxide precipitates. However, when the pH is higher than 9.5, the removal efficiency of HMs tends to be stable and the main reason was that the precipitation process was also affected by \( K_{sp} \). Meanwhile, the high pH environment would cause the formation of \( \text{R(OH)}_n \) precipitation to combine with water ionized OH⁻ to form \( \text{R(OH)}_{n+1}^- \) complexes, which will reduce the removal efficiency of heavy metal ions, so the pH chosen in this experiment was 9.5.

![Figure 2 Effect of solution pH on heavy metals removal](image)

3.2. Interaction between struvite and heavy metals
In order to study the removal efficiency of struvite for HMs in-depth, under the condition of pH 9.5, the effect of different additions of struvite on the removal of three HMs was explored, and the results
were shown in Figure 3. It can be seen from Figure 3(a) that as the quantity of struvite raised, the removal efficiency of the three HMs stabilize after gradually increasing, and the removal efficiency reaches higher than 90%. From Figure 3(b), the product obtained after the addition of 2.5g struvite was selected for measurement. It was found that the highest Fe content in the precipitate was 3.6 mg/g, followed by Cu (3.2 mg/g), and the Zn(2.7 mg/g). This meant the contact with struvite could effectively remove HMs from wastewater and indicated that struvite was an alternative method for removing HMs as a seed material.

Figure 3(a) Effect of various struvite quantities on heavy metals removal efficiency; (b) The contents of heavy metals in precipitate

3.3. Characterization analysis
The obtained product was characterized by XRD and SEM, and the result was shown in Figure 4. It can be seen from Figure 4(a) that the main component of the obtained product was still struvite, indicating that the interaction of struvite with HMs unchanged the material structure of the product. As shown in Figure 4(b) that the main morphology of the product was a rod-like structure, what's more, the surface of the product has a part collapse phenomenon. It is presumed that this phenomenon was to provide adsorption or nucleation growth sites for heavy metals to facilitate the removal of HMs.

Figure 4 (a) XRD and (b) SEM of the obtained precipitate

4. Conclusion
This paper investigated the influence of struvite crystals as seed materials on heavy metal removal, and the results showed that the pH is still the prominent process for HMs removal. Meanwhile, the addition of the struvite crystals could minimize HMs from wastewater in a depth way and promoted the removal efficiency of HMs. The series characteristics revealed the removal mechanism, indicating that HMs removal from wastewater depended on the surface collapse of struvite crystals. In a word, usage of struvite for treatment of the HMs from wastewater is a feasible approach.
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