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Size-dependent nanocrystal sorbent for copper removal from water

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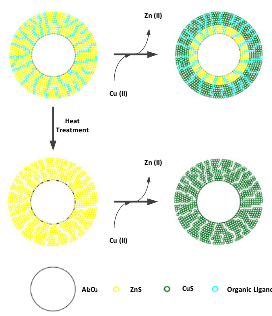
HIGHLIGHTS

- ZnS nanocrystals (NCs) sorbent was developed for Cu(II) removal from water.
- ZnS NCs layer thickness played an important role in Cu(II) removal.
- The adsorption capacity of ZnS NCs on Cu(II) is about 650 mg/g.
- The reaction mechanism of Cu(II) removal by ZnS NCs sorbent was investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, ZnS nanocrystals (NCs) was synthesized and investigated as a novel sorbent for the copper removal from waste water. According to the adsorption experiments, the copper removal efficiency is over 99.0% in one minute. The saturated adsorption capacity of ZnS NCs sorbent on copper is about 650 mg/g which is closed to the theoretic adsorption capacity. The influence of pH value, other metal ions and NCs sorbent size on copper removal efficiency were investigated, respectively. The ZnS NCs sorbent was characterized by TEM and XPS to reveal the reaction mechanism. It was found that the NCs layer thickness played an important role in copper removal by ZnS NCs sorbent. It is more difficult to remove the copper from water for the sorbents with thicker NCs layer. Heat treatment method promoted the copper removal performance of sorbent greatly. Additionally, the sorbent and the copper removed by sorbent could be reclaimed easily. Therefore, it is a promising method to remove the copper from water by ZnS NCs sorbent.

1. Introduction

Contamination of heavy metal in wastewater is a serious worldwide problem because of their adverse effect on the environment and human health [1–3]. Copper is one of the most widespread heavy metals due to its inexpensive and wide applications in industrial processes [2]. It posed a serious threat to human health and living organism which could cause stomach and intestinal problems [3]. Therefore, it is necessary to remove copper ions from the wastewater.

Many approaches, such as chemical precipitation [4,5], adsorption [6–8], cation exchange [9], electrochemical treatments [10,11] and membrane separation [12] have been developed for the removal of copper ions from wastewater. Among these technologies, adsorption is extensively used because it is simple, effective and economical. However, the sorbents always suffer from low efficiency and adsorption capacity, which limits their application [2,6]. Hereupon, it is highly desirable to develop novel sorbent with high adsorption capacity and efficiency.

In past decades, semiconductor nanocrystals (NCs) have been studied extensively due to their unique properties [13–15]. It is found that the NCs can be easily and quickly exchanged by some heavy metal ions [16–18]. Furthermore, the reaction time of cation

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exchange in the nanocrystals (NCs) is much shorter than that of the related systems of large size [19]. Therefore, the adsorption method based on cation exchange could provide a way to remove the copper from wastewater with high adsorption capacity and efficiency.

However, few researches about copper removal by NCs sorbent based on cation exchange have been reported yet. Furthermore, how the NCs size will affect the copper removal speed and degree, which is critical for its application in copper removal, attracts our interest. In this paper, we reported an effective ZnS NCs sorbent for copper removal from water. The influence of heat treatment on copper removal were investigated. Separation and regeneration study were also carried out.

2. Experimental methods

2.1. Material

Zinc chloride (>99%), Copper chloride (>99%), Mercuric chloride (>98%), Lead nitrate (>99%), Cadmium sulfate (>99%), Hydrochloric acid (37%), Alpha-Al_2O_3 (99.99%, 200 nm), Hexahydrate (>99%), Sodium sulfide (>99%), 1-butylamine (>99%), Ethylene glycol (>99%) and Triethylene glycol (>99%) were provide Aladdin Chemical (Shanghai, China). Thiourea (99%) was provided by Sigma–Aldrich (St. Louis, MO).

2.2. Preparation and heat treatment of ZnS NCs sorbent

Although the NCs sorbent could adsorb heavy metal ions, it is hard to separate the sorbents from water after adsorption experiment because of its nano-scale size. Thus, alpha-Al_2O_3 (200 nm) was used as the carrier of ZnS NCs sorbent in this research. It is easy to separate the sorbent from the water because its size is bigger than 200 nm. A solution of 2 mmol alpha-Al_2O_3 (200 nm) was mixed with 2 mmol $ZnCl_2$ and 200 mL ethylene glycol were placed in a 500 mL three-neck flask equipped with a condenser. A mixture of 3 mmol thiourea dissolved in 10 mL 1-butylamine and 40 mL ethylene glycol, were injected continuously into the reaction solution over 3 h by syringe pump at 180 °C. The four samples of the ZnS NCs sorbents were sampled from reaction solution at 0.5, 1.0, 2.0, 3.0 h, which were marked as L-0.5 h, L-1.0 h, L-2.0 h, L-3.0 h, respectively. Meanwhile, in order to investigate the influence of heat treatment on adsorption performance of sorbent, two ZnS NCs sorbents (L-2.0 h and L-3.0 h) were heated to 150 °C in a fixed bed reactor under nitrogen atmosphere for 1 h. The corresponding sorbent was marked as A-2.0 h and A-3.0 h, respectively.

2.3. Characterization

The microstructure of the sorbent was detected by Transmission electronic microscopy (TEM) (JEOL-2010, Tokyo, Japan), and the images were obtained electron microscope operating at 120 kV. The surface area of sorbents was detected by a surface area and pore size analyzer (NOVA 2200e, Quantachrome Instruments, USA). The pore volumes of all samples were calculated based on Barrett–Joyner–Halenda (BJH) method. The component ratio of sorbents was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES) (PS3520UVDD, Japan). X-ray photoelectron spectroscopy (XPS) was used to determine the change of oxidation states of ZnS NCs and copper on sorbents. X-ray photoelectron spectroscopy (XPS) spectra were acquired with a Kratos Axis Ultra^{DLD} spectrometer (Kratos Analytical, Japan) using a monochromatic Al Kα source (1486.6 eV). The analyzer uses hybrid magnification mode (both electrostatic and magnetic) and take-off angle is 90°. Under slot mode, the analysis area is 700 × 300 μm. Analysis chamber pressure is less than 5×10^{-9} Torr. Pass energy of 160 eV and 40 eV are normally used for survey spectra and narrow scan spectra, respectively. The energy step sizes of 1 eV and 0.1 eV were chosen for survey spectra and narrow scan spectra, respectively. In addition, binding energy (BE) range for a survey spectrum is 0–1200 eV. The X-ray source power is 75 W and 75–150 W for acquiring a survey spectrum and narrow scan spectra, respectively. The BE scale was calibrated according to the C 1s peak (284.8 eV) of adventitious carbon on the analyzed sample surface. The Kratos charge neutralizer system was used on all specimens except conductive samples.

2.4. Adsorption experiments

Copper usually exists as Cu^{2+} in wastewater. This paper chooses $CuCl_2$ as the target copper pollutant in wastewater [20,21]. For the adsorption study, a certain amount of ZnS NCs sorbents were added into a certain concentration of $CuCl_2$ solution with stirring (430 r/min). The solution was sampled and filtrated by filter (pore size: 220 nm) at different reaction time. Then, the Cu^{2+} concentration of the solution samples after adsorption were analyzed by continuum source atomic absorption spectrometry (ContrAA 700, Analytik Jena AG, Germany). In order to investigate the influence of other metal ions on the copper removal by ZnS NCs sorbent, a certain amount of Hg^{2+}, Pb^{2+} and Cd^{2+} were introduced into the $CuCl_2$ solution, respectively.

3. Results and discussion

3.1. Adsorption performance

The adsorption performance of ZnS NCs sorbent for copper removal from water was investigated. The $CuCl_2$ concentrations were range from 1.0 to 100.0 mg/L (Fig. 1). 100 mg ZnS NCs sorbent was added into 50 mL $CuCl_2$ solution with stirring (430 r/min) at pH 5.5 and the temperature was 25 °C. As shown in Fig. 1, the $CuCl_2$ removal efficiency was over 99.0% in one minute. In particular, the $CuCl_2$ concentration also decreased quickly from 100.0 mg/L (100 ppm) to below 0.001 mg/L (1.0 ppb). Obviously, ZnS NCs sorbent is very effective for the copper removal from wastewater.

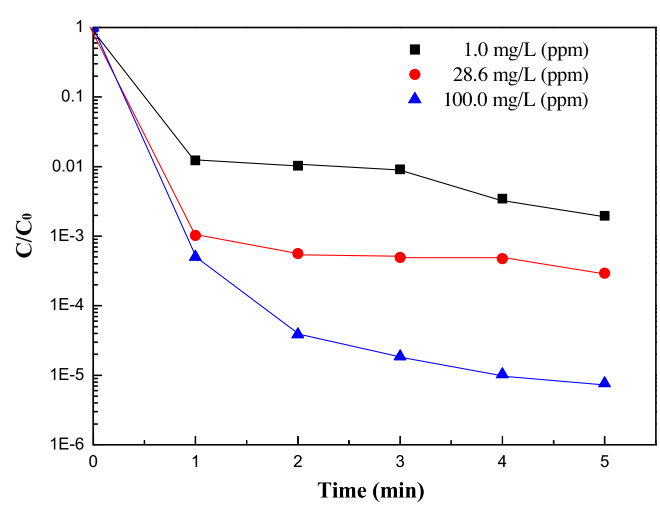

Fig. 1. The ratio of Cu^{2+} concentration at different treating time to initial Cu^{2+} concentration (C/C_0) as a function of time for copper removal by ZnS NCs (L-0.5 h). The initial $CuCl_2$ concentration were range from 1.0 to 100.0 mg/L. 100 mg ZnS NCs sorbent was added into 50 mL $CuCl_2$ solution with stirring (430 r/min) at the pH 5.5, temperature was 25 °C.