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Size-dependent nanocrystal sorbent for copper removal from water

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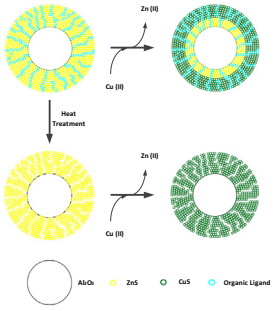
HIGHLIGHTS

- 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.

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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.

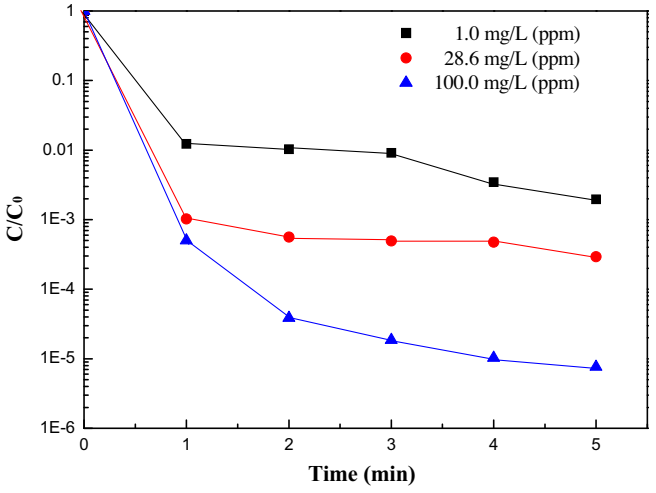

Fig. 1. The ratio of Cu^{2+} concentration at different treating time to initial Cu^{2+} concentration (C/C_0) as a function of time for copper removal by ZnS NCs (L-0.5 h). The initial $CuCl_2$ concentration were range from 1.0 to 100.0 mg/L. 100 mg ZnS NCs sorbent was added into 50 mL $CuCl_2$ solution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

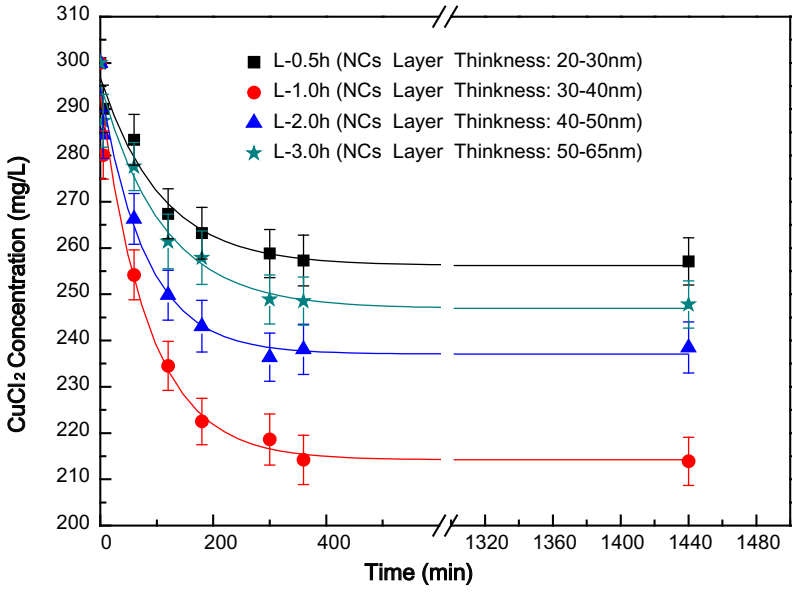

Fig. 2. Influence of ZnS NCs layer thickness on Cu^{2+} removal. 20 mg ZnS NCs sorbent was mixed with 100 mL $CuCl_2$ solution (300.0 mg/L) with stirring (430 r/min) at the pH 5.5, temperature was 25 °C, where the Cu^{2+} is highly excessive to the ZnS NCs contained in the four sorbents.

In order to investigate the influence of other metal ions on copper removal by ZnS NCs sorbent from water, several metal compounds, such as $HgCl_2$, $Pb(NO_3)_2$ and $CdSO_4$, were added into the $CuCl_2$ solution, respectively (Fig. S1, Supporting Information). According to Fig. S1, although the presence of Hg^{2+} decreased the Cu^{2+} removal reaction rate, the Cu^{2+} removal efficiency is still over 99.0% in 5 min. In addition, there is no obvious influence of other heavy metal cations and anions on the Cu^{2+} removal efficiency by the ZnS NCs sorbent.

3.2. Influence of NCs sorbent layer thickness on Cu^{2+} removal efficiency

Nanomaterials always have many special physical and chemical characteristics. Thus, the influence of NCs sorbent size on its performance in copper removal was investigated. Four ZnS NCs sorbents were tested, respectively. 20 mg sorbent was added into 100 mL $CuCl_2$ solution ($CuCl_2$ concentration: 300.0 mg/L) with stirring (430 r/min) at pH 5.5 and the temperature was 25 °C, where the Cu^{2+} is highly excessive to the ZnS NCs contained in the four sorbents.

From in the Fig. 2, it could be seen that L-1.0 h showed the best copper removal performance, then followed by L-2.0 h, L-3.0 h and L-0.5 h. According to the ICP analysis results of four sorbents (Table S1, Supporting Information), the atomic ratio of Zn to S is near to 1:1 and ZnS/Al_2O_3 mole ratios are close to 0.19:1, 0.49:1, 0.90:1 and 1:1 for the samples L-0.5 h, L-1.0 h, L-2.0 h and L-3.0 h, respectively. It is easy understand that the L-0.5 h showed the worst copper removal performance in four sorbents because its ZnS concentration was much less than that of other sorbents. Interestingly, L-1.0 h has the best copper removal efficiency although its ZnS component ratio is less than that of L-2.0 h and L-3.0 h. According to the mole ratios of removed $CuCl_2$ to ZnS NCs of sorbents (Fig. S2, Supporting Information), it could be found that about 98.7% Zn^{2+} of L-0.5 h and 97.0% Zn^{2+} of L-1.0 h was exchanged by Cu^{2+}. However, only 38.5% Zn^{2+} of L-3.0 h was exchanged by Cu^{2+} in the same solution. Obviously, most of ZnS NCs on L-2.0 h and L-3.0 h didn't react with the copper ions. From the TEM images (Fig. S3, Supporting Information) of four sorbents, it could be seen that the ZnS NCs coating layers follow the shape of supporting alpha-Al_2O_3 template, and the average ZnS NCs layer thickness of L-0.5 h, L-1.0 h, L-2.0 h and L-3.0 h were about 20–30 nm, 30–40 nm, 40–50 nm and 50–65 nm, respectively. Therefore, the ZnS concentration of sorbents is not the only factor that could affect the copper removal performance of sorbents, and the ZnS NCs layer thickness may played an important role in copper removal by ZnS NCs sorbent [21].

In order to improve the copper removal performance of L-2.0 h and L-3.0 h, these two sorbents were heated under 150 °C with N_2 atmosphere. As seen in Fig. 3, the final copper concentrations were 238.5 mg/L, 170.1 mg/L, 247.8 mg/L and 165.7 mg/L for L-2.0 h, A-2.0 h (heated), L-3.0 h and A-3.0 h (heated), respectively.

It could be seen that heated sorbents removed more copper ions than that untreated sorbents did. To clarify what the reason for the improvement of copper removal performance, we tested the surface area of the samples before and after heating treatment by BET. Surprisingly, the surface area of L-2.0 h and A-2.0 h were 9.9 m^2/g and 37.5 m^2/g, respectively. It could be seen that the surface area of sorbent increased significantly after be heated. Now, it is easy to understand why heat treatment can improve the copper removal efficiency. As mentioned before, just a part of Zn^{2+} could be exchanged by Cu^{2+} for the samples with thicker coating of ZnS layer, which is possibly because Cu^{2+} cannot diffuse through the whole ZnS layer and just exchange the shallow part of ZnS layer. When the samples were heated up to 150 °C, the organic ligands capping on the ZnS nanocrystals were partially removed and some unreated precursors were further decomposed, which produced many voids in the ZnS layer and then increased the surface area. Those voids were very helpful for the diffusion of Cu^{2+} into ZnS layers to exchange more Zn^{2+} ions.

3.3. The mechanism of heavy metals removal by ZnS NCs sorbent

During the copper ions removal experiments, the Zn^{2+} and Cu^{2+} concentrations in solution were both tested to investigate the reaction mechanism [22]. 100 mg ZnS NCs sorbent (L-1.0 h) was added into 50 mL $CuCl_2$ solution (Cu^{2+} concentration: 3.0 mmol/L) with stirring (430 r/min) at pH 5.5 and the temperature was 25 °C. As shown in Fig. 4, the Cu^{2+} concentration decreased from 3.0 to

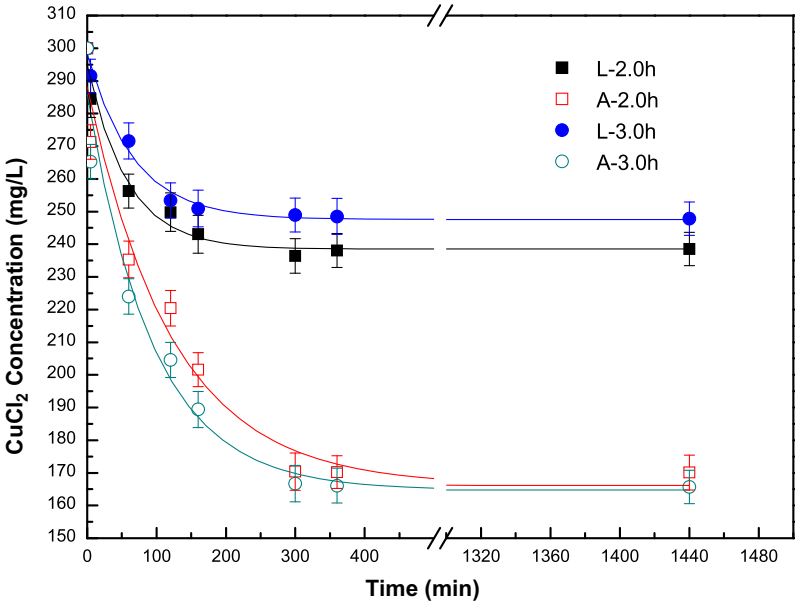

Fig. 3. Influence of heat treatment on ZnS NCs sorbent performance. 20 mg ZnS NCs sorbent was mixed with 100 mL $CuCl_2$ solution (300.0 mg/L) with stirring (430 r/min) at the pH 5.5, temperature was 25 °C.

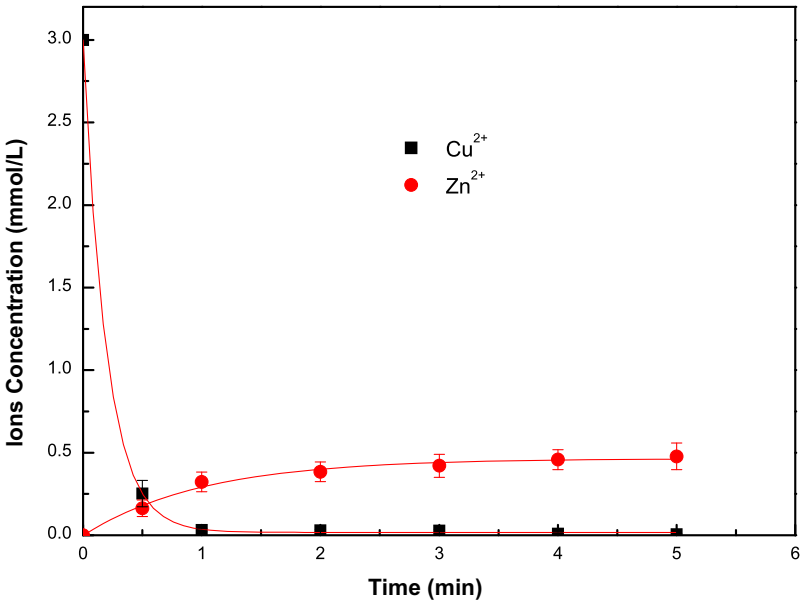

Fig. 4. The Cu^{2+} and Zn^{2+} concentration of solution in the copper removal process. 100 mg ZnS NCs sorbent (L-1.0 h) was added into 50 mL $CuCl_2$ solution (Cu^{2+} concentration: 3.0 mmol/L) with stirring (430 r/min) at the pH 5.5, temperature was 25 °C.

0.02 mmol/L in 1 min, the 99% Cu^{2+} was removed by ZnS NCs sorbents. On the contrary, the Zn^{2+} concentration increased slowly. Generally, the amount of Cu^{2+} removed from the solution should equal to that of Zn^{2+} released from the sorbent if Zn^{2+} was totally exchanged by Cu^{2+} based on cation exchange reaction. Therefore, the removal of Cu^{2+} by ZnS NCs was not only based on cation exchange, part of Cu^{2+} was removed through adsorption. After 24 h reaction, the Zn^{2+} concentration of solution increased to about 2.96 mmol/L which closes to the initial Cu^{2+} concentration. That means all of Zn^{2+} were finally exchanged.

In order to investigate the reaction mechanism of copper removal by ZnS NCs, the sorbent at different reaction time was tested by XPS [23] (Fig. 5). The binding energy of the observed photoelectron peaks of Cu $2p_{1/2}$ and $2p_{3/2}$ were 932.8 and 952.8 eV, respectively and which is consistent with the Cu-alloyed ZnS reference XPS spectrum [24]. This result indicates that Cu may be substituting for Zn in the wurtzite lattice and form the Cu-alloyed ZnS [25]. Therefore, there are two possible reaction pathways for Cu^{2+} removal by ZnS NCs, which could be deduced as follows. In the pathway 1, the Cu^{2+} was firstly adsorbed by ZnS NCs and formed adsorptive xCu · $ZnS_{(ad)}$. Then the xCu · $ZnS_{(ad)}$ converted to an intermediate product, $Cu_xZn_{1-x}S^*$ and simultaneously release Zn^{2+}. In the pathway 2, the Cu^{2+} directly reacted with ZnS NCs and formed $Cu_xZn_{1-x}S^*$ and release Zn^{2+} through the cation

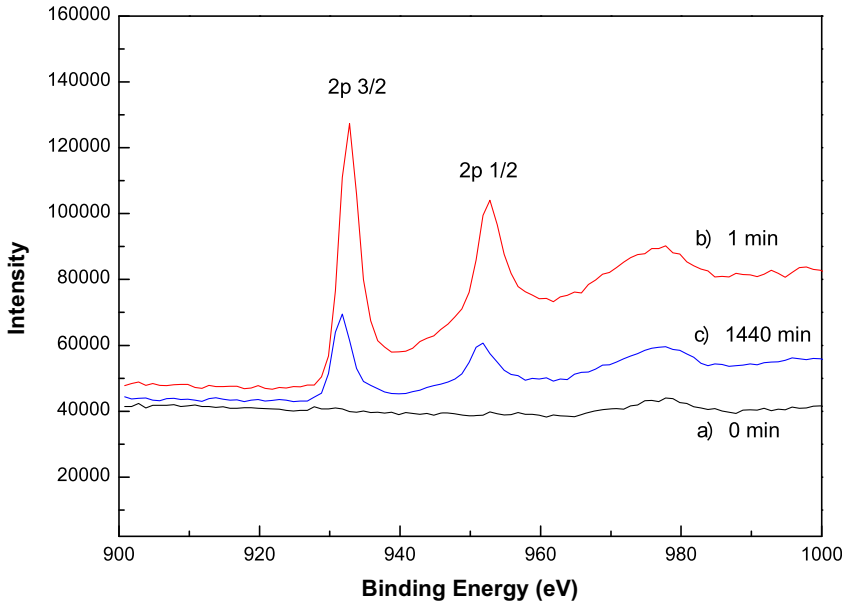

Fig. 5. XPS plot of the Cu 2p binding energy of ZnS NCs sorbents before and after copper removal. (a) Fresh sorbent; (b) sorbent after 1 min reaction; (c) sorbent after 24 h reaction. The samples for XPS runs were prepared by adding 100 mg ZnS NCs sorbent (L-0.5 h) into 50 mL $CuCl_2$ solution (100 mg/L) with stirring (430 r/min). Then, the sorbents were sampled after 1 min and 24 h reaction, respectively. The initial sorbent and the reacted sorbent were tested by XPS.

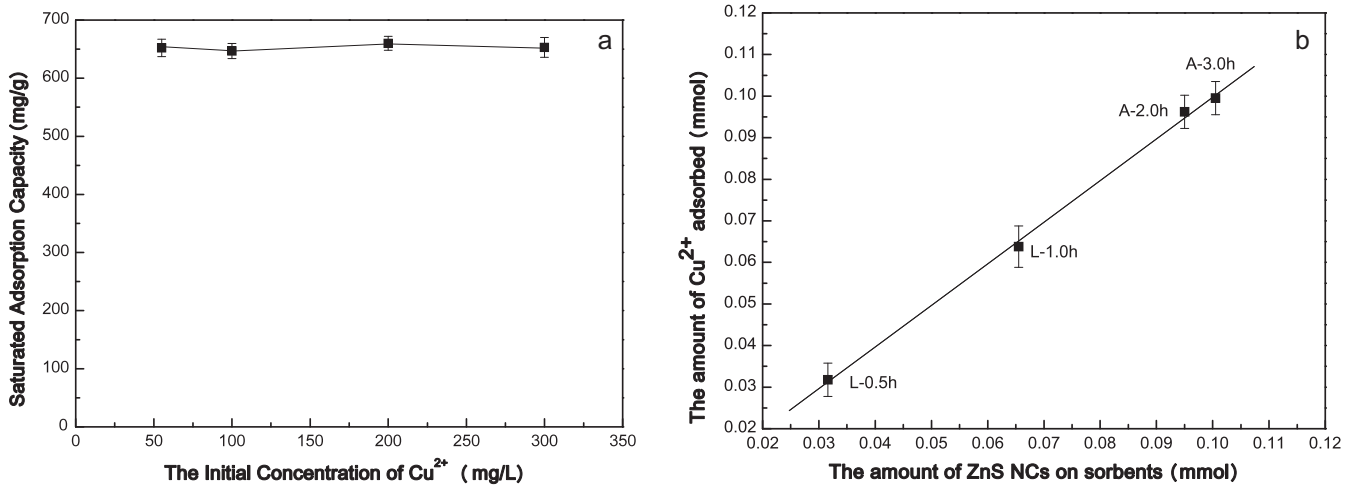

Fig. 6. Saturated adsorption capacity of ZnS NCs sorbent. (a) 10 mg ZnS NCs sorbent (L-1.0 h) was added into 100 mL $CuCl_2$ solution. The $CuCl_2$ concentration range is from 55.0 mg/L to 300.0 mg/L; (b) 20 mg ZnS NCs sorbents (L-0.5 h, L-1.0 h, A-2.0 h, A-3.0 h) were added into 100 mL $CuCl_2$ solution, respectively. The $CuCl_2$ concentration is 300.0 mg/L. The reaction temperature is 25 °C and the reaction time is 24 h at the pH 5.5, temperature was 25 °C.

exchange reaction, and if the Cu^{2+} is excess to Zn^{2+}, the $Cu_xZn_{1-x}S^*$ will finally turn to CuS. Eqs. (1) and (2) can be used to describe the reaction process.

Pathway 1

$$xCu^{2+} + ZnS \rightarrow xCu^{2+} \cdot ZnS_{(ad)} \rightarrow Cu_xZn_{1-x}S^* + xZn^{2+} \quad (1)$$

Pathway 2

$$xCu^{2+} + ZnS \rightarrow Cu_xZn_{1-x}S^* + xZn^{2+} \quad (2)$$

Since all of zinc ions were exchanged by Cu^{2+} eventually, the heavy metals removal by ZnS NCs sorbent belonged to cation exchange.

The influence of pH on the removal of Cu^{2+} by ZnS NCs sorbent was also investigated [26] (Fig. S4, Supporting Information). As shown in Fig. S4, the Cu^{2+} removal efficiency is over 99.9% when the pH value is from 1 to 6. There is no obvious effect of pH value on Cu^{2+} removal by ZnS NCs sorbent.

3.4. Adsorption capacity of ZnS NCs sorbent

To better demonstrate the behaviors between Cu^{2+} and ZnS NCs, the equilibrium isotherm of Cu^{2+} was studied at the initial Cu^{2+} concentration of 55–300 mg/L (Fig. 6a). The sorbent (L-1.0 h) was tested after 24 h adsorption to ensure that the adsorption equilibrium was reached. It can be seen that the saturated adsorption capacity of ZnS NCs on Cu^{2+} is about 650 mg/g if calculated by ZnS NCs themselves with the initial Cu^{2+} concentration range from 55.0 mg/L to 300.0 mg/L, which is larger than other reported sorbents [27–30]. Meanwhile, the saturated adsorption capacity of ZnS NCs on Cu^{2+} didn't show obvious difference with the increase of initial copper concentration. Additionally, the mole ratio of Cu^{2+}

adsorbed by sorbent to ZnS NCs on sorbent closed to 1:1 under different experimental condition (Fig. 6b). This also indicates that the saturated adsorption capacity of sorbent is related with the amount of ZnS NCs. The adsorption isotherm model studies were conducted (Fig. S5, Supporting Information). The adsorption of Cu (II) on ZnS NCs was better estimated by Langmuir model with a correlation coefficient (R^2) of 0.9995 under the studied range, implying that the Cu(II) adsorption process is mainly monolayer.

3.5. Reclaim of copper and ZnS NCs sorbent

The reclaim of copper adsorbed by the ZnS NCs sorbent is crucial in practical application and it is also significant that avoid causing the second pollution. The sorbent after Cu^{2+} absorption was treated by HNO_3 solution, the HNO_3 solution concentration is from 8 to 1 mol/L. It was found that the color of the sorbent turned to white quickly. Chemical analysis demonstrates that 99% copper sulfide on the sorbent dissolved into HNO_3 solution. It is easy to adsorb and accumulate the copper from the waste water containing low concentration copper ions and reclaim it from the sorbent. While, the carrier of sorbent, alpha-Al_2O_3 was left after be treated by HNO_3 solution. It could be used to synthesize new sorbent again.

4. Conclusions

It has been demonstrated that the ZnS NCs sorbent could remove the copper from water effectively, which can remove 99% Cu^{2+} in one minute. Its saturated adsorption capacity and reaction rate is much better than that of most of reported sorbents. The saturated adsorption capacity of ZnS NCs is about 650 mg/g. The mechanisms of Cu^{2+} removal were cation exchange through ICP and XPS analysis. The ZnS NCs layer thickness of sorbent plays an important role in copper removal and found the ZnS NCs layer thickness were 30–40 nm that remove the highest efficiency. Meanwhile, the heat treatment could improve its adsorption performance on copper by removing the organic ligand on sorbent and increasing its surface area. Based on the experiment results, ZnS NCs sorbent have potential applications for removing copper from contaminated water.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2015.08.151.

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