



Research paper

A novel method for the sequential removal and separation of multiple heavy metals from wastewater



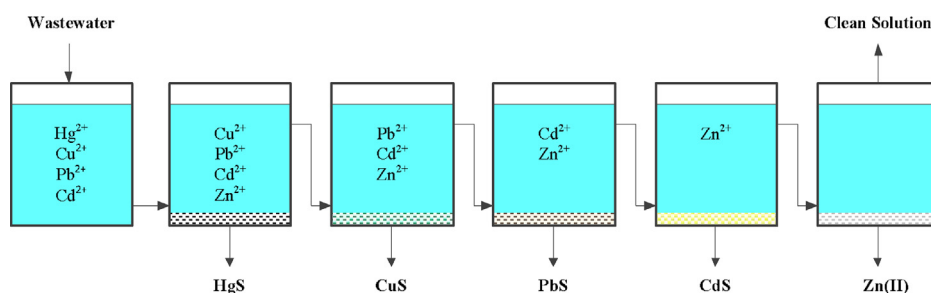
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HIGHLIGHTS

- A novel method was developed for the removal and separation of heavy metals.
- ZnS Sorbent showed extraordinary performance for multiple heavy metals removal.
- The heavy metal ions were removed based on the ion exchange reactions.
- K_{sp} of heavy metal sulfides is the determining factor for the metal adsorption selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method was developed and applied for the treatment of simulated wastewater containing multiple heavy metals. A sorbent of ZnS nanocrystals (NCs) was synthesized and showed extraordinary performance for the removal of Hg^{2+} , Cu^{2+} , Pb^{2+} and Cd^{2+} . The removal efficiencies of Hg^{2+} , Cu^{2+} , Pb^{2+} and Cd^{2+} were 99.9%, 99.9%, 90.8% and 66.3%, respectively. Meanwhile, it was determined that solubility product (K_{sp}) of heavy metal sulfides was closely related to adsorption selectivity of various heavy metals on the sorbent. The removal efficiency of Hg^{2+} was higher than that of Cd^{2+} , while the K_{sp} of HgS was lower than that of CdS . It indicated that preferential adsorption of heavy metals occurred when the K_{sp} of the heavy metal sulfide was lower. In addition, the differences in the K_{sp} of heavy metal sulfides allowed for the exchange of heavy metals, indicating the potential application for the sequential removal and separation of heavy metals from wastewater. According to the cumulative adsorption experimental results, multiple heavy metals were sequentially adsorbed and separated from the simulated wastewater in the order of the K_{sp} of their sulfides. This method holds the promise of sequentially removing and separating multiple heavy metals from wastewater.

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1. Introduction

Wastewater from the metallurgical, mining and battery manufacturing industries, among others, usually contains many types of heavy metal ions [1]. These have attracted increasing attention because of their toxicity and other adverse effects on public health

and the environment [2–4]. Meanwhile, these heavy metals are also valuable resources that are worth recycling. Thus, it is significant to remove and recycle heavy metals from industrial wastewater.

Many technologies have been developed for the removal of heavy metals from water, such as extraction, adsorption, membrane separation, ion exchange, photocatalysis and chemical precipitation [5–11]. Among these technologies, adsorption has been widely used because it is simple, economical and the materials are easily available [12,13]. Moreover, with the development of nanotechnology, nanosorbents have shown higher efficiency and

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faster adsorption rates for heavy metal removal compared with traditional sorbents [14]. Adsorption should be an ideal method for the removal of heavy metals. However, industrial wastewater usually contains multiple heavy metals that compete for active sites on sorbents [15]. It is difficult to separate and recycle mixed heavy metals adsorbed on sorbents. Therefore, sequential removal and separation of multiple heavy metals from contaminated water is still a challenging task.

In recent years, the cation exchange method has become a convenient tool to produce materials that have morphologies, shapes and structures that are difficult to determine by conventional synthetic methods [16,17]. For instance, to prepare HgS or PbS nanocrystals (NCs), an easily synthesized nanostructure, such as that of CdS NCs, was synthesized as a template. Then, CdS NCs were easily and quickly exchanged to HgS or PbS NCs by introducing Hg^{2+} or Pb^{2+} into the synthetic system of CdS NCs [18]. Based on their intrinsic cation exchange properties, metal sulfide NCs sorbents were applied to remove heavy metals from polluted water and showed an extraordinary adsorption rate and capacity [19–23]. Furthermore, the mutual exchange character of metal sulfides opens a new window for the separation of multiple heavy metals from wastewater. If the metal sulfide NCs sorbent is added to wastewater that contains multiple heavy metals, the heavy metals can be adsorbed in the order of the stability of their adsorption products because of the mutual exchange character of metal sulfides. Ultimately, the heavy metal with the most stable sulfide will be the first heavy metal adsorbed and can be easily separated from the other heavy metals. Likewise, the other heavy metals will be separated one by one. Hence, these features can be utilized to sequentially remove and separate multiple heavy metals from wastewater. However, there is little research reporting this adsorption and separation method based on cation exchange and its feasibility needs to be verified.

In this paper, a new method was developed for the multiple heavy metals sequential removal and separation from wastewater based on cation exchange. A ZnS NCs sorbent was synthesized and was applied in the removal of heavy metal from simulated wastewater. Then, mutual exchange and cumulative adsorption experiments were conducted to evaluate the sorbents performance on multiple heavy metals removal and separation.

2. Experimental methods

2.1. Material

Alpha- Al_2O_3 (99.99%, 200 nm), zinc chloride (>99%), ethylene glycol (>99%), 1-butylamine (>99%), mercury chloride (>99%), cupric nitrate (>99%), lead nitrate (>99%), and cadmium chloride (>99%) were provided by Aladdin Chemical (Shanghai, China). Thiourea (99%) was provided by Sigma-Aldrich (St. Louis, MO).

2.2. Synthesis of ZnS NCs sorbents

Alpha- Al_2O_3 (2.0 mmol; 200 nm) was mixed with 2.0 mmol of ZnCl_2 and 200.0 mL of ethylene glycol in a 500.0-mL three-neck flask equipped with a condenser. A mixture of 3.0 mmol of thiourea dissolved in 10.0 mL of 1-butylamine and 40.0 mL of ethylene glycol was injected continuously into the reaction solution at a temperature of 180 °C over a period of 3.0 h using a syringe pump. Three samples of ZnS NCs sorbents were sampled from the reaction mixture at 0.5, 1.0 and 3.0 h, which were marked as S-0.5 h, S-1.0 h and S-3.0 h, respectively.

2.3. Characterization

Morphology observations and energy dispersive X-ray (EDX) analysis of the NCs sorbents were conducted using high-resolution transmission electron microscope (HRTEM, JEOL-2010, Japan), operating at 120 kV. The X-ray diffraction (XRD) patterns were recorded using a Shimadzu XRD-6000 (Japan). The surface area of sorbents was detected by a surface area and pore size analyzer (NOVA 2200e, Quantachrome Instruments, USA).

2.4. Adsorption experiments

2.4.1. Adsorption performance

To evaluate the suitability of ZnS NCs sorbent for the removal of various heavy metals from wastewater, four heavy metals were tested as targets. A total of 100.0 mg of ZnS NCs sorbent (S-0.5 h) was added to 50 mL of simulated heavy metal wastewater that contained HgCl_2 , $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ and CdCl_2 . The initial heavy metals concentrations were all 1.0 mmol/L. The pH value of the heavy metal solutions was approximately 5.5. All batch adsorption experiments were performed by mixing NCs sorbent with a certain concentration of heavy metal solution with stirring (400 r/min) at 25 °C. The solutions were sampled at different reaction times and filtered through a 220-nm membrane analyzer. The heavy metals concentration of solution samples was analyzed by continuum source atomic absorption spectrometry (ContrAA 700, Germany) and inductively coupled plasma optical emission spectrometry (ICP-OES) (PS3520UVDD, Japan). The removal efficiency of the heavy metals was calculated using the equation:

$$\eta = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

where η represents the heavy metal ion removal efficiency (%) and C_0 and C_t are the initial and instantaneous concentrations of heavy metal ions (mmol/L), respectively. All batch adsorption experiments were conducted for three times under the same condition. The accuracy of the data reported here was within 5%.

2.4.2. Adsorption isotherm

Adsorption isotherm experiments were conducted by mixing 20.0 mg of sorbent (S-1.0 h) with 50.0 mL of a heavy metal solution in a sealed vial with a concentration ranging from 5.0 to 678.0 mg/L. The vials were stirred for 24 h to reach equilibrium. The pH value of the heavy metal solutions was approximately 5.5. The amount of heavy metal ions adsorbed on the sorbent under equilibrium conditions was obtained from the following equation:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of heavy metal ions (mg/L), respectively; V is the volume of heavy metal solution (L); m denotes the mass of the sorbent (g).

The isotherm data thus obtained were fitted using the classical Langmuir and Freundlich models. The two typical adsorption isotherms can be expressed as [24]:

$$\text{Langmuir model: } \frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} \times K_L} \quad (3)$$

$$\text{Freundlich model: } \log Q_e = \log K_F + \frac{1}{n} \times \log C_e \quad (4)$$

where Q_e is the adsorption capacity (mg/g), C_e is the equilibrated concentration of heavy metal ions (mg/L), Q_{\max} is the saturated adsorption capacity (mg/g), and K_L and K_F refer to the affinity parameter of the Langmuir sorption constant and Freundlich adsorption capacity, respectively. $\frac{1}{n}$ is the Freundlich adsorption intensity parameter.

2.4.3. Adsorption kinetics

The adsorption kinetics of ZnS NCs sorbent was conducted by adding 20.0 mg of sorbent (S-1.0 h) to 50.0 mL of a heavy metal solution (300.0 mg/L) at a pH of 5.5 with stirring (400 r/min) at room temperature for 120 min. Pseudo-first-order and pseudo-second-order kinetic models were applied to interpret the adsorption kinetics to investigate the mechanisms and processes of the adsorption. These kinetics models are given as follows [25]:

$$\text{Pseudo-first-order kinetic model: } \ln(Q_e - Q_t) = \ln Q_e - K_1 \times t \quad (5)$$

$$\text{Pseudo-second-order kinetic model: } \frac{t}{Q_e} = \frac{1}{K_2 \times Q_e^2} + \frac{t}{Q_e} \quad (6)$$

where Q_e is the adsorption capacity at equilibrium (mg/g), Q_t is the amount of metal adsorbed at time t (mg/g), K_1 is the pseudo-first-order adsorption rate constant (min^{-1}), and K_2 is the pseudo-second-order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). R_1^2 and R_2^2 are the corresponding correlation coefficients.

2.4.4. The adsorption selectivity of ZnS NCs sorbent toward different heavy metals

Selectivity studies of the ZnS NCs sorbent to different heavy metals were performed by adding different dosages of ZnS NCs sorbent to 50.0 mL of simulated wastewater containing Hg^{2+} , Cu^{2+} , Pb^{2+} and Cd^{2+} . The concentration of heavy metal ions was 0.4 mmol/L. The pH value of the heavy metal solution was approximately 5.5. In all, 10.0–100.0 mg of the ZnS NCs sorbent (S-0.5 h) was added to the solution. The solution was then stirred at 400 r/min for 24 h. Furthermore, the binary separation factor α_j^i was applied to evaluate the selectivity of ZnS NCs sorbent for different heavy metal ions. The value of α_j^i is a measure of the preference for one ion over another during ion exchange and can be expressed as followed [26]:

$$\alpha_j^i = \frac{q_i \times C_j}{q_j \times C_i} \quad (7)$$

where α_j^i represents the dimensionless separation factor of ion i with respect to ion j . C_i and C_j are the aqueous-phase concentrations of ions i and j , respectively. The values of q_i and q_j are the solid-phase concentrations of ions i and j , respectively.

2.4.5. Mutual exchange and adsorption

To evaluate the mutual exchange performance of heavy metal ions on the metal sulfide NCs sorbents, a series of heavy metal sulfide (CdS, PbS and CuS) NCs sorbents were prepared. These heavy metal sulfide NCs sorbents were prepared according to the following steps. First, 200.0 mg of ZnS NCs sorbent (S-0.5 h) was added to 200.0 mL each of a CdCl_2 , $\text{Pb}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$ solution (5.0 mmol/L) with stirring (400 r/min), replacing Zn^{2+} with Cd^{2+} , Pb^{2+} and Cu^{2+} , respectively. Second, the sorbents were separated from the solution after 24 h of cation exchange and adsorption and were dried at 100°C for 2 h. The main components of these heavy metal sulfide NCs sorbents were CdS, PbS and CuS, respectively (Fig. S1, Supporting information).

100.0 mg of CdS NCs, PbS NCs and CuS NCs sorbents were added to 50 mL of $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and HgCl_2 solutions with stirring (400 r/min), respectively. The $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and HgCl_2 concentrations were all 1.0 mmol/L. The pH value of the heavy metal solutions was approximately 5.5.

2.4.6. Cumulative adsorption experiments

A cumulative adsorption experiment was conducted to test and verify the feasibility of a technology for the sequential removal and separation of multiple heavy metals. Firstly, four beakers were used as adsorption reactors, labelled reactor A, reactor B, reactor C and reactor D. Each reactor was loaded with 50.0 mg of ZnS NCs sorbent (S-1.0 h), and the corresponding sorbents were marked as

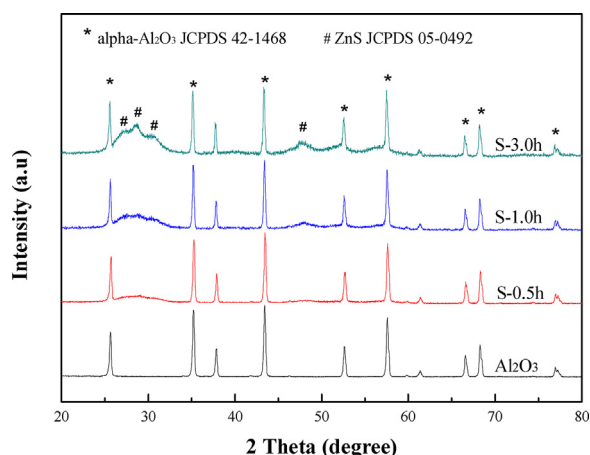


Fig. 1. The XRD patterns of Al_2O_3 and ZnS NCs sorbents.

sorbent A, sorbent B, sorbent C and sorbent D, respectively (Fig. S2, Supporting information). Secondly, 50.0 mL of a mixed solution of the four heavy metals (the concentrations of Hg^{2+} , Cu^{2+} , Pb^{2+} and Cd^{2+} were all 1.5 mmol/L) was injected into reactor A with stirring (400 r/min). After 3.0 h of adsorption, the mixed solution was filtered and injected into reactor B. The above experimental adsorption steps were repeated by injecting the filtrate into reactors C and D. After the first round of experiments (Run 1) was finished, sorbents A–D were added to reactors A–D, respectively. Another 50.0 mL of a fresh mixed solution of heavy metals was passed through reactors A–D again to conduct the second round of experiments (Run 2). After each round of experiments, the sorbents from the adsorption reactors were analyzed to calculate the concentrations of the four heavy metals in the sorbents.

3. Results and discussion

3.1. Characterization

The results of powder X-ray diffractogram (XRD, Fig. 1) identified the samples were mixtures of wurtzite ZnS NCs and alpha- Al_2O_3 . Those sharp peaks and weak peaks were from alpha- Al_2O_3 nanoparticles and wurtzite ZnS NCs, respectively. The transmission electron microscopy (TEM) images of ZnS NCs sorbents (S-0.5 h, S-1.0 h and S-3.0 h) was shown Fig. S3 (Supporting information). It could be seen that all alpha- Al_2O_3 nanoparticles have been fully coated with ZnS NCs layers. The average ZnS NCs thickness of S-0.5 h, S-1.0 h and S-3.0 h are about 20–25 nm, 35–40 nm and 55–65 nm, respectively. Meanwhile, the coating layer was composed of ZnS NCs around 4–8 nm (Fig. S4, Supporting information). Chemical analysis using EDX spectrometry (Fig. S5, Supporting information) indicates that the mole ratios of ZnS/ Al_2O_3 were close to 0.21:1, 0.44:1 and 1:1 for the sorbents S-0.5 h, S-1.0 h and S-3.0 h, respectively. As shown in Table S1 (Supporting information), the surface area of S-0.5 h, S-1.0 h and S-3.0 h were $15.9 \text{ m}^2/\text{g}$, $13.8 \text{ m}^2/\text{g}$ and $9.5 \text{ m}^2/\text{g}$, respectively.

3.2. Adsorption performance

The removal performance of the ZnS NCs sorbent for the various heavy metals is shown in Fig. 2. From Fig. 2, it can be seen that the removal efficiencies of Hg^{2+} , Cu^{2+} , Pb^{2+} and Cd^{2+} after 5 min were over 99.9%, 99.9%, 90.8% and 66.3%, respectively. Obviously, the ZnS NCs sorbent (S-0.5 h) was able to remove these heavy metals quickly and efficiently. The analytical results of the products show that the major reaction products were HgS, CuS, PbS and CdS. In addition, the removal performances of the ZnS NCs sorbent (S-0.5 h)

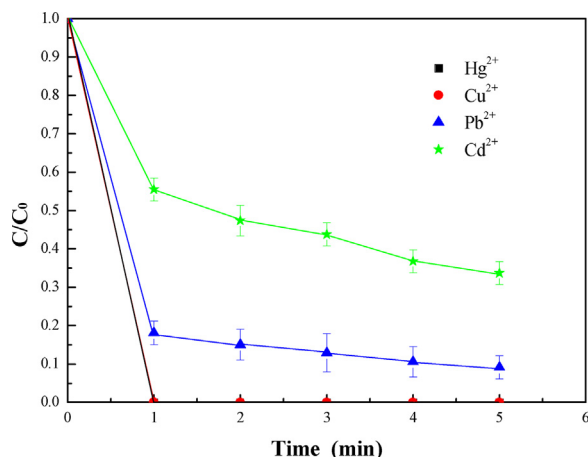


Fig. 2. The adsorption of heavy metals by ZnS NCs sorbent. One-hundred milligrams of ZnS NCs sorbent (S-0.5 h) was added to 50 mL of HgCl_2 , $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ and CdCl_2 solutions with stirring (400 r/min). The initial heavy metals concentrations were all 1.0 mmol/L. The pH value of the heavy metal solutions was approximately 5.5.

for heavy metals under different initial heavy metal concentrations from 100.0 mg/L to 1.0 mg/L were investigated (Table S2, Supporting information). All four heavy metals were removed efficiently. From the heavy metal removal experiments, it was found that the removal efficiencies of these four heavy metals were related to the solubility product constants (K_{sp}) of their sulfides. The K_{sp} values of HgS , CuS , PbS and CdS were approximately 1.6×10^{-52} , 6.3×10^{-36} , 8.0×10^{-28} and 8.0×10^{-27} between 18 and 25 °C [27]. The removal efficiency of a heavy metal is higher when the K_{sp} of its sulfide is lower. Accordingly, the removal efficiency of Hg^{2+} is higher than that of Cd^{2+} .

Sometimes other metal ions in wastewater or the pH value may affect the adsorption of a particular heavy metal by a sorbent. However, there is no apparent effect of other metal ions, such as Ca^{2+} and Co^{2+} , on the removal of heavy metals by ZnS NCs sorbent according to previous research [23,28]. Additionally, ZnS NCs sorbent are stable when the pH value of the wastewater is greater than 3 [23,28]. Consequently, ZnS NCs sorbent could be an ideal choice for the removal of heavy metals from wastewater.

3.3. Adsorption isotherms

Fig. 3 presents the typical adsorption isotherms of Hg^{2+} on a ZnS NCs sorbent (S-1.0 h) at a pH of 5.5 in the studied concentration ranges. The fitting results based on the two isotherm models are shown in Fig. 3. It can be seen that the adsorption of Hg^{2+} on ZnS NCs sorbent was better estimated by the Langmuir model with a correlation coefficient (R^2) of 0.999 for Hg^{2+} concentrations ranging from 5.0 to 678.0 mg/L. The Langmuir model was also better than the Freundlich model for fitting the adsorption isotherm of ZnS NCs sorbent (S-1.0 h) for Cu^{2+} , Pb^{2+} and Cd^{2+} (Fig. S6 and Table S3, Supporting information).

3.4. Adsorption kinetics

The adsorption kinetics parameters are key factors for the design of adsorption reactors in industrial applications. The fitting results based on the two kinetic models are shown in Fig. 4. The values for the kinetic models are shown in Table S4 (Supporting information). It is clear that the pseudo-first-order kinetic model fitted well with the kinetic data.

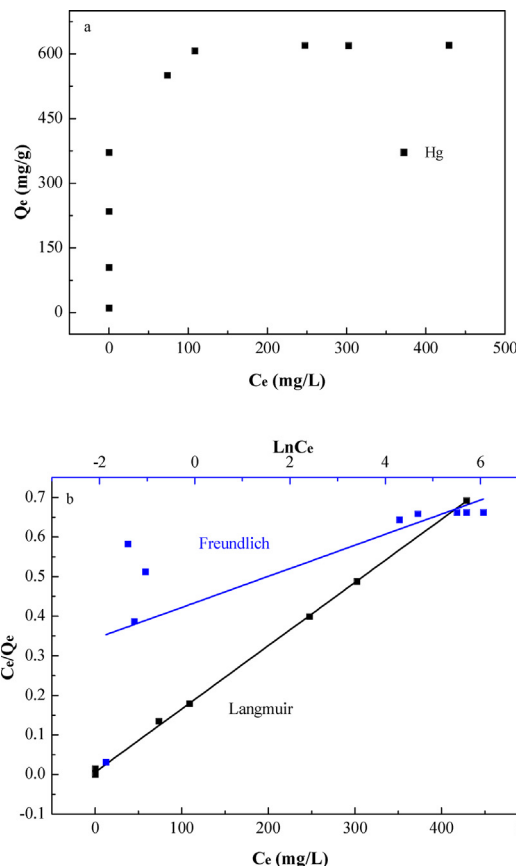


Fig. 3. Adsorption isotherm of Hg^{2+} on ZnS NCs sorbent. Twenty milligrams of sorbent (S-1.0 h) was added to 50.0 mL of the heavy metals solution in sealed vials with concentrations ranging from 5.0 to 678.0 mg/L. The vials were stirred for 24 h to reach equilibrium. The pH value of the heavy metal solutions was approximately 5.5.

Table 1
Separation factor (α_j^i) of different heavy metal ions.

$j \setminus i$	Hg^{2+}	Cu^{2+}	Pb^{2+}
Cu^{2+}	1,329.2		
Pb^{2+}	45,464	34.2	
Cd^{2+}	210,910.9	158.7	4.6

3.5. The adsorption selectivity of ZnS NCs sorbents toward different heavy metals

As shown in Fig. 5, when only 10.0 mg of sorbent (S-0.5 h) was added to 50.0 mL of the mixed solution, the removal efficiencies of Hg^{2+} , Cu^{2+} , Pb^{2+} and Cd^{2+} were 99.8%, 34.8%, 1.0% and 0.2%, respectively. The removal efficiencies of Cu^{2+} , Pb^{2+} and Cd^{2+} gradually increased with the increasing of sorbent dosage. From Table 1, it can be seen that the separation factors of Hg^{2+} with respect to Cu^{2+} , Pb^{2+} and Cd^{2+} were 1329.2, 45464.0 and 210910.9, respectively. Therefore, Hg^{2+} could more easily be adsorbed by ZnS NCs than Cu^{2+} , Pb^{2+} and Cd^{2+} . Interestingly, the adsorption selectivity of the sorbent for various heavy metals was also related to the K_{sp} of their sulfides. A heavy metal is preferentially adsorbed by the ZnS NCs sorbent when the K_{sp} of the heavy metal sulfide is lower. Thus, Hg^{2+} was first adsorbed by ZnS NCs sorbent, followed by Cu^{2+} , Pb^{2+} and Cd^{2+} . The high adsorption selectivity of the ZnS NCs sorbent provides the possibility for separating multiple heavy metals.

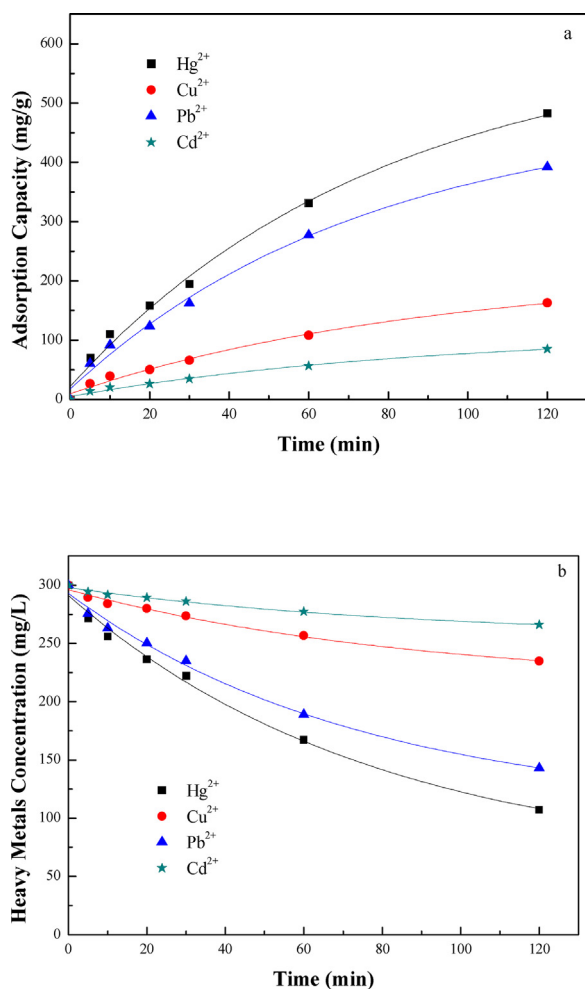


Fig. 4. Adsorption kinetics of heavy metal ions on ZnS NCs sorbent. Twenty milligrams of sorbent (S-1.0 h) was added to 50.0 mL of the heavy metals solution. The heavy metals concentration was 300.0 mg/L. The stirring rate was 400 r/min. The pH value was approximately 5.5.

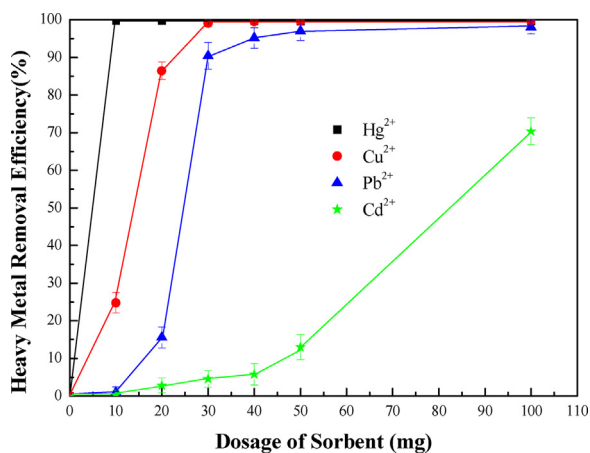


Fig. 5. The adsorption selectivity of ZnS NCs sorbent (S-0.5 h) toward different heavy metals.

Ten to one-hundred milligrams of ZnS NCs sorbent (S-0.5 h) was added to 50 mL of the mixed heavy metal solution with stirring (400 r/min) for a 24 h reaction time. The heavy metal concentrations in the mixed solution were all 0.4 mmol/L. The pH value of the heavy metal solutions was approximately 5.5.

3.6. The mutual exchange adsorption procedure of heavy metals

To test the performance of the used sorbents (S-0.5 h), CdS NCs, PbS NCs and CuS NCs sorbents were used to treat the simulated wastewater containing Pb²⁺, Cu²⁺ and Hg²⁺, respectively. For a nanosorbent, its size is usually the critical parameter that affects its adsorption performance. Previous research has also demonstrated that a small-size sorbent has a better adsorption capacity and adsorption rate than a larger one [23,28]. Therefore, the NCs size and layer thickness of CdS, PbS and CuS NCs sorbents are important to their removal performance for heavy metals. According to the TEM of CdS, PbS and CuS NCs sorbents, which are shown in Fig. 6, it can be seen that all of the ZnS, CdS, PbS and CuS NCs were present as coatings on the surface of alpha-Al₂O₃ and that the layer thickness of the NCs was 20–25 nm. In addition, as shown by HRTEM (Fig. S7, Supporting information), the coating layer is composed of approximately 4–8 nm NCs. There is no remarkable change of the layer thickness or size of the NCs after cation exchange. Theoretically, the used sorbents could also effectively remove heavy metals. Fig. 7 shows that the Hg²⁺, Cu²⁺ and Pb²⁺ removal efficiencies were approximately 99.7%, 86.5% and 39.1% in 5 min, respectively. The results of the adsorption experiment indicated that the used sorbents could continue to remove other heavy metals. Moreover, the concentrations of the heavy metal ions were detected during the adsorption process. From Fig. 8, it can be seen that the Hg²⁺ concentration decreased quickly with an increase in the Cu²⁺ concentration, which meant that Hg²⁺ was adsorbed by the sorbent while Cu²⁺ was released from the sorbent. Meanwhile, the amount of removed Hg²⁺ was close to the amount of released Cu²⁺, which implied that Hg²⁺ was replaced by Cu²⁺. Similar results were found when PbS and CdS NCs sorbents were used to remove Cu²⁺ and Pb²⁺, respectively (Fig. S8, Supporting information). This result indicates that Hg²⁺, Cu²⁺ and Pb²⁺ were replaced by Cu²⁺, Pb²⁺ and Cd²⁺ based on the ion exchange reaction, respectively. The reaction pathways could be deduced as following reactions.



The above results provided us with a possible opportunity to remove and separate multiple heavy metals sequentially. For example, when ZnS NCs sorbent is added to simulated wastewater containing multiple heavy metals, those metals can be adsorbed by ZnS NCs and generate HgS, CuS, PbS and CdS at the same time. Then, the CuS, PbS and CdS will be converted to additional HgS and will release Cu²⁺, Pb²⁺ and Cd²⁺ if there is enough Hg²⁺ in the wastewater. Eventually, most of the adsorption product on the sorbent will be HgS, which is easy to be separated from the mixed solution. The rest of the Cu²⁺, Pb²⁺ and Cd²⁺ in the mixed solution can be removed and separated by using the same treatment.

3.7. The sequential removal and separation of heavy metals

Cumulative adsorption experiments were conducted to test and verify the feasibility of the sequential removal of multiple heavy metals and the separation technology. The experimental results are shown in Fig. 9.

As shown in Fig. 9a (Run1), it can be seen that most of the Hg²⁺, Cu²⁺, Pb²⁺ and Cd²⁺ were adsorbed by the sorbents of reactors A, B, C and D, respectively. The mole ratio of heavy metals to sorbents in Table 2 showed that the mole ratios of Hg²⁺, Cu²⁺ and Pb²⁺ in sorbent A were approximately 82.1%, 10.7% and 7.2%, respectively. Then, the mole ratio of Hg²⁺ increased to approximately 91.0% after the second round of experiments (Run2). This result indicates that these four heavy metals could initially be separated by ZnS NCs

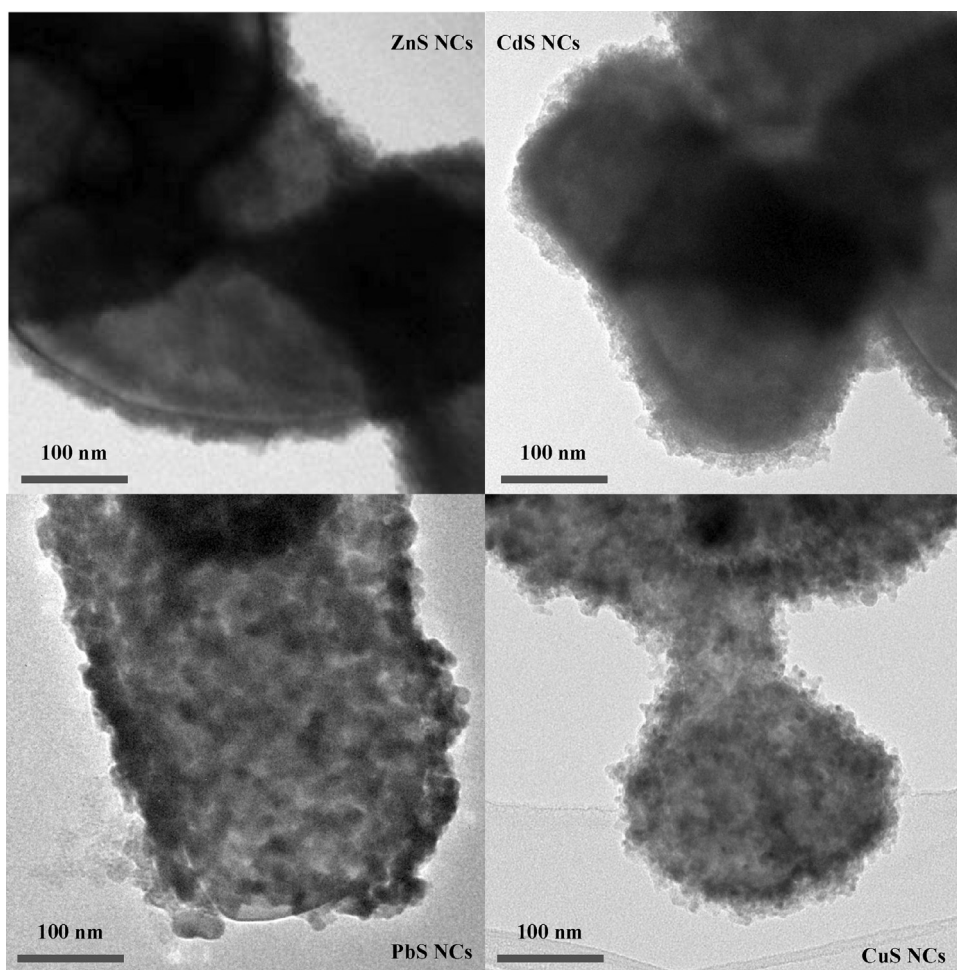


Fig. 6. TEM images of ZnS, CdS, PbS and CuS NCs sorbents.

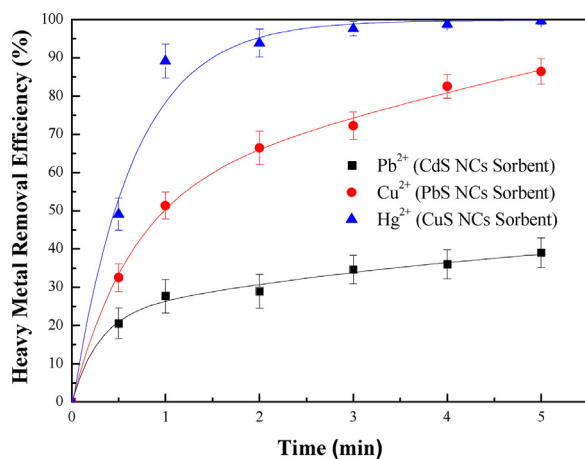


Fig. 7. The mutual substitution adsorption of heavy metals. One-hundred milligrams of CdS, PbS and CuS NCs sorbents (S-0.5 h) were added to 50 mL of $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and HgCl_2 solutions with stirring (400 r/min), respectively. The $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and HgCl_2 concentrations were all 1.0 mmol/L. The pH value of the heavy metal solutions was approximately 5.5.

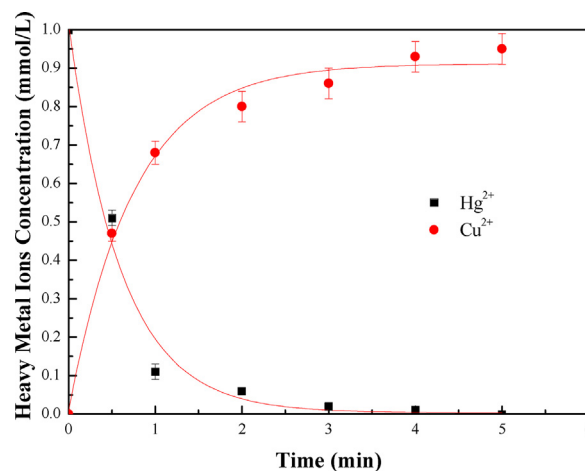


Fig. 8. Hg^{2+} and Cu^{2+} concentrations in solution in the mercury removal process. One-hundred milligrams of CuS NCs sorbents were added to 50 mL of a HgCl_2 solution with stirring (400 r/min). The HgCl_2 concentrations were all 1.0 mmol/L. The pH value of the heavy metal solutions was approximately 5.5.

sorbent. The separation effect will be improved if the experimental conditions are optimized. Finally, all of these heavy metals could be exchanged by Zn^{2+} . It is easy to find a particular sorbent such as raw

or modified dolomite to remove Zn^{2+} from wastewater [29]. Eventually, all of these heavy metals could be removed and separated sequentially.

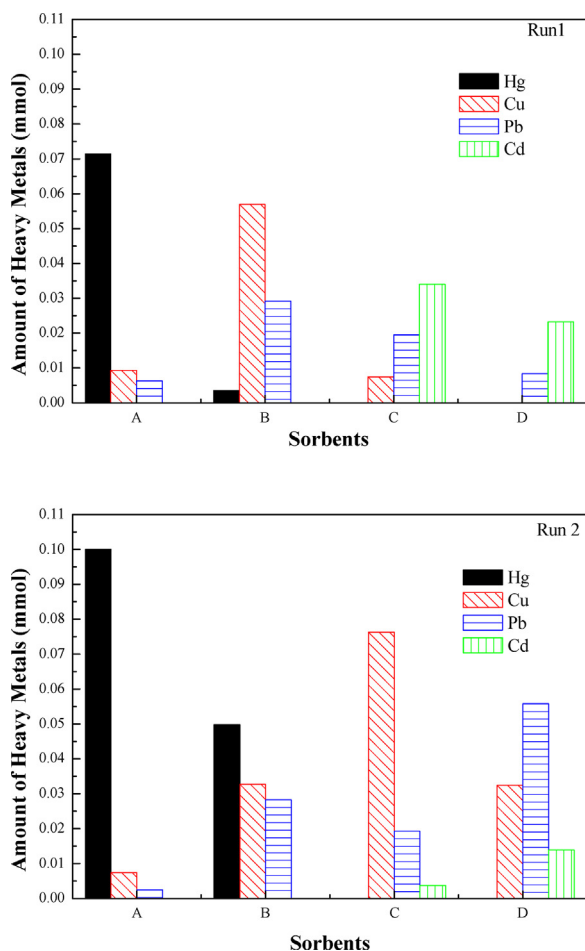


Fig. 9. The cumulative adsorption experimental results.

Table 2
Mole Ratio of Heavy Metals in Each Sorbent.

Sorbent	Hg (%)	Cu (%)	Pb (%)	Cd (%)
A (Run1)	82.1	10.7	7.2	0
B (Run1)	3.9	63.5	32.6	0
C (Run1)	0	12.3	32.0	55.7
D (Run1)	0	0	26.5	73.5
A (Run2)	91.0	6.7	2.3	0
B (Run2)	44.9	29.5	25.5	0
C (Run2)	0.1	76.8	19.4	3.7
D (Run2)	0.1	31.7	54.7	13.6

4. Conclusions

A ZnS nanocrystal sorbent was synthesized for the heavy metals removal from wastewater. It showed an extraordinary adsorption capacity to aqueous heavy metals ions based on the ion exchange reaction. Meanwhile, it was found that the heavy metal is more preferred to be adsorbed when the K_{sp} of its sulfide is lower. And the heavy metal adsorbed on sorbent could be replaced by other heavy metal when the sulfide of the latter is more stable than that of the former. This mutual substitution character of metal sulfides was utilized for the separation of multiple heavy metals. According to the cumulative adsorption experiments results, all of the other heavy metals could be adsorbed and separated from the wastewater one by one. The results showed that this sequential adsorption and separation method based on cation exchange is a promising technology to remove and reclaim multiple heavy metals from wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2017.08.072>.

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