

# Rapid and Effective Adsorption of Mercury(II) in Aqueous Solution Using CuS Composites Supported by SiO<sub>2</sub> Aerogel

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**Abstract**—Nowadays, pollution caused by heavy metals has become an urgent problem to be solved today, especially Hg(II) in heavy metals can cause diarrhea, neurological weakness and serious life threatening. Therefore, new materials are urgently needed to adsorb Hg(II) ions in water. Herein, we loaded sulfide (CuS) particles onto SiO<sub>2</sub> aerogel obtained from boron slag, which was used to prepare new SiO<sub>2</sub>/CuS adsorbents. The influence of pH in the solution, the initial Hg(II) ion concentration, contact time, and co-existing cations on the adsorption behavior of mercury(II) ions by SiO<sub>2</sub>/CuS was investigated. At the optimal conditions, the removal rate and adsorption amount of mercury(II) ions by SiO<sub>2</sub>/CuS reached 93.16% and 232.90 mg/g within 60 min. The results show that the adsorption process of SiO<sub>2</sub>/CuS is consistent with the PSO model. The adsorption mechanism of SiO<sub>2</sub>/CuS on Hg(II) ions is a chemisorption process.

**Index Terms**—Adsorption, SiO<sub>2</sub> aerogel, mercury (II), copper sulfide

## I. INTRODUCTION

The rapid development of the world and the increase in human activities have caused many environmental problems and irreversible pollution of the environment [1–3]. The increase of common organic pollutants such as dyes, phenols and toxic heavy metal ions has led to serious pollution of water bodies [4–6], and heavy metal ions such as mercury ions (Hg(II)), cadmium ions (Cd(II)) and nickel ions (Ni(II)), at very low concentrations will make water bodies toxic [7], and it is worrying that these heavy metal ions will keep moving in the water. Therefore, it is urgent to remove harmful heavy metal ions from polluted water bodies.

Sulfur, which belongs to the VI main group element with oxygen, has a high affinity for Hg(II). The metal sulfides used for mercury removal mainly include copper sulfide, calcium sulfide, iron sulfide, zinc sulfide, etc. Studies have shown that the loading of sulfur in SiO<sub>2</sub> aerogel is an important factor affecting the effectiveness of mercury removal, and the pure metal sulfide itself is composed of sulfur and metal atoms, and the coverage of sulfur is maximized, so it has good performance of mercury removal [8]. Metal sulfides can be obtained by sulfiding metal oxides with sulfur solutions or sulfur-containing gases, or by preparing pure metal substances by co-precipitation [9].

Boron mud contains a large amount of elemental silicon, the content varies slightly depending on the boron mud production process, the elemental silicon content is generally around 25%, the crystalline form of elemental silicon in boron mud is relatively single, mainly present in quartz,

which makes the elemental silicon in boron mud very easy to extract, and the alkali leaching method is generally used to extract the elemental silicon in boron mud, the boron mud is immersed in a specific concentration of alkali, and the filtrate is collected by filtration [10]. Zhang and Ning *et al.* [11] tried to use molten sodium hydroxide to separate the elemental silicon and made some progress. The filtrate obtained from the alkali leaching method can be simply purified to obtain a solution of water glass, which is widely used and is now a common industrial raw material for the preparation of various silicon products such as mesoporous materials of silicon [12]. Although the recycling of boron sludge waste has been studied by scholars, very few of them can be industrially produced, mainly because the production cost of boron sludge waste reuse is too high and the added value of the produced products is low, which has no economic benefits [13]. Therefore, it is urgent to find a new practical route for using boron sludge waste. The extraction of silicon elements from boron sludge to prepare SiO<sub>2</sub> aerogel may be a practical approach, and the preparation of SiO<sub>2</sub> aerogel from boron sludge has not been reported in the literature [14].

According to the above results, in order to explore the application of SiO<sub>2</sub> aerogel, based on the characteristics of good adsorption of sulfide, this study produced a simple process to introduce CuS into SiO<sub>2</sub> aerogel, and made SiO<sub>2</sub>/CuS.

## II. MATERIALS PREPARATION

The process of preparing SiO<sub>2</sub> aerogel using water glass as the silicon source is as follows: dilute the water glass with pure water, adjust the pH of the diluted water glass to 2, and hydrolyze it at these two pH values for several hours, and then adjust the pH value using ammonia and hydrochloric acid, and after it gels, add ethanol for aging, leave it for a period of aging, remove the aging solution, add hexane solvent replacement, and after a period of replacement, remove the modified aerogel was dried in an oven at a gradient temperature and under normal pressure to obtain SiO<sub>2</sub> aerogel.

To obtain SiO<sub>2</sub>/CuS, SiO<sub>2</sub> aerogel (0.5 g) and 100 ml of water were added to the flask and sonicated for 0.5 h. A certain amount of ammonium sulfide and CTAB were added to the above mixture and then 0.65 g of copper sulfate solution was added dropwise to the above solution and stirred for 3 h.

Boron sludge is obtained locally. Cetyltrimethyl-Ammonium Bromide (CTAB), ammonium sulfide solution and copper sulfate (CuSO<sub>4</sub>·5H<sub>2</sub>O) were purchased from Tianjin Daomao Chemical Reagent Company (Tianjin, China). Mercurium nitrate was supplied by Guizhou Tongren Tailuier Chemical Plant (Guizhou, China).

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The adsorption capacity ( $Q_e$ , mg/g) of the adsorbent C/CuS and the corresponding removal efficiency ( $R$ , %) were measured based on Eqs. (1) and (2).

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

$$R = \frac{(C_0 - C_e)}{C_0} \cdot 100\% \quad (2)$$

where,  $C_0$  (mg/L) and  $C_e$  (mg/L) are respectively the initial concentration of mercury (II) ions and the equilibrium concentration at adsorption equilibrium.  $m$  (g) is the mass of the adsorbent C/CuS, and  $V$  (L) is the volume of the solution containing heavy metal mercury(II) ions.

### III. RESULTS AND DISCUSSION

The change of pH during adsorption has a great influence on the adsorption process, and we used solutions with different pH values (pH = 2–9) for adsorption. Fig. 1 shows the effect of SiO<sub>2</sub>/CuS on Hg(II) removal and zeta potential at different pH values. Zeta potential gradually decreases with pH = 2–9, and the SiO<sub>2</sub>/CuS surface shows positive charge when pH < 3.8. When pH = 2–4, the removal ability of SiO<sub>2</sub>/CuS increased rapidly. The removal capacity of SiO<sub>2</sub>/CuS increased slightly when pH = 4–7, while the adsorption capacity decreased slightly when the pH = 4–9. According to the properties related to the functional groups on the surface of SiO<sub>2</sub>/CuS, the adsorption capacity was maximum when pH = 7.

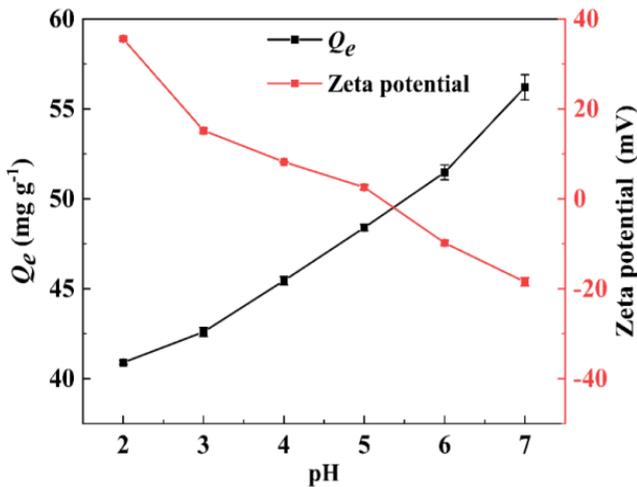


Fig. 1. The effect of pH on the adsorption capacity and zeta potential of SiO<sub>2</sub>/CuS for Hg(II).

Fig. 2 investigates the effect of different ion concentrations ( $C_0$ ) on the adsorption capacity of SiO<sub>2</sub>/CuS. It can be clearly found that the removal capacity of SiO<sub>2</sub>/CuS increases rapidly with the change of Hg(II) ion content when  $C_0 = 50$ –350 mg/L. When the content of Hg(II) reached 350 mg/L, the SiO<sub>2</sub>/CuS removal capacity stabilized. When  $C_0 = 350$ –450 mg/L, the adsorption amount of Hg(II) ions increased slowly. This is because the increase in concentration will improve the active sites of the adsorbent, but too large a concentration will lead to saturation of the sites and affect the removal efficiency.

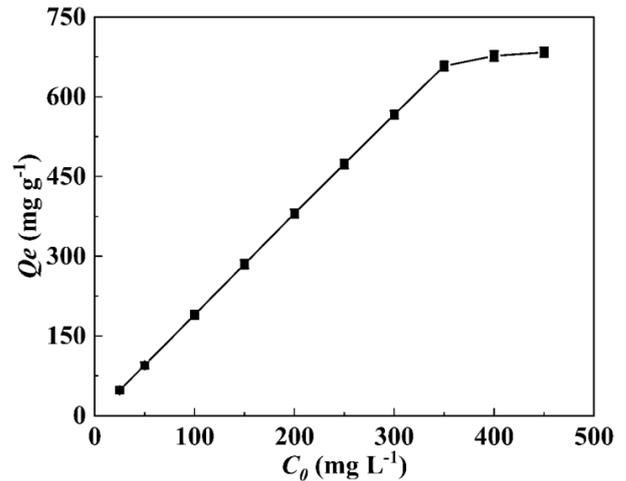


Fig. 2. The relationship between the initial concentration of Hg(II) and the adsorption effect of SiO<sub>2</sub>/CuS.

The isothermal model curves are shown in Figs. 3 and 4, where the  $R^2$  values of Langmuir ( $R^2=0.9885$ ) are higher than the  $R^2$  values of Freundlich ( $R^2=0.9678$ ). The theoretical  $Q_m$  ( $Q_m=680.32$  mg/g) of SiO<sub>2</sub>/CuS calculated from the L model agrees with the experimental value. It shows that the removal process of Hg(II) ions by SiO<sub>2</sub>/CuS follows the Langmuir model and the adsorption process is chemisorption process.

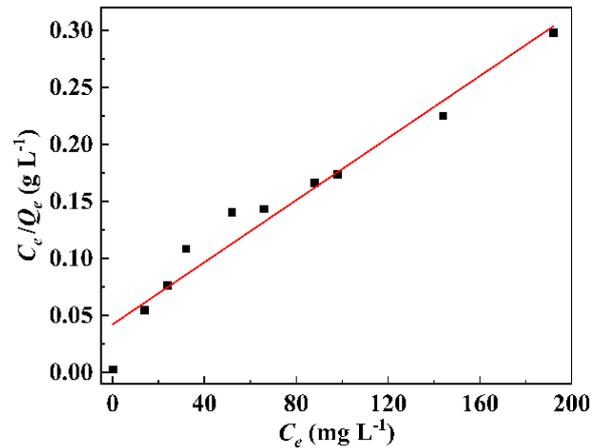


Fig. 3. Langmuir isotherm plots for the adsorption Hg(II) ions.

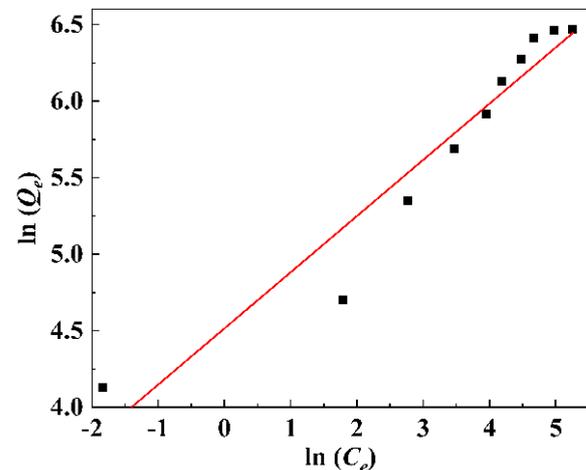


Fig. 4. Freundlich isotherm plots for the adsorption Hg(II) ions.

Fig. 5 shows the variation of removal capacity with contact time. When the adsorption time was varied from 0–180 min. In the initial stage of SiO<sub>2</sub>/CuS adsorption (60 min), the rate of SiO<sub>2</sub>/CuS removal gradually decreased and finally reached the adsorption equilibrium. Because, SiO<sub>2</sub>/CuS has abundant removal sites, the repulsive force between the Hg(II) ions adsorbed on the surface of SiO<sub>2</sub>/CuS and the Hg(II) ions in solution will exist with time change, resulting in no significant change in the adsorption amount.

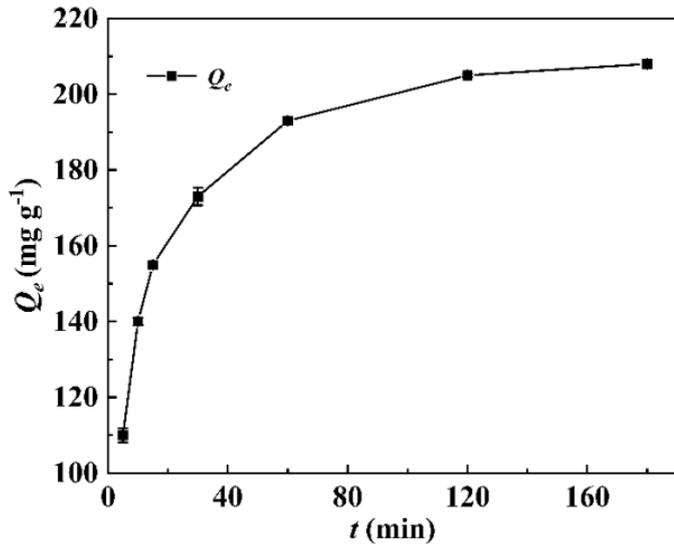


Fig. 5. The relationship between the contact time and the adsorption effect of SiO<sub>2</sub>/CuS.

To investigate the removal mechanism, in this study, pseudo-first order (PFO) and pseudo-second order (PSO) models were investigated.

Figs. 6 and 7 show the adsorption isotherms of SiO<sub>2</sub>/CuS. PSO (R<sup>2</sup> = 0.9993) is better than PFO (R<sup>2</sup> = 0.9808), which also indicates that PSO is consistent with the adsorption process of SiO<sub>2</sub>/CuS. The removal of Hg(II) ions by SiO<sub>2</sub>/CuS is a chemisorption process.

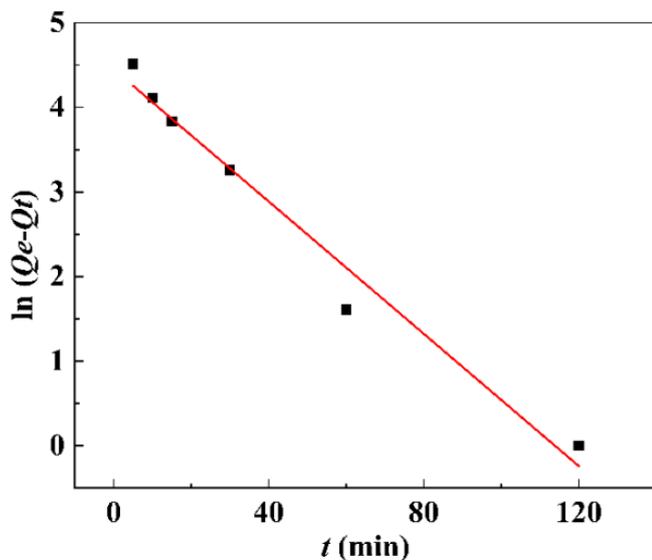


Fig. 6. Fit of kinetic data to pseudo-first-order model.

The coexistence of cations affects the adsorption sites of SiO<sub>2</sub>/CuS. The effect of the presence of cations on SiO<sub>2</sub>/CuS was investigated as shown in Fig. 8. It can be found that the presence of coexisting cations does not compete for the removal ability of SiO<sub>2</sub>/CuS, and the adsorbent of SiO<sub>2</sub>/CuS has good selectivity for Hg(II) ions (The initial concentration of all cations was 0.01 M).

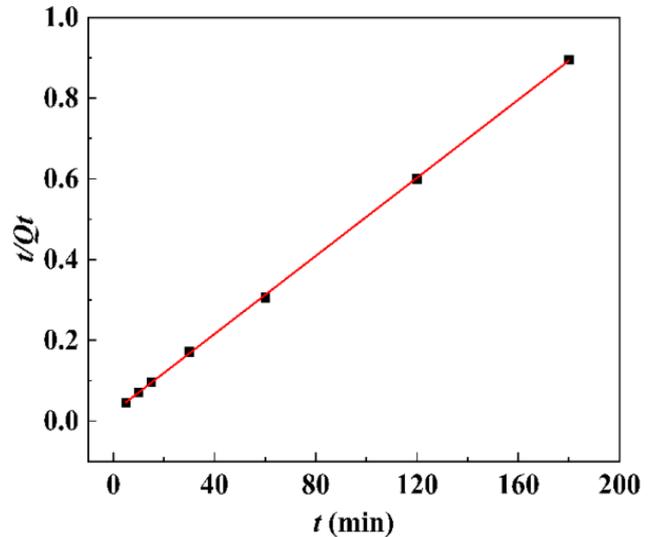


Fig. 7. Fit of kinetic data to pseudo-second-order model.

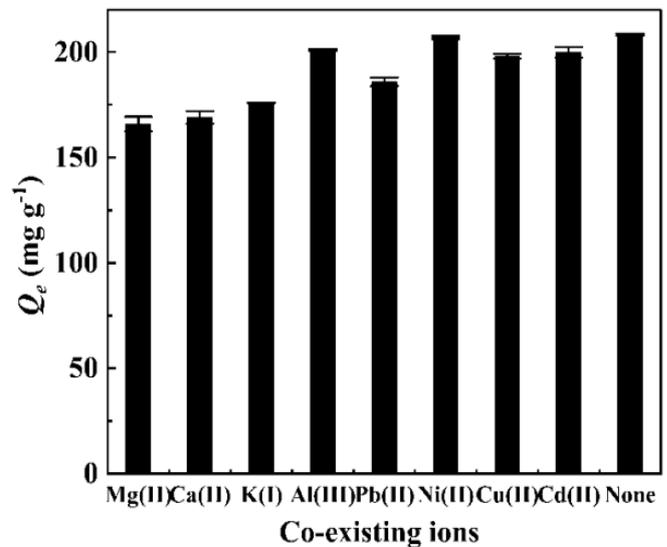


Fig. 8. Effect of co-existing ions on adsorption Hg(II) ions.

#### IV. CONCLUSION

We developed an efficient adsorbent by introducing copper sulfide on the surface of SiO<sub>2</sub> aerogel extracted from boron mud. The adsorption capacity and removal rate were 232.90 mg/g and 93.16% at pH 7 with 20 mg C/CuS, 50 mL of 100 mg/L Hg(II) solution for 1 h. The adsorption effect was good.

#### FUNDING

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Heavy metal ions are widely present in the wastewater.

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