Synthesis of amino-functionalized silicon fiber cloth composite for effective removal of Cu (II) from wastewater

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Abstract. In this paper, amino modified silica fiber cloth (KSF) was prepared by the chemical grafting method. The SEM, FTIR and TGA techniques were employed for the characterization of the silica fiber cloth (SF) and KSF. FTIR analysis suggests that functional amino groups of γ-aminopropyl triethoxysilane (KH550) were grafted on the surface of KSF. The influence of single factor on adsorption performance was studied. The results showed that the adsorption capacity of KSF can reach 178.46 mg·g⁻¹, the experimental adsorption data were fitted closely by pseudo-second-order kinetic model, adsorption isotherms were simulated well by Langmuir model. Thermodynamic analysis revealed that the adsorption process was endothermic, entropy-driven and spontaneous. The adsorption-desorption experiments demonstrated that KSF showed no significant removal efficiency loss even after ten consecutive cycles, indicating the good stability of prepared KSF material. Our findings suggested the KSF can serve as potential candidates for the practical application of wastewater containing heavy metals.

1. Introduction

Copper is widely used in electrical, metal finishing, painting, wood manufacturing, pigment, and other industries. And this results in an increase of Cu²⁺ content in the environment [1]. If people intake long-term or excessive copper, it will lead to copper poisoning and even death [2]. Therefore, it is essential to remove excess copper in industrial wastewater before it is discharged into surface water and groundwater [3].

There have been many technologies including membrane separation, chemical precipitation, electrochemical removal, ion exchange and adsorption. Among the existing techniques, adsorption is considered to be an effective and low-cost technique for removing toxic heavy metal ions in wastewater [4]. In recent years, adsorbents constructed from inorganic oxide systems have shown excellent performances in removing heavy metals in wastewater [5]. SiO₂ materials are particularly prominent for removing heavy metals, due to its large surface area, excellent thermal stability and easy modification [6]. Many research teams around the world have conducted studies on the silica-based adsorbents, showing that they have the potential to be used as high-efficiency heavy metal adsorbents [7-8]. However, it is still limited in environmental application because silica has limited active functional groups. To overcome this limitation, promising functional modified silica materials have recently been used to remove toxic substances in wastewater [6,9].
In the literature [10], the fabric has a good effect on removing Cu\(^{2+}\) ions from water, and its adsorption capacity for Cu\(^{2+}\) ions can reach 122.4 mg∙g\(^{-1}\). Other studies have shown that the hydrogen bonds on the interface increase after the reaction of SiO\(_2\) and KH550 [11]. Combined with the above research, we prepared an amino-functionalized silica fiber material (KSF) by modifying with silane coupling (KH550). The adsorption ability of SFK for Cu\(^{2+}\) ion was investigated by pH, initial Cu\(^{2+}\) ion concentration, adsorption temperature, regeneration and reuse. We also studied adsorption kinetics, isotherms and thermodynamics to understand the mechanism of KSF adsorption of Cu\(^{2+}\) ion. From the perspective of green chemistry, this research has achieved the purpose of recyclability and expanded the application of silicon-based cellulose materials in the field of heavy metal governance, providing a theoretical basis for its use as an adsorption material.

2. Materials and methods

2.1. Materials
γ-aminopropyl triethoxysilane (KH550, NH\(_2\)(CH\(_2\))\(_3\)Si(OC\(_2\)H\(_5\))\(_3\)) was purchased from Youpu Chemical Co., Ltd. (Nanjing, China); Silica fibre cloth was purchased from HANO New Materials Co., Ltd. (Anhui, China); sodium hydroxide, acetone, hydrochloric acid, hydrogen nitrate, copper sulfate, and absolute ethanol were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Methods
First, the silica fiber cloth (10 g) was soaked in acetone for 24 h, and plastic wrap was used to seal the beaker mouth to prevent acetone volatilization, in order to remove the organic solvent or pollutants on its surface. Then a certain quantity of silica fiber cloth was impregnated in 6 mol·L\(^{-1}\) HNO\(_3\) and stirred at 60 °C for 1 h. Then it was washed repeatedly with distilled water to neutral and dried at 110 °C for 5 h, named SF. Add 0.8 mL KH550 to 50 mL absolute ethanol in stoppered conical flask, after stirring for 1 h, then 2 g of SF was added and reacted at 80 °C for 12 h in a thermostatic oscillator. Finally, the resulting sample was washed with anhydrous ethanol to remove excess coupling agent, and dried at 60 °C, denoted as KSF.

2.3. Characterization
SEM images were recorded by scanning electron microscopy (S-4800, Japan). FTIR spectra were performed by Fourier transform infrared spectroscopy ( Nicolet 5700, Thermo, America) in the wavenumber range from 4000 to 400 cm\(^{-1}\). The thermo gravimetric analysis (TGA) of SF and KSF was carried out by using a TAQ 600 instrument (TA Instruments, Inc., USA) thermo-gravimetric analyzer at a heating rate of 10 °C min\(^{-1}\) from 30 to 800 °C under N\(_2\) atmosphere. The Cu\(^{2+}\) ion residual concentration was measured by atomic absorption spectrophotometry (AAS, WFX-120, Beijing Rayleigh Analytical Instrument Co., Ltd.).

2.4. Batch adsorption experiment
Sorption of Cu\(^{2+}\) on SF and KSF was carried out by batch adsorption technology in 50 mL polyethylene centrifuge tube, and a series of adsorbents and stock solutions were added to them to achieve the required concentrations of different components. And adjust the system to the desired pH with 0.1 mol·L\(^{-1}\) HCl or NaOH. All adsorption experiments were repeated three times, and used the mean values for data analysis. The Cu\(^{2+}\) adsorption sample (KSF-Cu) was obtained after adsorption of Cu\(^{2+}\) and drying. The removal efficiency (φ) and adsorption capacity (q, mg∙g\(^{-1}\)) were determined by Formulas (1) to (2):

\[
\varphi = \frac{c_0 - c}{c_0} \times 100\% \quad (1)
\]

\[
q = \frac{(c_0 - c) \times v}{w} \quad (2)
\]
where \(c_0\) (mg·L\(^{-1}\)) and \(c\) (mg·L\(^{-1}\)) are the Cu\(^{2+}\) ion initial concentration and Cu\(^{2+}\) ion final concentration in the solution, respectively. \(w\) (g) is the dosage of adsorbent, \(v\) (L) is the volume of adsorption solution.

2.5. Desorption experiment

KSF-Cu was added to 20 mL 0.1 mol·L\(^{-1}\) HCl solution, stirred for 4 h at 800 rpm. Then sample was carried out 10 consecutive adsorption-desorption experiments to study its regeneration performance.

3. Results and discussion

3.1. Characterization of the adsorbents

Figure 1 presents the SEM images of KSF and SF. As can be seen from Figure 1(a), the morphology and size of KSF after modified of KH550 (Figure 1(b)) was similar to that of SF, indicating that KH550 grafted onto the surface of SF had no significant effect on the microstructures of SF. And the surface of KSF becomes rough and there are many fine particles on the surface of the fiber, mainly because the extra KH550 accumulated on the surface of KSF.

Figure 2 showed the absorption peaks at 462 cm\(^{-1}\), 787 cm\(^{-1}\) and 1012 cm\(^{-1}\) are the characteristic peaks of Si−O−Si. The wide absorption peak at 3353 cm\(^{-1}\) is the characteristic peak of Si−OH and O−H stretching vibration. The absorption peak at 1633 cm\(^{-1}\) is assigned to the O−H bending vibration. Compared with SF, the absorption peaks at 2937.5 cm\(^{-1}\) and 2883.2 cm\(^{-1}\) are characteristic peaks of stretching vibration in methyl and methylene groups on KSF [12]. The above results verify that KH550 was successfully grafted to the surface of KSF.

It was found that the total weight loss of SF and KSF in Figure 3 was 2.15 wt% and 9.74 wt%, respectively. In the study temperature range, the weight loss of SF comes from the loss of its physically adsorbed water and structural water. For KSF, except for the loss of moisture below 300 °C, the grafted organic components (KH550) begin to rapidly decompose at temperatures above 300 °C, which were the steps of the decomposition of organic ingredients grafted on the surface of KSF, and the breaking of a chemical bond between KH550 and KSF. Obviously, the weight loss rate of KSF was much higher.
than that of SF over the investigated temperatures range, further verifying that KH550 was successfully grafted onto the surfaces of SF, which is consistent with FTIR analysis.

Figure 4. Evaluation of Cu$^{2+}$ ion adsorption with varying the initial pH solution (a), adsorbent dosage (b), initial concentration (c) and reaction temperature (d).

3.2. Adsorption studies
As shown in Figure 4(a), the removal efficiency increased significantly from pH 2 to 5, and then slowly changed. At a lower pH value, owing to the strong electrostatic repulsion between the protonated amino groups of KSF and Cu$^{2+}$ ions, and therefore reduces the adsorption. As the pH value increases, due to the increase in the deprotonation of the amino group of KSF, it is easier to form a chelate between Cu$^{2+}$ ions and KSF, and therefore increased the adsorption. However, Cu$^{2+}$ is easy to form into precipitate when the pH value exceeds 5.6. In the range of pH in this study, pH 5 is the optimal solution for Cu$^{2+}$ adsorption.

As shown in Figure 4(b), with the increase of the dosage of the adsorbent, the removal efficiency of Cu$^{2+}$ increased, and when the dosage of adsorbent reached 16 mg, the removal efficiency of Cu$^{2+}$ can be close to 100%. This may be the greater the amount of adsorbent, the more active adsorption sites are provided. Therefore, 10 mg is selected for further research.

As shown in Figure 4(c), with the increase of initial Cu$^{2+}$ ion concentration, the removal efficiency gradually decreased, and when the concentration of Cu$^{2+}$ is lower than 100 mg·L$^{-1}$, the removal efficiency remains above 95%. This can be explained that the adsorption sites are unsaturated when the initial concentration is low, while the competition between ions for available adsorption sites increases at higher concentrations, and therefore, the adsorption sites are saturated and the complexation of Cu$^{2+}$ and KSF became difficult.

As shown in Figure 4(d), the removal efficiency gradually increases with the increase of temperature, which indicates that Cu$^{2+}$ adsorption is an endothermic process.

3.3. Adsorption kinetics
The pseudo-first-order kinetic model, pseudo-second-order kinetic model, and the intraparticle diffusion model was calculated by Formulas (3) to (5):
\[ q_t = q_e (1 - e^{-k_1 t}) \]  
\[ q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \]  
\[ q_t = k_p \sqrt{t} + C \]

where \( k_1 (\text{min}^{-1}) \), \( k_2 (\text{g} \cdot \text{mg}^{-1} \text{min}^{-1}) \) and \( k_p (\text{mg} \cdot \text{g}^{-1} \text{min}^{-1/2}) \) are the rate constants of the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models, respectively. Figure 5(a) and 5(b) are the adsorption curves of the pseudo-first-order and pseudo-second-order models, respectively. The removal of Cu\(^{2+}\) was very fast at the beginning, slowed down after a period of time, and then decreased after 60 minutes, indicating that the equilibrium was quickly reached in 60 minutes. Table 1 showed the fitting parameters of the kinetic model. Compared with the pseudo-first-order model, it is found that the theoretical adsorption capacity \( (q_{e, \text{cal}} = 96.85 \text{ mg} \cdot \text{g}^{-1}) \) calculated by pseudo-second-order model is closer to the experimental data \( (q_{e, \text{exp}} = 94.68 \text{ mg} \cdot \text{g}^{-1}) \), and the corresponding \( R^2 \) value was also considerably higher, which indicates that pseudo-second-order adsorption data is in agreement with adsorption of Cu\(^{2+}\).

Figure 5(c) is the fitting curve of the intra-particle diffusion model. It can be seen that the graph does not pass the origin, but shows a multi-linear relationship, which indicates that intraparticle diffusion is not the only rate-controlling step. The first stage belongs to the fast adsorption stage (external diffusion), that is, the adsorbate diffuses to the external surface of the adsorbent through the solution, and the second stage belongs to the slow adsorption stage (intra-particle diffusion), which corresponds to the diffusion of adsorbent molecules within the adsorbent. Table 1 shows the value of the external diffusion rate constant \( (k_{p1} = 23.3442 \text{ mg} \cdot \text{g}^{-1} \text{min}^{-1/2}) \) is greater than intra-particle diffusion rate constant \( (k_{p2} = 0.1089 \text{ mg} \cdot \text{g}^{-1} \text{min}^{-1/2}) \), which suggested that the removal efficiency of Cu\(^{2+}\) was higher at first owing to large surface area and sufficient active adsorption sites of the KSF.

![Figure 5. Adsorption kinetic model fitting of KSF: (a) pseudo-first-order kinetic model; (b) pseudo-second-order kinetic model; (c) intraparticle diffusion model.](image)

| Table 1. Kinetic parameters of Cu\(^{2+}\) onto KSF. |
|------------------------|------------------------|--------------------|
| Kinetic models         | Parameters             | Values             |
| pseudo-first-order     | \( k_1 (\text{min}^{-1}) \) | 0.6493             |
|                        | \( q_e (\text{mg} \cdot \text{g}^{-1}) \) | 91.4389            |
|                        | \( R^2 \)              | 0.9723             |
| pseudo-second-order    | \( k_2 (\text{g} \cdot \text{mg}^{-1} \text{min}^{-1}) \) | 0.009              |
|                        | \( q_e (\text{mg} \cdot \text{g}^{-1}) \) | 96.8575            |
|                        | \( R^2 \)              | 0.9805             |
|                        | \( k_p (\text{mg} \cdot \text{g}^{-1} \text{min}^{-1/2}) \) | 23.3442            |
|                        | \( C_1 \)              | 13.8199            |
| intraparticle diffusion | \( k_{p2} (\text{mg} \cdot \text{g}^{-1} \text{min}^{-1/2}) \) | 0.1089             |
| model                  | \( (R_1)^2 \)          | 0.83355            |
|                        | \( C_2 \)              | 93.3828            |
|                        | \( (R_2)^2 \)          | 0.9853             |
3.4. Adsorption isotherms

The Langmuir model and Freundlich model can be calculated using Formulas (6) to (7):

\[ q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \]  
(6)

\[ q_e = K_F c_e^n \]  
(7)

where \( q_m \) (mg·g\(^{-1}\)) is the maximum theoretical adsorption capacity, \( K_L \) (L·mg\(^{-1}\)) is the Langmuir adsorption isotherm constant. \( K_F \) ((mg·g\(^{-1}\))·(mg·L\(^{-1}\))^\(n\)) and \( n \) (dimensionless) are the Freundlich isotherm constants. Both Langmuir and Freundlich models are commonly used to understand the adsorption behaviors and its mechanisms of heavy metal ions [13]. As shown in Figure 6 and Table 2, it suggested that the Langmuir isotherm model was more suitable to describe the adsorption behavior of Cu\(^{2+}\) on KSF based on the higher correlation coefficients, which indicating that the adsorption of Cu\(^{2+}\) on the homogeneous distribution of active sites of KSF was monolayer adsorption. The theoretical maximum adsorption capacity fitted by Langmuir model is 178.46 mg·g\(^{-1}\). As can be observed, the Freundlich constant \( n \) is between 0.1 and 1, which indicated that the adsorption process is a favorable process.

![Figure 6. Adsorption isotherm models for Cu\(^{2+}\) adsorption: (a) Langmuir model; (b) Freundlich model.](image)

| Table 2. Adsorption parameters of Langmuir and Freundlich isotherm models. |
|-------------------|-------------------|-------------------|
| Isotherm models   | Parameters        | Values            |
| Langmuir          | \( q_m \) (mg·g\(^{-1}\)) | 178.46            |
|                   | \( K_L \) (L·mg\(^{-1}\)) | 0.1712            |
|                   | \( R^2 \)          | 0.9832            |
|                   | \( K_F \)          | 25.2507           |
| Freundlich        | \((\text{mg}·\text{g}^{-1})·(\text{mg}·\text{L}^{-1})^n\) | 25.2507           |
|                   | \( n \)            | 0.3345            |
|                   | \( R^2 \)          | 0.8090            |

3.5. Thermodynamic analysis

The thermodynamic parameter can be calculated by Formulas (8) to (10):

\[ \Delta G^o = -RT \ln k_c \]  
(8)

\[ k_c = \frac{c_e}{c_0} \]  
(9)

\[ \ln k_c = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \]  
(10)

where \( R \) and \( T \) (K) are the universal gas constant and temperature, respectively. \( k_c \) and \( c_0 \) (mg·L\(^{-1}\)) are the equilibrium adsorption constant and the concentration of Cu\(^{2+}\) ion on the adsorbent, respectively. In an effort to understand the nature of the adsorption process of Cu\(^{2+}\) onto KSF, the changes in Gibbs free energy (\( \Delta G^o \)), enthalpy (\( \Delta H^o \)) and entropy (\( \Delta S^o \)) are computed in Figure 7 [14]. \( \Delta G^o \) is negative, and the negative values become more negative as the temperature increases in the range of 293 to 313 K in Table
3, implying that the removal of Cu\(^{2+}\) by the KSF is spontaneous, and at higher temperatures, the process is thermodynamically more favorable. \(\Delta H^0\) is positive, indicating that the adsorption process is endothermic in nature. And \(\Delta S^0\) is positive, indicating that the randomness of the solid-solution interface increases, which implied that the adsorption process was entropically favored.

**Table 3.** Thermodynamic parameters for Cu\(^{2+}\) adsorption on KSF.

| T/K  | \(\Delta G^0\)/kJ·mol\(^{-1}\) | \(\Delta H^0\)/kJ·mol\(^{-1}\) | \(\Delta S^0\)/J·mol\(^{-1}\)k\(^{-1}\) |
|------|-----------------|-----------------|-----------------|
| 293  | -5.03           |                 |                 |
| 298  | -6.23           |                 |                 |
| 303  | -7.43           | 65.53           | 240.81          |
| 308  | -8.64           |                 |                 |
| 313  | -9.84           |                 |                 |

3.6. Desorption and regeneration

After ten cycles of adsorption, the regeneration studies of KSF is shown in Figure 8. The results showed that the removal efficiency of KSF did not decrease significantly after repeated ten adsorption−desorption cycles, and the adsorption efficiency of Cu\(^{2+}\) was still over 90%. These results indicate that KSF has high stability and reusability for effectively removing Cu\(^{2+}\) from aqueous solution.

![Figure 7. Van’t Hoff plot for Cu\(^{2+}\) adsorption at different temperatures.](image)

![Figure 8. Regeneration studies of KSF.](image)

4. Conclusions

(1) FTIR analysis suggested that functional amino groups of KH550 were grafted on the surface of KSF. And KSF is excellent for removal of Cu\(^{2+}\) from aqueous solution, it could efficiently remove Cu\(^{2+}\) ions under the conditions of pH 5, initial concentration of 100 mg·L\(^{-1}\), and adsorbent dosage of 0.01 g.

(2) Adsorption kinetics study showed that the pseudo-second-order kinetics model could fit the experimental data well. The adsorption isotherm indicated that the Langmuir model can fit the adsorption of Cu\(^{2+}\) well, indicating that the adsorption of Cu\(^{2+}\) occurs on homogeneous distribution of active sites on the surface of KSF. Adsorption thermodynamics revealed endothermic, entropy-driven and spontaneous nature of the adsorption.

(3) The adsorption-desorption experiments demonstrated that KSF showed no significant removal efficiency loss even after ten consecutive cycles, indicating the good stability and regeneration performance of prepared KSF material.

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