Article

Study on the Performance of Composite Adsorption of Cu$^{2+}$ by Chitosan/β-Cyclodextrin Cross-Linked Zeolite

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Abstract: In order to remove Cu$^{2+}$ from wastewater, a kind of microsphere adsorbent (SCDO) with high efficiency for Cu$^{2+}$ adsorption was prepared by the microdrop condensation method, where chitosan (CTS) and sodium alginate (SA) were used as the matrix to crosslink β-cyclodextrin (β-CD) and zeolite (Zeo). The structure and properties of SCDO were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Upon that, the adsorption performance of SCDO for Cu$^{2+}$ was studied, in which the effects of pH, initial concentration, dosage, adsorption time and temperature were investigated. The results showed that the removal rate of Cu$^{2+}$ reached 97.08%, and the maximum adsorption capacity was 24.32 mg/g with the temperature at 30 °C, the dosage of SCDO at 12 g/L, the initial concentration of Cu$^{2+}$ at 100 mg/L, the pH of the solution at 6.0 and the adsorption time at 120 min, respectively. The adsorption process of Cu$^{2+}$ by SCDO occurred in accordance with quasi-second-order kinetics model and Langmuir adsorption isotherm. After four repeats of continuous adsorption and desorption, the regenerative removal rate of Cu$^{2+}$ could still reach 84.28%, which indicated that SCDO had outstanding reusability.

Keywords: microspheres; chitosan; β-cyclodextrin; zeolite; Cu$^{2+}$ adsorption

1. Introduction

Copper is an essential trace element for life, but excessive copper is harmful to people, animals and plants. The main sources of copper pollution are copper compounds produced by copper and zinc mining and smelting, metal processing, machinery manufacturing, iron and steel production and electroplating [1]. When these copper compounds are discharged into water, they will pollute the water. Copper concentration in drinking water shall not exceed 1.0 mg/L. Therefore, it is very important to remove copper ions from water.

At present, technologies such as ion exchange, membrane treatment and reverse osmosis have been widely used in the removal of heavy metal ions. However, these methods have their own shortcomings [2]. For example, the removal of metal ions is incomplete, requiring higher reagents and energy, producing toxic sludge or other wastes, and taking a long time to desorb [3]. Adsorption is considered as an effective method to treat heavy metal pollution in wastewater [4]. The principle of adsorption method is to use the porous structure of adsorbent and the physical properties of large surface area to adsorb pollutants in water, to achieve the purpose of removing heavy metals in water [5]. It is simple in operation, low in application cost and good in treatment effect, so it is widely used to remove heavy metal pollution in water. The core of adsorption method lies in the selection of adsorbent, and high-quality adsorbent can reduce the initial investment and operating cost of the treatment process and improve the treatment effect [6].

In recent years, many studies have focused on finding cheap and efficient adsorbents such as waste biopolymers, clay minerals and chitosan [7]. Chitosan is the N-deacetylation of chitin with amino and chitin structures, which is an environmentally friendly adsorption
material [8]. As a natural polymer chelating agent, chitosan has active groups such as amino (-NH$_2$) and hydroxyl (-OH) groups, and is easy to form complexes with metal ions, so it is widely used in the adsorption of heavy metals in wastewater [9]. However, chitosan is easy to dissolve in acidic solution, easy to be lost during use and has a certain degree of swelling, which limits its application in some systems [10,11]. Therefore, physical/chemical modification of chitosan is required. Majid Arvand et al. prepared a modified with 3,4-dimethoxybenzaldehyde chitosan derivative for the removal of Cd$^{2+}$ from water. At pH 6.5, the maximum adsorption capacity of Cd$^{2+}$ reached 217.4 mg/g, and the adsorption process conformed to the Langmuir isotherm model [12]. Chen et al. used chitosan-modified multiwalled carbon nanotubes for the removal of U(VI) from wastewater. The maximum adsorption capacity was at pH = 7, which reached 71 mg/g [13]. Sodium alginate is a natural macromolecular organic substance, which can effectively remove heavy metals from water [15]. Sodium alginate is very hydrophilic, and can react with calcium in aqueous solution by ion exchange, and polymerize to form stable water-based gel balls [16]. This spheroidization property makes it an ideal framework for the preparation of composite adsorbents. Therefore, the combination of sodium alginate and chitosan to prepare a composite adsorbent can achieve the effect of enhancing the adsorption performance [17].

β-cyclodextrin is the product of cyclodextrin glucosyltransferase acting on starch and contains a cavity structure that can encapsulate compounds of suitable size [18]. Studies have shown that using a cross-linking agent to cross-link chitosan and β-cyclodextrin, the obtained product can be used for water treatment [19]. On the one hand, the amino group on the chitosan molecule is used to adsorb metal ions by electrostatic attraction; on the other hand, the resistance of the cavity structure of β-cyclodextrin is easy to encapsulate metal ions. Therefore, the polymer formed by cross-linking chitosan and β-cyclodextrin can significantly enhance the adsorption capacity of metal ions. Zeolite is an inorganic crystalline microporous mineral with large porosity, good cation exchange and screening ability [20]. Several studies have shown that the incorporation of an inorganic matrix (Zeo) can enable composite adsorbents with stable porous structures and higher acid resistance [21,22].

Based on this, a kind of microsphere adsorbent (SCDO) with high efficiency for Cu$^{2+}$ adsorption was prepared by microdrop condensation method, where chitosan (CTS) and sodium alginate (SA) are used as the matrix, to crosslink β-cyclodextrin (β-CD) and zeolite (Zeo). The enveloping effect of β-cyclodextrin ring structure increases the adsorption capacity of SCDO for Cu$^{2+}$, and the incorporation of inorganic matrix (Zeo) makes SCDO have a stable porous structure and higher acid resistance. The additional SA improves the loss of CTS, which is beneficial to the separation from wastewater after adsorption, and overcomes the difficulty of absorbents recover. The adsorption process and mechanism of SCDO were investigated, which benefits the practical copper-containing wastewater treatment.

2. Materials and Methods
2.1. Materials
Chitosan (CTS), sodium alginate (SA), β-cyclodextrin (β-CD), zeolite, epichlorohydrin, calcium chloride, sodium hydroxide, hydrochloric acid (HCl), nitric acid (HNO$_3$) and anhydrous copper sulfate were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All solutions were prepared by deionized water. All the chemicals were of analytical grade.
2.2. Preparation and Characterization of SCDO

2.2.1. Preparation of SCDO

SA (2.0 g) was dissolved in 50 mL deionized water and stirred magnetically at 60 °C for 1 h to obtain a uniform viscous solution containing 4.0% SA. Then we added 1 g CTS and continued stirring to obtain a solution. Weighed 0.5 g of dried Zeo and added it to 50 mL 4.0% β-CD solution, dispersed it ultrasonic for 20 min, poured the mixed solution into SA solution, and stir continuously until it was completely mixed. The solution was left to stand until air bubbles were removed. Then the uniform solution was dropped into 5% CaCl$_2$ solution with a 20 mL syringe and condensed into microspheres with an average particle size of about 4.5 mm instantly. After a curing time of 30 min, 2 mL of epichlorohydrin was added, the crosslinking reaction was heated in a water bath of 60 °C for 2 h, and then curing was continued for 30 min. After filtration, residual calcium chloride and epichlorohydrin were repeatedly rinsed with deionized water to remove them. Finally, the microspheres were freeze-dried in vacuum at −60 °C for 24 h to constant weight for use.

2.2.2. Characterization

The microstructure of SCDO was observed by scanning electron microscopy (SEM, Zeiss Supra55, Oberkochen, Germany). The elemental composition and surface functional groups of SCDO were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi+, Thermo Fisher, Waltham, MA, USA). The crystallinity was tested by X-ray diffractometer (XRD, D/MAX 2500, Tokyo, Japan). The functional groups of SCDO were determined by Fourier Transform infrared spectrometer (FTIR, IS50, Santa Clara, CA, USA). The concentration of Cu$^{2+}$ was measured by flame atomic absorption spectrometer (AAS, novAA-300, Perkinelmer Ltd., Waltham, MA, USA).

2.3. Adsorption Experiments

In this experiment, anhydrous CuSO$_4$ was dissolved in deionized water, simulated solutions of different concentrations were configured in conical bottles, and a certain amount of SCDO (2–12 g/L) was put into the simulated solution for adsorption. The effects of pH (1.0–6.0), adsorption time (0–300 min) and initial concentration (10–100 mg/L) on Cu$^{2+}$ adsorption were investigated. The solution pH value was adjusted with 0.1 mol/L HCl and 0.1 mol/L NaOH. The concentration of Cu$^{2+}$ was measured by AAS after the supernatant was diluted by a certain multiple after the oscillation by a thermostatic oscillator. Three parallel samples were set for each group of experiments, and the experimental results were averaged for data analysis. The Cu$^{2+}$ removal rate ($R$) and adsorption capacity $Q_e$ (mg/g) of SCDO were obtained by calculation, and calculated by Equations (1) and (2):

\[
R = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\%. \quad (1)
\]

\[
Q_e = \frac{V \times (C_0 - C_t)}{m}. \quad (2)
\]

where $R$—removal rate; $Q_e$—adsorption capacity at equilibrium, mg·g$^{-1}$; $C_t$—represents the concentration of Cu$^{2+}$ remaining in the solution at a certain time, mg·L$^{-1}$; $C_0$—initial concentration of Cu$^{2+}$, mg·L$^{-1}$; $V$—Cu$^{2+}$ solution volume, L; $m$—SCDO mass, g.

2.4. The Principles for the Cu$^{2+}$ Determination

In this experiment, the flame atomic absorption method was used to determine Cu$^{2+}$ in water. The characteristic spectral radiation of the element to be measured is emitted by the hollow cathode lamp, which is absorbed by the basic atoms of the element to be measured in the sample vapor generated by the flame atomic instrument. By measuring how much the characteristic radiation is absorbed, the content of the element to be measured is obtained.

The steps of measurement:
Pretreatment of samples: Take 100 mL of water sample and put it into a 200 mL beaker, then add 5 mL of nitric acid, and heat it on a hot plate for digestion. Steam to about 10 mL, then add 5 mL of nitric acid and 2 mL of perchloric acid, and continue digestion until about 1 mL.

Determination of samples: Select the analysis line and adjust the flame by parameter. The instrument is zeroed with 0.2% nitric acid, and the blank sample and sample are drawn in to measure their absorbance. After subtracting the absorbance of the blank sample, find the metal concentration in the sample from the calibration curve. It can also be read from the instrument.

Calibration curve: Put 0 mL, 0.5 mL, 1 mL, 3 mL, 5 mL and 10 mL of the absorption standard solution into six volumetric flasks (100 mL), respectively, and dilute to volume with 0.2% nitric acid. Then measure the absorbance according to the steps of sample determination, and draw a calibration curve.

The concentration of Cu\textsuperscript{2+} can be read from the instrument (AAS).

2.5. The Data Analysis

(1) Adsorption kinetics fitting: Lagergren quasi-first-order and quasi-second-order kinetic models were used to fit the adsorption kinetics of Cu\textsuperscript{2+} by SCDO, and the best fitting model was selected according to the value of linear regression correlation coefficient [23]. The kinetic model equations are as follows:

\[
Q_t = Q_e \left(1 - e^{-K_1t}\right)
\]

(3)

\[
Q_t = \frac{K_2Q_e^2t}{1 + k_2Q_e^2t}
\]

(4)

where \(t\)—adsorption time, min; \(K_1\)—quasi-first-order kinetic rate constant, min\(^{-1}\); \(K_2\)—quasi-second-order kinetic rate constant, g\(\cdot\)\(\text{mg}\cdot\text{min}\)\(^{-1}\); \(Q_t\)—the adsorption capacity at a certain moment, mg\(\cdot\)g\(^{-1}\); \(Q_e\)—equilibrium adsorption capacity, mg\(\cdot\)g\(^{-1}\).

(2) Adsorption isotherm fitting: Langmuir and Freundlich models were used to fit the adsorption process of Cu\textsuperscript{2+}. The isotherm model equations [24] are shown in Equations (5) and (6), respectively:

\[
Q_e = \frac{Q_mC_e}{1 + bC_e}
\]

(5)

\[
Q_e = K_F C_e^{1/n}
\]

(6)

where \(Q_m\)—theoretical maximum adsorption capacity, mg\(\cdot\)g\(^{-1}\); \(Q_e\)—equilibrium adsorption capacity, mg\(\cdot\)g\(^{-1}\); \(C_e\)—the concentration of Cu\textsuperscript{2+} at adsorption equilibrium, mg\(\cdot\)L\(^{-1}\); \(b\)—Langmuir model constant, L\(\cdot\)mg\(^{-1}\); \(n\) and \(K_F\) (mg\(\cdot\)g\(^{-1}\))—Freundlich model constant.

2.6. Desorption and Regeneration Experiment

When SCDO adsorbed Cu\textsuperscript{2+} saturated, 0.1 mol/L HNO\textsubscript{3} solution was used as desorption agent to desorption SCDO after adsorption. After adsorption, SCDO loaded with Cu\textsuperscript{2+} was placed in 150 mL desorption medium HNO\textsubscript{3} solution and vibrated at 160 r/min for 120 min at 30 °C. Then, SCDO was washed with deionized water and adsorbed again. After adsorption, SCDO was saturated and desorbed.

3. Results and Discussion

3.1. Micromorphology Analysis

The surface images and SEM images of SCDO before and after adsorption are shown in Figure 1. As can be seen from Figure 1a,b, SCDO is a white spherical particle with good spherical morphology and uniform particle size, averaging about 4.5 mm. After adsorption
of Cu$^{2+}$, SCDO turns blue. As can be seen from Figure 1c,d, the microscopic morphology of SCDO is irregular, with rough and uneven surface, porous network structure and relatively uniform pores on the cross section. When Cu$^{2+}$ enters the channel of SCDO, because of the channel resistance, it is difficult for Cu$^{2+}$ to get rid of the bondage, which improves the adsorption capacity of SCDO to Cu$^{2+}$ and helps to increase the adsorption capacity.

![Figure 1](image-url)

Figure 1. (a,b) SCDO surface map before and after adsorption; (c) SEM image of SCDO surface; (d) SEM image of cross section.

3.2. XRD Analysis

Figure 2 shows the XRD patterns of SA, CTS, β-CD, Zeo and SCDO. The XRD patterns of CTS showed three strong characteristic peaks at 2θ = 10°, 20° and 28°, indicating the existence of crystallization region of CTS [25]. Due to the presence of a large number of amino and hydroxyl groups in CTS molecules, strong intramolecular and intermolecular hydrogen bonds can be formed, leading to the existence of crystallization zones in the molecular structure of CTS [26]. The crystallization peaks of Zeo were 7.05°, 10.03°, 12.3°, 15.9°, 21.5°, 23.8°, 25.9°, 26.9°, 29.8°, 30.68°, 34.03°, 44° and 52.4°, and no obvious characteristic peaks were observed in SCDO. This finding indicates that Zeo becomes amorphous in the SCDO matrix. Due to the strong interaction between composites, the crystallization of zeolite is limited [27]. The XRD patterns of β-CD show multiple diffraction peaks, which indicate that β-CD has an amorphous structure. XRD patterns of SCDO were observed. SCDO was similar to SA. The strength of the characteristic peak weakened at 2θ = 20° and shifted to the left at 2θ = 18°, indicating that the hydrogen bond strength of CTS was weakened after CTS composite crosslinking, leading to the decrease of CTS crystallinity. At the same time, a new characteristic peak appeared at 2θ = 18°, which was attributed to the ionic bond cross-linking between -NH$_3^+$ in CTS and -COO$^-$ in β-CD, which increased the crystallinity [28].
3.3. FTIR Analysis

The FTIR images of SCDO before and after Cu\textsuperscript{2+} adsorption were analyzed. Figure 3 shows that before adsorption, the wave numbers of 1313 cm\textsuperscript{-1} and 1596 cm\textsuperscript{-1} are the stretching vibration of C–OH and C=C, and the strong absorption band at 1021 cm\textsuperscript{-1} is the skeleton vibration band of Si–O–Si [29]. A broad band appears in the wave number range of 3300–3500 cm\textsuperscript{-1}, which is attributed to the stretching vibration of N–H bond or O–H bond [30,31]. After the adsorption of Cu\textsuperscript{2+}, the intensity of the characteristic peak changed to some extent, from 1430 cm\textsuperscript{-1} and 1636 cm\textsuperscript{-1} to 1421 cm\textsuperscript{-1} and 1618 cm\textsuperscript{-1}, and the intensity of the characteristic peak at 1368 cm\textsuperscript{-1} also decreased significantly. It shows that -COO\textsuperscript{-} interacts with Cu\textsuperscript{2+} [32]. The change of peak intensity from 3327 cm\textsuperscript{-1} to 3382 cm\textsuperscript{-1} after adsorption indicates that the -NH\textsubscript{2} group is involved in the Cu\textsuperscript{2+} adsorption process [33], while the peaks of other functional groups have no significant change. It can be seen that the amino, hydroxyl and carboxyl groups in SCDO play a major role in the adsorption of Cu\textsuperscript{2+}, which further indicates that the adsorption of Cu\textsuperscript{2+} by SCDO is mainly chemical adsorption.

3.4. XPS Analysis

SCDO was characterized by XPS, and its elemental composition and surface functional groups were analyzed. It can be seen from Figure 4a that there are C, O, Si, Ca, N and other elements in the full spectrum of SCDO. The appearance of Si and N element peaks indicates
that Zeo and CTS are successfully loaded. Figure 4b shows the C 1s high-resolution spectrum. C=C/C–C/C–H corresponds to the binding energy of 284.4 eV, C=O corresponds to the binding energy of 285.3 eV, C=O corresponds to the binding energy of 286.3 eV, and O–C=O bond corresponds to the binding energy of 287.9 eV [34,35], indicating that there are oxygen-containing functional groups in SCDO. Figure 4c shows the high-resolution spectrum of O 1s. O–H corresponds to a binding energy of 531.2 eV, C-OH corresponds to a binding energy of 532.2 eV, and C=O corresponds to a binding energy of 532.9 eV [36], which is consistent with infrared analysis. Figure 4d is a high-resolution spectrum of Ca 2p. The binding energies of Ca 2p3/2 and Ca 2p1/2 are 347.7 eV and 351.3 eV [37], respectively, which corresponds to Ca2+, indicating that Ca2+ interacts with carboxyl in SCDO.

![Figure 4](image_url)

Figure 4. (a) XPS spectra of SCDO; (b) C 1s; (c) O 1s; (d) Ca 2p.

3.5. BET Analysis

Figure 5 shows the N2 adsorption–desorption isotherms and corresponding pore size distribution curves of SCDO. When the relative pressure p/p0 was in the range of 0–0.6, the adsorption capacity of SCDO increased slightly, indicating the existence of micropores. A rapid uptake was observed from 0.8 to 1.0, indicating mesopores structures with the SCDO. Figure 5a shows that the adsorption isotherm of SCDO exhibits a hysteresis loop, indicating that it contains not only a microporous structure but also a mesoporous structure. The BJH pore size distribution of SCDO in Figure 5b also confirms that the microspheres have a large number of micropores and mesopores concentrated between 1 nm and 20 nm, which provide usable adsorption sites for heavy metal adsorption.
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3.6. Effect of pH

The solution pH value can affect the adsorption capacity of \( \text{Cu}^{2+} \) by affecting the chemical properties of the solution and the existence of functional groups on the surface of the adsorbent [38]. In the experiment, the pH ranges from 1.0 to 6.0, because \( \text{Cu}^{2+} \) precipitates in the form of \( \text{Cu(OH)}_2^+ \) when the pH exceeds 6.5 [39]. As shown in Figure 6, the adsorption amount of \( \text{Cu}^{2+} \) by SCDO increases with the increase of pH, and reaches the maximum value when pH is 6.0. This is because under strong acidic conditions, there are more \( \text{H}^+ \) and \( \text{Cu}^{2+} \) in the solution to participate in competitive adsorption, which makes the surface of SCDO protic and reduces the adsorption capacity of \( \text{Cu}^{2+} \) [40]. When pH increased gradually, \( \text{H}^+ \) concentration decreased and protonated functional groups deprotonated, so competitive adsorption weakened. Therefore, SCDO can remove \( \text{Cu}^{2+} \) more effectively at higher pH [41]. At a pH of >4.0, the removal rate was slightly improved, indicating that the electrostatic interaction is not the main factor for the \( \text{Cu}^{2+} \) binding [42]. Based on the above analysis, the subsequent experiments were carried out at pH 6.0.
was set as 12 g/L in this experiment. The removal rate of SCDO gradually decreased and tended to be gentle, while the adsorption amount showed a trend of gradual increase. When the initial concentration of Cu$^{2+}$ was 10 mg/L, the removal rate was 80%, but the adsorption amount was 4 mg/g. When the dosage increased from 8 g/L to 12 g/L, the removal rate changed from 88% to 91%, with a small change in the removal rate. The adsorption capacity of Cu$^{2+}$ by SCDO was gradually saturated. As the adsorption sites of SCDO increase, the concentration of Cu$^{2+}$ in the solution gradually decreased, and the total adsorption capacity was much higher than the amount of remaining Cu$^{2+}$ in the solution, so the adsorption capacity decreased. Based on the above analysis, the dosage was set as 12 g/L in this experiment.

As shown in Figure 7, the influence of SCDO dosage on Cu$^{2+}$ adsorption was explored. It can be seen that the removal rate of Cu$^{2+}$ increases with the increase of dosage, while the adsorption amount decreased gradually. When the dosage was 2 g/L, the removal rate was 52%, but the adsorption capacity was higher than the other five groups. This is because the Cu$^{2+}$ content in the solution is higher than the adsorption capacity of SCDO, and SCDO has been saturated, resulting in a low removal rate. When the dosage increased to 8 g/L, the removal rate increased significantly from 52% to 88%, because the adsorption capacity of SCDO was close to the Cu$^{2+}$ content in the solution. When the dosage increased from 8 g/L to 12 g/L, the removal rate changed from 88% to 91%, with a small change in the removal rate. The adsorption capacity of Cu$^{2+}$ by SCDO was gradually saturated. As the adsorption sites of SCDO increase, the concentration of Cu$^{2+}$ in the solution gradually decreased, and the total adsorption capacity was much higher than the amount of remaining Cu$^{2+}$ in the solution, so the adsorption capacity decreased. Based on the above analysis, the dosage was set as 12 g/L in this experiment.

3.7. Effect of SCDO Dosage

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Figure 6. The effect of pH on the adsorption of Cu$^{2+}$.

Figure 7. Effect of dosage of SCDO on adsorption of Cu$^{2+}$.
3.8. Effect of the Initial Concentration of Cu$^{2+}$ Solution

As shown in Figure 8, the initial concentration range of Cu$^{2+}$ for SCDO adsorption was explored. It can be seen that with the increase of the initial concentration of Cu$^{2+}$, the removal rate of SCDO gradually decreased and tended to be gentle, while the adsorption amount showed a trend of gradual increase. When the initial concentration of Cu$^{2+}$ was 10 mg/L, SCDO may not reach adsorption saturation due to the relatively small amount of Cu$^{2+}$ in the solution, so Cu$^{2+}$ can be effectively removed from the solution. However, when the concentration of Cu$^{2+}$ was 100 mg/L, all free sites on the SCDO surface were saturated for adsorption. Therefore, with the increase of the initial concentration of Cu$^{2+}$, the removal rate gradually decreased, but the removal rate of Cu$^{2+}$ still maintained more than 80%.

![Figure 8. Effect of initial concentration on adsorption of Cu$^{2+}$.](image)

3.9. Effect of Contact Time on Adsorption

As shown in Figure 9, the optimal adsorption saturation time was explored. It can be seen that the adsorption capacity of SCDO for Cu$^{2+}$ increased rapidly within 0 to 90 min, which was due to the numerous free adsorption sites and the large specific surface area on the surface of SCDO, resulting in a higher contact probability between Cu$^{2+}$ and the binding sites [43]. Subsequently, the binding site was gradually occupied by Cu$^{2+}$, and the adsorption rate gradually slowed down and leveled off. When the adsorption time reached 120 min, the adsorption equilibrium was established. By studying the relationship between the adsorption capacity and time, the optimal adsorption time of Cu$^{2+}$ was determined to be 120 min.

![Figure 9. Effect of contact time on adsorption.](image)

3.10. Study of Adsorption Kinetics

Adsorption is a physicochemical process in which solute is transferred from liquid phase to adsorbent surface. Kinetic studies can establish mathematical models for surface adsorption, diffusion within particles and diffusion outside liquid film, and better reflect the adsorption mechanism. The initial concentration of Cu$^{2+}$ was set at 100 mg/L (25 mL) for adsorption kinetics experiment. The adsorption was carried out in the period of (5–240 min) to explore the rule of SCDO's adsorption process of Cu$^{2+}$ with time. Figure 10 shows the kinetic fitting curve, and the fitting parameters are shown in Table 1. It can be seen that the correlation coefficient $r^2$ of quasi-second-order kinetic fitting is 0.9998, which is larger than that of quasi-first-order kinetic fitting, and the equilibrium adsorption capacity ($Q_{e,cal}$) obtained by quasi-second-order kinetic model fitting is 24.41 mg/g, which is closer to the actual adsorption capacity ($Q_{e,exp}$). Therefore, quasi-second-order kinetics is more consistent with the process of SCDO adsorption of Cu$^{2+}$. This indicates that SCDO adsorption of Cu$^{2+}$ should be a chemisorption process.
Actual $Q_{e,\text{exp}}$ (mg/g) 

| $C_0$ (mg/L) | Quasi-First Order Dynamics | Quasi-Second Order Dynamics |
|-------------|-----------------------------|----------------------------|
|             | $Q_{e,\text{cal}}$ (mg/g)  | $k_1$ (min$^{-1}$) | $r^2$ | $Q_{e,\text{cal}}$ (mg/g) | $k_2$ (g (mg h)$^{-1}$) | $r^2$ |
| 100         | 22.11                       | 0.4989                   | 0.9750 | 24.41            | 0.0834                   | 0.9998 |

### 3.11. Study on Adsorption Isotherm Model

The initial concentration of Cu$^{2+}$ was set at 10–100 mg/L (25 mL), the reaction temperatures were set at 303.15 K, 313.15 K, 333.15 K, and the dosage of SCDO was set at 12 g/L to explore the influence of different temperatures on the adsorption of Cu$^{2+}$. The fitting curve is shown in Figure 11. It can be seen that the equilibrium adsorption capacity increases with the increase of temperature, indicating that the adsorption of SCDO to Cu$^{2+}$ increases with the increase of temperature within a certain range. Table 2 shows the isothermal fitting parameters. At the same temperature, the fitting correlation coefficient $r^2$ of Langmuir model is greater than that of Freundlich model, which indicates that SCDO’s adsorption of Cu$^{2+}$ is more consistent with Langmuir isothermal adsorption model and belongs to monomolecular adsorption. That is, the surface adsorption capacity of SCDO is uniform, and there is no interaction between the adsorbed Cu$^{2+}$. The theoretical maximum adsorption capacity ($Q_{e,\text{cal}}$) of Cu$^{2+}$ obtained by Langmuir fitting is close to the experimental
value. At the same time, the relative parameters \(1/n\) obtained by Freundlich isothermal adsorption model were in the range of 0–1, which proved that SCDO had good adsorption performance for \(\text{Cu}^{2+}\).

![Figure 11. Isotherm fitting curve of SCDO.](image)

| Temperature (K) | Actual \(Q_m\) (mg·g\(^{-1}\)) | \(Q_{e,cal}\) (mg·g\(^{-1}\)) | \(b\) (L·mg\(^{-1}\)) | \(r^2\) | \(K_F\) (mg·g\(^{-1}\)) | \(1/n\) | \(r^2\) |
|----------------|-------------------------------|------------------|----------------|-----|----------------|-----|-----|
| 303.15         | 14.40                         | 16.88            | 0.0338         | 0.9906 | 1.54          | 0.6099 | 0.9837 |
| 313.15         | 17.34                         | 18.58            | 0.0824         | 0.9941 | 3.12          | 0.4940 | 0.9639 |
| 333.15         | 20.28                         | 21.16            | 0.3842         | 0.9952 | 7.11          | 0.3537 | 0.9766 |

### 3.12. Mechanism Analysis of \(\text{Cu}^{2+}\) Adsorption

(1) XPS analysis before and after SCDO adsorption of \(\text{Cu}^{2+}\): The XPS spectra before and after SCDO adsorption of \(\text{Cu}^{2+}\) are shown in Figure 12. After adsorption of \(\text{Cu}^{2+}\), a new peak of elemental Cu appeared. In addition, in the high-resolution Cu 2p spectrum, binding energy values of 933.4/953.2 eV and 934.7/954.7 eV are assigned to Cu 2p\(_{3/2}\) and Cu 2p\(_{1/2}\), respectively. The results show that the existing form of Cu is mainly Cu\(^{2+}\), which further indicates that Cu\(^{2+}\) is adsorbed onto SCDO. Figure 12(c) shows Al—O, C—O, Si—O, and O−H bonds at binding energies 531.3 eV, 532.0 eV, 532.8 eV, and 533.4 eV, respectively. After the adsorption of Cu\(^{2+}\), the binding energy value of O 1s shifted to a higher binding energy, indicating that hydroxyl and carboxyl groups were involved in the adsorption process of Cu\(^{2+}\). Figure 12(d) shows the C 1s spectra before and after SCDO adsorption. After adsorption of Cu\(^{2+}\), the binding energies of C−C/C=C, C—O, C=O and O−C=O peaks shifted to 284.7 eV, 285.6 eV, 286.6 eV and 288.0 eV, indicating that the interaction between carboxyl groups and Cu\(^{2+}\) occurred.
3.12. Mechanism Analysis of Cu²⁺ Adsorption

(1) XPS analysis before and after SCDO adsorption of Cu²⁺: The XPS spectra before and after SCDO adsorption of Cu²⁺ are shown in Figure 12. After adsorption of Cu²⁺, a higher binding energy, indicating that hydroxyl and carboxyl groups were involved in the interaction between carboxyl groups and Cu²⁺ occurred. From the point of view of practical application, high efficiency adsorbent must have stability and repeatability. In order to explore the reusability of SCDO, 0.1 mol/L HNO₃ solution was used as desorption agent for Cu²⁺ desorption. Since -NH₂ in CTS can chelate with both metal ions and H⁺, there is a balance between them, and dilute acid can be used to desorb SCDO after adsorption [44]. Lone pair electrons on N atoms of the -NH₂ group can bind to Cu²⁺ or H⁺ through electron pair sharing to form coordination complexes.

The adsorption process mainly involves the following reactions:

\[
R—OH + Cu^{2+} + H_2O \rightarrow R—OCu—OH + 2H_3O^+ \quad (7)
\]

\[
R—COOH + Cu^{2+} + H_2O \rightarrow (R—COO)_2Cu + H_3O^+ \quad (8)
\]

\[
R—NH_2 + Cu^{2+} + H_2O \rightarrow NH_2(CuOH)^+ \quad (9)
\]

\[
R—NH_3^+ + CuCl^3- \rightarrow R—NH_3^+ CuCl^3- \quad (10)
\]

\[
R—NH_2 + Cu^+ \rightarrow R—NH_3^+ \quad (11)
\]

3.13. Desorption and Regeneration Experiment

From the point of view of practical application, high efficiency adsorbent must have stability and repeatability. In order to explore the reusability of SCDO, 0.1 mol/L HNO₃ solution was used as desorption agent for Cu²⁺ desorption. Since -NH₂ in CTS can chelate with both metal ions and H⁺, there is a balance between them, and dilute acid can be used to desorb SCDO after adsorption [45]. As shown in Figure 13, after four consecutive adsorption–desorption experiments, the adsorption capacity of Cu²⁺ by SCDO decreased significantly during the adsorption–desorption cycle. Therefore, the removal rate of Cu²⁺ by SCDO did not decrease after four adsorption–desorption cycles. At the same time, it can be seen from the SEM application that SCDO still maintains a uniform particle size and after SCDO adsorption of Cu²⁺ are shown in Figure 12. After adsorption of Cu²⁺, a higher binding energy, indicating that hydroxyl and carboxyl groups were involved in the interaction between carboxyl groups and Cu²⁺ occurred. From the point of view of practical application, high efficiency adsorbent must have stability and repeatability. In order to explore the reusability of SCDO, 0.1 mol/L HNO₃ solution was used as desorption agent for Cu²⁺ desorption. Since -NH₂ in CTS can chelate with both metal ions and H⁺, there is a balance between them, and dilute acid can be used to desorb SCDO after adsorption [44]. Lone pair electrons on N atoms of the -NH₂ group can bind to Cu²⁺ or H⁺ through electron pair sharing to form coordination complexes.

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R—NH_2 + Cu^{2+} + H_2O \rightarrow NH_2(CuOH)^+ \quad (9)
\]

\[
R—NH_3^+ + CuCl^3- \rightarrow R—NH_3^+ CuCl^3- \quad (10)
\]

\[
R—NH_2 + Cu^+ \rightarrow R—NH_3^+ \quad (11)
\]
from 24.01 mg/g to 21.07 mg/g, without significant loss of adsorption capacity, and the regeneration removal rate of Cu\(^{2+}\) still reached 84.28%. SCDO remained stable throughout the experiment and demonstrated good reusability, which is a key factor in practical application. It can be seen from Figure 14 that SCDO still maintains a uniform particle size after four adsorption–desorption cycles. At the same time, it can be seen from the SEM spectrum that the pore size of SCDO becomes larger, which is beneficial to increase the removal efficiency of SCDO for Cu\(^{2+}\). Therefore, the removal rate of Cu\(^{2+}\) by SCDO did not decrease significantly during the adsorption–desorption cycle.

Figure 13. SCDO regenerate Cu\(^{2+}\) by desorption.

Figure 14. (a) Surface map of SCDO after desorption. (b–d) SEM image of SCDO cross section after 4 cycles of adsorption-desorption.

3.14. Comparison of the Capacity for Cu\(^{2+}\) with Reported Adsorbents

To verify the adsorption performance of SCDO for Cu\(^{2+}\), we compared the prepared adsorbent with several reported adsorbents. Table 3 lists the maximum adsorption capacity
of different adsorbents for Cu$^{2+}$. By comparison, it can be seen that the adsorption capacity of SCDO prepared in this study is better than that of most adsorbents reported in the literature.

| Adsorbent                                      | $Q_m$ (mg/g) | Reference |
|------------------------------------------------|--------------|-----------|
| Chitosan-coated sand                          | 8.18         | [46]      |
| Composite cryogels                            | 2.50         | [47]      |
| PVA and carboxymethyl cellulose composite hydrogels | 5.5          | [48]      |
| Mesoporous titania beads                      | 8.4          | [49]      |
| Chitosan-nanoSiO$_2$ nanocomposite            | 6.683        | [30]      |
| Nanoscale magnetite                           | 8.9          | [50]      |
| cross-linking chitosan/rectorite nano-hybrid composite microspheres | 20.49        | [51]      |
| SCDO                                           | 24.32        | This study |

4. Conclusions

A kind of microsphere adsorbent (SCDO) with high efficiency for Cu$^{2+}$ adsorption was prepared by microdrop condensation method, where chitosan (CTS) and sodium alginate (SA) are used as the matrix, to crosslinking β-cyclodextrin (β-CD) and zeolite (Zeo). SEM characterization analysis showed that SCDO had a rough surface, a three-dimensional network structure and a porous structure in the transverse section. FTIR and XPS analysis showed that groups such as -OH, -NH$_2$ and -COOH were involved in the adsorption process of Cu$^{2+}$. The results showed that with the pH at 6.0, SCDO dosage at 12 g/L, and adsorption time at 120 min, respectively. SCDO reached adsorption equilibrium, the removal rate of Cu$^{2+}$ reached 97.08%, and the maximum adsorption capacity reached 24.32 mg/g. The adsorption process of Cu$^{2+}$ conformed to quasi-second-order kinetics model and Langmuir adsorption isotherm, which indicating that the adsorption process was mainly chemical adsorption and monolayer adsorption. Continuous adsorption-desorption experiments showed that SCDO had good regenerative ability. After four times of continuous adsorption and desorption, the adsorption capacity decreased from 24.01 mg/g to 21.07 mg/g, without obvious loss of adsorption capacity. In summary, these results revealed that the prepared adsorbents could be considered as effective and promising materials for remove of Cu$^{2+}$ in wastewater.

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