Preparation of In Situ ZIF-9 Grown on Sodium Alginate/Polyvinyl Alcohol Hydrogels for Enhancing Cu (II) Adsorption from Aqueous Solutions

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Abstract
Metal–organic framework materials (ZIF-9) were loaded on Sodium alginate/polyvinyl (PVA/SA) hydrogel by in situ growth method for adsorption of heavy metal Cu (II). The structure of hydrogels composited with MOFs and polymers was designed to improve the poor mechanical properties of natural polymer gel materials and the inconvenience of powdered MOFs materials in practical applications. The adsorption results showed that the optimum adsorption process of Cu (II) pH was 5.0. The adsorption kinetics and isotherm suggest that the adsorption process follows the Freundlich isotherm and the pseudo-second-order models. The experimental maximum adsorption capacity was 98.98 mg/g, 2.6 times and 1.5 times higher than ordinary SA and PVA/SA hydrogel spheres. Synthesized hydrogel spheres were characterized by FT-IR, SEM, XRD, and XPS, which confirmed that MOF materials have grown in situ on PVA/SA hydrogel spheres. More importantly, PVA/SA@ZIF-9 exhibited exceptional mechanical stability and showed excellent recycling capability in the cyclic adsorption process.

Keywords Sodium alginate hydrogel · ZIF-9 · Cu (II) · adsorption

1 Introduction

Industrial wastewater containing a large number of heavy metal ions is directly or indirectly discharged into natural water bodies, which seriously threatens the water resources that human beings rely on [1]. Among the many heavy metal ions, copper, as an essential trace element for animals and humans, can help iron transfer proteins and plays an important role in the catalytic process of heme formation. Of course, heavy metal, copper can also be harmful in excess, since Copper ions denature proteins. When the copper in the body accumulates to a certain amount, symptoms such as developmental stagnation, physiological lesions, and even death, the current large-scale application of copper in industry and life has also made the problem of copper pollution increasingly serious.

The commonly used treatment methods for heavy metal pollution in water are chemical precipitation [2], electrochemical treatment [3], membrane treatment [4], ion exchange [5], and adsorption methods. Among them, the adsorption method has the advantages of simple operation, low cost, and environmental friendliness, making it become one of the most potential technologies widely used in treating heavy metal pollution in water [6–9]. A large number of adsorbent materials have already been applied to the treatment of heavy metal pollution in water, such as modified cellulose materials [10, 11], activated carbon fiber material [11], nanocrystalline materials [12], magnetic nanomaterials [13], etc. However, seeking high-efficiency and novel adsorption materials and applying them to the field of heavy metal treatment in water is still a hot research topic for scholars. In recent years, the application of hydrogel adsorbs treating heavy metals in water has received extensive attention. The hydrogel material is a polymer compound that has abundant adsorption active sites on its network polymer chain, such as -OH, -NH2, -COOH, -SO3H, -CONH2, etc., so it can remove the target metal ions from the contaminated water by effectively interacting with the target metal. Based on environmental friendliness and economic cost considerations, natural polymer materials have been widely used in heavy metal pollution treatment in water [14]. Common natural polymers include cellulose, chitosan, sodium...
alginate, etc. Among them, sodium alginate, as a natural polysaccharide, is rich in carboxyl (−COOH) and hydroxyl (−OH) functional groups. It reacts with multivalent metal ions such as Ca(II) and Fe(III) to form a gel with a three-dimensional network structure, which has the advantage of good solid–liquid separation when used in water. In addition, it has the advantages of good biocompatibility, biodegradability, comprehensive source, and economic availability. However, applying a single sodium alginate hydrogel material also has shortcomings, such as limited adsorption active sites and poor mechanical properties, which limit its practical use due to possible difficulties such as disintegration. It has been reported that biochar, cellulose, gelatin, and other materials are blended and embedded with sodium alginate to enhance their mechanical strength and other properties. Li et al. prepared apatite/attapulgite/alginate composite hydrogels to adsorb aqueous solution methylene blue (MB). It was stated that the apatite and attapulgite particles enhanced the hydrogel structure. At the same time, the composite gel with attapulgite and apatite added increased the porosity and effectively active adsorbed sites, improving the affinity of the hydrogel surface. Compared to conventional alginate hydrogels, it has a higher adsorption capacity.

Metal–organic frameworks (MOFs), as a new type of porous material, usually have the advantages of high porosity, large surface area, and controllable composition. These benefits allow MOFs to be synthesized by various methods and widely studied in wastewater treatment and resource recovery applications. However, most of the current MOFs reported are in powder form. The practical application of powdered MOFs was limited due to the disadvantages of poor processability, recyclability, and potential safety hazards of dust formation. Some processing steps are required to address these issues to improve the machinability of MOFs in practical applications. The easiest way is to bond MOFs particles using a binder to form bulky particles directly. However, this often reduces surface area and severe pore plugging. Another approach is combining MOFs with other materials to create composite materials, which produce synergistic effects that enhance material functionality. ZIF-9 is a powdered MOFs material prepared with Co(II) as a metal ion and benzimidazole (bIm) as an organic ligand. Like most other powdered MOFs, there are certain defects in the practical application process.

Therefore, the final product combines the advantages of the natural polymer material SA containing significant adsorption functional groups porous structure of MOFs materials, using PVA/SA hydrogels as the matrix, loading ZIF-9 by in situ growth method hydrogels in this study. It solves the problems of poor mechanical properties of SA hydrogels and inconvenient application of MOFs powder materials. Conventional methods characterized the prepared PVA/SA@ZIF-9 composites; total reflection Fourier transform infrared spectroscopy (ATR-FTIR), field emission scanning electron microscopy (FE-SEM), and X-ray electron spectroscopy (XPS), Brunauer, Emmett and Teller Specific Surface Area (BET), X-ray diffraction. Finally, the prepared PVA/SA@ZIF-9 material was applied to Cu(II) adsorption. The adsorption pH, adsorption kinetics, adsorption isotherm, adsorption thermodynamics, and recycling performance during the adsorption process were studied by adsorption experiments, which verified the application potential of the adsorbent.

2 Materials

SA (C₆H₇NaO₆)m, PVA (C₂H₄O)n, calcium chloride (CaCl₂), Cobalt Nitrate Co(NH₃)₂·6H₂O, Benzimidazole (bIm), N, N’-Dimethylformamidamide (DMF) were obtained from Macklin Biochemical Co., Ltd (Shanghai, China), cupric nitrate (Cu(NO₃)₂·3H₂O), hydrochloric acid (HCl), sodium hydroxide (NaOH), and sodium chloride (NaCl) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). A stock Cu(II) solution of 1000 mg/l was prepared and further diluted to the desired levels for later use.

3 Experiment and Methods

3.1 Preparation of PVA/SA Gel Spheres

2.81 g SA powder was dissolved in 100 ml of PVA (2.48%, w/v) as solution A. After stirring vigorously for 3 h, the PVA/SA solution was dropped into 300 ml CaCl₂ solution (2.4%, w/v) with a syringe needle. The PVA/SA hydrogels obtained were soaked in the CaCl₂ solution for 24 h to ensure complete gelation. The uncross-linked calcium ions on the surface of the hydrogels were washed with distilled water. According to the different contents of sodium alginate SA (2.5, 3.0, 3.5, 4 g), the as-prepared PVA/SA composite hydrogels were named PVA/SA-2.5, PVA/SA-3.0, PVA/SA-3.5, PVA/SA-4.0. A part of hydrogels was stored in water for later use. The rest of the hydrogel spheres were freeze-dried.

3.2 Preparation of PVA/SA@ZIF-9 Gel Spheres

The PVA/SA hydrogels were placed in 100 ml 58.7 g/l Co(NO₃)₂·6H₂O N, N’-Dimethylformamide solution and stirred for 12 h. Hydrogels were washed with N, N’-Dimethylformamide solution three times to remove unab sorbed ions. Then all hydrogels were added to 23.5 g/l benzimidazole N, N’-Dimethylformamide solution, and
6 ml of ammonia water was slowly added dropwise during stirring. After being stirred for 12 h, hydrogels were washed with \( N, N' \)-Dimethylformamide solution three times to remove unbound benzimidazole. The PVA/SA@ZIF-9 composite hydrogels were dried in a vacuum drying oven at 60 °C and stored to use in Cu(II) adsorption.

### 3.3 Adsorption Experiment

The Cu(II) solution was obtained by diluting 1000 mg/l Cu(II) stock solution (Cu(NO\(_3\))\(_2\)·3H\(_2\)O) by the stepwise dilution method and sealed at 4 °C. 0.05 g of PVA/SA hydrogel adsorbents were added to 50 ml of Cu(II) solution with a concentration of 20–500 mg/l and shaken at a constant temperature shaker (160 rpm). The pH of the Cu(II) solution was adjusted between 2 and 6 with 0.1 mol HCl/NaOH solution. The effect of adsorption time on the capacity of Cu(II) solution was investigated. The remaining concentration of Cu(II) in the solution after adsorption was confirmed by ICP-OES. The removal rate of Cu(II) by the adsorbent (R, %), the adsorption capacity (q\(_e\), mg/g) corresponding to any time t (min), and the equilibrium adsorption capacity (q\(_e\), mg/g) were calculated as follows:

\[
R(\%) = \frac{C_0 - C_e}{C_0} \times 100
\]

\[
q_t = \frac{C_0 - C_t}{m} \times V
\]

\[
q_e = \frac{C_0 - C_e}{m} \times V
\]

where \( C_0, C_t, C_e \) represent the Cu(II) concentration (mg/l) in the solution at the initial time, time t, and equilibrium, respectively; m is the dry weight of the adsorbent; V is the Cu(II) solution (L) volume. The experimental adsorption data are the average value of two or more repeated experiments.

### 3.4 Adsorption–Desorption Experiments

The desorption steps were as follows: The PVA/SA@ZIF-9-Cu(II) hydrogels were put into 50 ml of 0.2 mol/l HCl with mechanically stirring at 200 rpm at 25 °C for 2 h. Then the hydrogels above were repeatedly washed with deionized water until the pH of the aqueous solution was neutral, and then the regeneration of PVA/SA@ZIF-9 hydrogels was repeated 8 times for the Cu(II) adsorption.

### 3.5 Characterization Analysis

Fourier transform infrared (FTIR, Nicolet 6700 Thermo fisher, USA) spectroscopy was used to analyze the functional groups of hydrogels and adsorption mechanism at the scanning wavenumber range from 650 to 4000 cm\(^{-1}\), the resolution was 4 cm\(^{-1}\), and the reflection accessory was diamond-ATR. The morphology of the composite hydrogels was investigated by field emission scanning electron microscope treated with gold spraying (SEM, JSM-6610LV, Tokyo, Japan). X-ray diffraction (XRD, D8 FOCS, Germany) was used to explore the crystalline structure of composite hydrogels with CuK\(_\alpha\) radiation from 5°~65°. The detection voltage was 40 kV, the analysis current was 40 mA, and the scanning rate was 3°~5°/min. A 200 mg sample was weighed for specific surface area testing to calculate the specific surface area of PVA/SA and PVA/SA@ZIF-9 using the Brunauer, Emmett and Teller Specific Surface Area (BET) method and N\(_2\) adsorption–desorption isotherms at 77 K to evaluate their pore structure. Vacuum degassing for 6 h at 120 °C. (Autosorb-iQ2, Quantachroe, USA). The chemical elements were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB, Thermo Fisher, USA) spectrometer before and after modification and adsorption. The binding energy was corrected with C 1s (284.8 eV). Avantage software processed the resulting spectrum for peak separation.

### 4 Results and Discussion

#### 4.1 Analysis of Preparation Materials

##### 4.1.1 FT-IR Analysis

The FTIR spectra of SA, PVA/SA, ZIF-9, PVA/SA@ZIF-9, and PVA/SA@ZIF-9-Cu hydrogels were shown in Fig. 1. The wideband at 3600–3000 cm\(^{-1}\) corresponded to the stretching vibration of -OH[29]. The peaks at 2800–3000 cm\(^{-1}\) were attributed to the C-H (-CH or -CH\(_2\)) stretching vibration. Since PVA was rich in -OH and C-H groups, the FTIR spectra of PVA/SA, -OH, and C-H stretching vibration are significantly more robust than SA hydrogels. In addition, the peaks of 1620 and 1419 cm\(^{-1}\) were the asymmetric and symmetric stretching vibrations of carboxylate (-COO\(^-\)), respectively[30]. The peaks at 1070 cm\(^{-1}\) were due to the C–OH bond of the alcoholic hydroxyl group[31]. In the FTIR spectra of PVA/SA-ZIF-9, the peaks of 3440 cm\(^{-1}\) belong to the benzimidazole -NH stretching vibration. Since PVA was rich in -OH and C-H groups, the FTIR spectra of PVA/SA, -OH, and C-H stretching vibration are significantly more robust than SA hydrogels. In addition, the peaks of 1620 and 1419 cm\(^{-1}\) were the asymmetric and symmetric stretching vibrations of carboxylate (-COO\(^-\)), respectively[30].
was successfully grown in situ on the PVA/SA hydrogels from the results above. After the PVA/SA@ZIF-9 hydrogels were combined with Cu(II), -COO-groups belonging to the carboxylate moved to the low frequency (from 1620 to 1600 cm\(^{-1}\), 1419 to 1410 cm\(^{-1}\)); the positions of the characteristic peaks changed obviously, which indicated that the hydrogels material participated various reactions during the possible process of Cu(II) adsorption.

### 4.1.2 Morphological Characteristics of SA, PVA, PVA/SA/@ZIF-9

Figure 2a showed the morphology of SA under the emission scanning electron microscope; the surface of SA was relatively smooth and flat. Figure 2b showed the morphology of PVA/SA. Compared with the SA hydrogel, the material after composite PVA has a more apparent lamellar structure, which was conducive to the diffusion of heavy metal ions during the adsorption process of the material and increased the active adsorption sites of the material. Figure 2c was the SEM image of ZIF-9, the Crystal structure was shown in the upper right corner, the pore structure image of the hydrogel (Fig. 2d) showed that ZIF-9 crystals are attached and embedded, and its porous structure has not changed due to the loading of ZIF-9.
4.1.3 XRD Analysis

Figure 3 shows the XRD pattern of the ZIF-9 and PVA/SA/@ZIF-9 composite material, showing that the XRD pattern of the PVA/SA/@ZIF-9 composite was consistent with the ZIF-9 pattern, indicating that the crystal structure of ZIF-9 was supported by PVA/SA hydrogel through in situ growth method was not affected. A few characteristic peaks of ZIF-9 were weakened, probably because ZIF-9 was coated by sodium alginate and polyvinyl alcohol in PVA/SA hydrogel. However, it also shows that PVA/SA/@ZIF-9 composite material preparation was successful.

4.1.4 BET Analysis

The BET test was used to investigate the effect of the in-situ growth of ZIF-9 on the surface of PVA/SA hydrogels on the material’s porous structure. The N2 adsorption–desorption isotherms and pore size distributions of PVA/SA and PVA/SA/@ZIF-9 hydrogels was shown in Fig. 4. The surface area and average pore diameter of PVA/SA were 6.2481 m²/g and 26.56 nm, while the surface area and the average pore diameter of PVA/SA@ZIF-9 were 70.1531 m²/g and 15.43 nm, which could be attributed to the high specific surface area of ZIF-9. Compared with PVA/SA hydrogels, PVA/SA/@ZIF-9 exhibited a larger specific surface area, indicating by loading ZIF-9 in situ growth to PVA/SA hydrogels, significantly increased the specific surface area of the material and was beneficial to the adsorption process.

4.1.5 XPS Analysis

The element binding energy of PVA/SA, PVA/SA@ZIF-9, and PVA/SA@ZIF-9-Cu were further investigated by using XPS. As shown in Fig. 5a, the characteristic peak of N 1s can be observed around 399.5 eV in the PVA/SA/@ZIF-9 hydrogel spectrum. When PVA/SA/@ZIF-9 hydrogel adsorbed Cu(II), a Cu 2p spectrum appeared, indicating that Cu(II) was adsorbed on PVA/SA/@ZIF-9 hydrogel. The characteristic peak of Ca 2p disappears in the PVA/SA/@ZIF-9-Cu hydrogel spectrum, which may be caused by the ion exchange between Cu(II) and Ca(II). The gel morphology of the adsorbent is not destroyed after the adsorption, which proves that the primary interaction with the associated Ca(II) was not completely replaced. In the high-resolution XPS spectrum of O 1s (Fig. 6b), it was found that PVA/SA/@ZIF-9 had different peaks of 533.5, 532.5, and

![Fig. 3 XRD patterns of ZIF-9, PVA/SA/@ZIF-9](image)

![Fig. 4 N2 adsorption and desorption isotherms of PVA/SA and PVA/SA/@ZIF-9, corresponding pore size distributions](image)
531.2 eV, which were the binding energies by C–OH, C = O, and C–O–C of the composite hydrogel, respectively[33]. While the hydrogel adsorbed Cu(II), its peak value transferred to 533.0, 531.5, and 530.2 eV, respectively. The C 1 s spectrum (Fig. 6c) shows three peaks, in which 287.4 and 285.5 eV were ascribed to C = O and C-O of the composite hydrogel, and 284.1 eV was the binding energy of C–C[34], respectively. When the material was combined with Cu(II), the binding energies of C = O, C-O, and C–C transferred to 287.3 eV, 285.3 eV, and 283.5 eV, respectively, indicating that the adsorption process of Cu(II) by composite hydrogel materials involves oxygen-containing functional groups. The peaks of 399.9 and 399.5 eV in the N 1 s (Fig. 5d) XPS spectrum of PVA/SA@ZIF-9 hydrogel were the binding energies of -NH- and -N = of benzimidazole in ZIF-9, respectively[35]. After adsorption of Cu(II), the binding energy of N peak transferred to 398.8 and 397.4 eV, respectively. The intensity of the N 1 s peak was observed to decrease, indicating that ZIF-9 in the composite hydrogel had an adsorption effect on Cu(II).

The FTIR and XPS results suggest that the carboxyl and hydroxyl functional groups had cation exchange and complexing with Cu(II) PVA/SA@ZIF-9 hydrogels and Cu (II) ions, at the same time physical adsorption also played a role. The adsorption mechanism was described in Fig. 7.

4.2 Target Cu Ions Removal Experimental Studies

4.1.6 Effects of pH

The pH of the aqueous solution directly affects the form of adsorbate in the water and the chemical properties of the adsorbent. Therefore the SA, PVA/SA PVA/SA@ZIF-9 hydrogels were added to the initial Cu(II) concentration of 50 mg/l when the pH value of the solution was 2–6. the results were shown in Fig. 7. The three adsorbents have a
similar overall change trend under different initial pH values of the solution. As the pH increases from 2 to 6, the removal efficiency of Cu(II) by the three materials increases gradually. PVA/SA and PVA/SA@ZIF-9 reached the maximum removal rate of Cu(II) at pH 5 and then decreased. And PVA/SA@ZIF-9 has a significantly higher removal rate of Cu(II) than the other materials under the research conditions, which may be due to the improved number of adsorption sites and adsorption-specific surface area after composite ZIF-9 material. At lower pH, the removal rate is correspondingly lower due to the competitive effect between H\(^+\) and Cu\(^{2+}\) for adsorption sites [36]. The competitive relationship weakened when the pH value gradually increased, Cu\(^{2+}\) had more opportunities to contact the unoccupied adsorption sites, which led to an increase in the removal rate. It was observed in this study that the reduced removal rate of Cu(II) at pH = 6 may be due to the formation of partial copper hydroxide precipitation, and functional groups such as -COOH and -OH in the adsorbent cannot interact with this state of Cu(II) binding. In summary, the experimental content of this chapter selects pH 5 as the experimental condition for subsequent adsorption experiments.

4.1.7 Adsorption Kinetics and Adsorption Isotherms

To study the interaction mechanism between hydrogels and Cu(II) and evaluate its adsorption capacity, two typical adsorption isotherm models, the Langmuir theoretical model
and Freundlich theoretical are used to fit the experimental results, and their nonlinear forms are as follows:

\[ q_e = \frac{K_L q_m c_e}{1 + K_L c_e} \quad (4) \]

\[ q_e = K_F c_e^n \quad (5) \]

where \( q_m \) is the theoretical maximum adsorption capacity of the adsorbent (mg/g); \( K_L \) is related to the adsorption energy Langmuir constant (L/mg); \( K_F \) represents the Freundlich constant \([(mg/g)/(mg/l)^{1/n}] \) related to the adsorption capacity of the multilayer, \( n \) is a dimensionless parameter. Figure 8a depicted the adsorption of Cu(II) on SA, PVA/SA-2.5, PVA/SA-2.8, PVA/SA-3.0, PVA/SA-3.5, PVA/SA-4 hydrogels adsorption isotherm at room temperature. As shown in the Figure, in the lower initial Cu(II) concentration range, the adsorption capacity of the adsorbent increases sharply. And with improving the initial concentration, the adsorption capacity increases slowly, the reason was the number of available active sites changed on the adsorbent surface. These results also suggest that with the increase of initial Cu(II) concentration, the total amount of adsorbed Cu(II) increases, and the adsorption capacity of PVA/SA@PAM-2.8 hydrogels was higher than that of SA, PVA/SA, and PVA/SA-3.0, PVA/SA-3.5, PVA/SA-4. The increase of SA content resulted in more hydroxyl (-OH) and carboxyl (-COOH) groups in the PVA/SA hydrogel. Therefore, a higher Cu(II) adsorption capacity can be obtained. However, the adsorption capacity decreased slightly with the further increase of SA concentration, which was caused by the reducing the chances of adsorbate capturing binding sites that were due to excessive crosslink density, similar to the work reported[37]. In addition, it can be seen from Fig. 8b that the introduction of porous material ZIF-9 by in situ growth on PVA/SA-2.8 hydrogel improves the adsorption specific surface area of the hydrogel material and enhances the adsorption performance of the composite material. Based on this, PVA/SA@ZIF-9 (SA content 2.8) was selected as the adsorbent for subsequent adsorption experiments.

![Fig. 8 a The adsorption isotherms of Cu(II) on SA, PVA/SA-2.5, PVA/SA-2.8, PVA/SA-3.0, PVA/SA-3.5, PVA/SA-4 hydrogels; b Adsorption isotherms of Cu(II) on SA, PVA/SA-2.8 and PVA/SA@ZIF-9 hydrogels; c PVA/SA@ZIF-9-Cu hydrogels adsorption kinetic curves](image-url)
Table 1 shows the results and correlation coefficients obtained by fitting the Langmuir model and the Freundlich model to the experimental data. According to the correlation coefficient ($R^2$), it can be seen that the adsorption data of SA, PVA/SA, and PVA/SA@ZIF-9 show a better fit with the Freundlich model. In addition, the obtained constants $R_L$ and $n$ are between 0 and 1, which indicates that the adsorption reaction is easy to proceed with [38]. Besides, the Langmuir adsorption isotherm calculated that the maximum adsorption capacity of PVA/SA@ZIF-9 for Cu(II) was 116.22 ± 3.73 mg/g, and the experimental value was 98.98 mg/g, which was about SA (39.79 ± 1.02 mg/g) and PVA/SA (71.31 ± 2.01 mg/g) 2.9 and 1.6 times. The results indicate that the composite porous material ZIF-9 has significantly enhanced the Cu(II) adsorption capacity of PVA/SA hydrogels.

Kinetic processes are also critical for evaluating potential adsorbent materials for practical applications. Figure 9c depicts Cu(II) adsorption kinetics on PVA/SA@ZIF-9 gel spheres at different initial concentrations (50, 100, and 200 mg/l). In this experiment, pseudo-second-order and pseudo-first-order kinetic models are used to fit the experimental data, and their nonlinear forms are as follows:

$$q_t = q_e(1 - e^{-K_1t})$$  
$$q_t = \frac{k_2q_e^2t}{1 + k_2q_et}$$

where, $K_1$ (1/min) and $K_2$ [g/(mg min)] and $t$ (min) are the rate constants associated with the pseudo-first-order kinetic model, the rate constant and time of the pseudo-second-order kinetic model, respectively.

The influence of contact time on the adsorption efficiency of Cu(II) was discussed (Fig. 8c). The adsorption capacity of PVA/SA@ZIF-9-Cu increased rapidly from 41.76 to 68.2 mg/g as the time increased from 1 to 6 h at the initial concentration was 200 mg/l. Then, the increased rate of adsorption capacity decreased with the extension of adsorption time, which indicated that the adsorption active sites were gradually depleted, and the adsorption reached saturation. The rapid absorption rate in the initial phase was due to sufficient unoccupied adsorption sites and a large concentration gradient as the driving force; the Cu (II) in the solution slowly penetrated the PVA/SA@ZIF-9 composite hydrogels and occupied the internal active sites. After the active areas were gradually

| Adsorbent          | Langmuir isotherm | Freundlich isotherm |
|--------------------|-------------------|---------------------|
|                    | $q_m$ (mg/g)      | $K_L$ (L/mg)       | $R_L$ | $R^2$ | $K_F$ (mg/g) | $n$ | $R^2$ |
| SA                 | 39.79             | 0.025               | 0.0816–0.3798 | 0.933 | 10.934 | 0.2040 | 0.9714 |
| PVA/SA-2.5        | 66.862            | 0.024               | 0.0844–0.3720 | 0.916 | 16.833 | 0.3626 | 0.9949 |
| PVA/SA-2.8        | 71.31             | 0.023               | 0.0881–0.3620 | 0.934 | 17.280 | 0.3116 | 0.9925 |
| PVA/SA-3.0        | 63.906            | 0.019               | 0.1047–0.3232 | 0.953 | 12.949 | 0.2632 | 0.9891 |
| PVA/SA-3.5        | 57.99             | 0.026               | 0.0787–0.3884 | 0.959 | 16.506 | 0.2417 | 0.9753 |
| PVA/SA-4.0        | 58.592            | 0.024               | 0.0851–0.3702 | 0.946 | 15.485 | 0.3094 | 0.9075 |
| PVA/SA@ZIF-9      | 116.22            | 0.010               | 0.1818–0.2157 | 0.975 | 11.569 | 0.3524 | 0.9920 |

Fig. 9 a Effect of temperature on the adsorption of Cu(II) on PVA/SA@ZIF-9 b van’t Hoff’s curves
saturated, resulting in a decrease in the adsorption rate of Cu(II) until equilibrium is reached [33]. Based on the results above, a reaction time of 12 h was used as the reaction condition for the subsequent adsorption experiments.

Table 2 presents the results of relevant experimental data by pseudo-first-order and pseudo-second-order kinetic models. It is shown that the linear correlation coefficient of the pseudo-second-order kinetic model ($R^2 = 0.981, 0.992, \text{and } 0.991$) was better than that of the pseudo-first-order kinetic model ($R^2 = 0.975, 0.981, \text{and } 0.962$) at different initial concentrations (50, 100, and 200 mg/l). Therefore, the adsorption process of Cu(II) on PVA/SA@ZIF-9 composite hydrogels was chemical adsorption [39].

4.1.8 The Effect of Temperature and Adsorption Thermodynamics

Thermodynamic studies were carried out at 293.15, 298.15, 303.15, 308.15, 313.15 K temperature, respectively. The results were shown in Fig. 9a. With the increase in temperature, the adsorption of Cu(II) by PVA/SA increased. The adsorption process was endothermic.

The thermodynamic parameters such as enthalpy change $\Delta H^0$ (KJ/mol), entropy $\Delta S^0$ [J/(mol K)], and Gibbs free energy $\Delta G^0$ (KJ/mol) in the adsorption process are calculated by the following formula:

$$\ln K_T = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$  \hspace{1cm} (8)

$$\Delta G^0 = -RT \ln K_T$$  \hspace{1cm} (9)

$$K_T = \frac{q_e}{C_e}$$  \hspace{1cm} (10)

Table 2 Adsorption kinetic parameters of PVA/SA@ZIF-9 for different initial Cu(II) concentrations

| $C_0$ (mg/l) | $q_{e,exp}$ (mg/g) | Pseudo first-order model | Pseudo second-order model |
|---------------|------------------|-------------------------|--------------------------|
|               | $q_{e,cal}$ (mg/mg) | $k_1$ (1/min) | $R^2$ | $q_{e,cal}$ (mg/mg) | $k_1$ [g/(mg min)] | $R^2$ |
| 50            | 44.2             | 47.5 ± 2.2             | 0.0036 | 0.9757 | 63.9 ± 3.9 | 0.00005 | 0.9811 |
| 100           | 58.4             | 59.7 ± 1.2             | 0.0004 | 0.9816 | 76.1 ± 2.3 | 0.00006 | 0.9920 |
| 200           | 76.2             | 71.9 ± 1.5             | 0.0119 | 0.9625 | 81.2 ± 1.3 | 0.00019 | 0.9915 |

Table 3 Thermodynamic parameters of Cu(II) adsorption by PVA/SA@ZIF-9

| Temperature(K) | $\ln K_T$ | $\Delta G^0$ (KJ/mol) | $\Delta H^0$ (KJ/mol) | $\Delta S^0$ [J/(mol K)] |
|----------------|------------|-----------------------|-----------------------|--------------------------|
| 293            | 1.87       | -4.55                 | 19.5814               | 82.2562                  |
| 298            | 2.03       | -5.03                 |                       |                          |
| 303            | 2.05       | -5.17                 |                       |                          |
| 308            | 2.22       | -5.68                 |                       |                          |
| 313            | 2.42       | -6.29                 |                       |                          |
Pb(II), Hg(II), and Cu(II)) indicates that PVA/SA@ZIF-9 can be used in some specific. It has high application potential in wastewater treatment.

4.1.10 Recycling Performance Evaluation Experiment

The recycling performance of PVA/SA@ZIF-9 hydrogels is shown in Fig. 10, and the experimental results suggest the adsorption capacity Cu(II) of the PVA/SA@ZIF-9 hydrogels decreased slightly with using dilute acid as the eluent to regenerate the adsorbent after several cycles of adsorption and desorption experiments. The adsorption capacity from the first to the eighth time was 44.2–38.2 mg/g, which maintained an excellent removal effect. The structure of the hydrogels remained intact and presented no apparent difference (Fig. 11).

5 Conclusion

The PVA/SA composite hydrogel material prepared by in situ growth composite ZIF-9 significantly enhanced the adsorption effect of sodium alginate hydrogel on Cu(II). The experimental results show that complexation, cation exchange, and physical adsorption are the main adsorption mechanisms, and -OH and -COOH in the composite material are involved in the adsorption process and the result of ion exchange between Ca\(^{2+}\) and Cu\(^{2+}\). PVA/SA@ZIF-9 shows the maximum adsorption capacity for Cu(II) (98.98 mg/g) under optimal conditions, approximately 2.6 and 1.5 times that of ordinary SA and PVA/SA hydrogels. Besides, adsorption potential for different metal ions results shows it also has good application prospects in lead and mercury adsorption. The adsorption–desorption cycle performance research experiments further demonstrated the excellent adaptability and mechanical stability of PVA/SA@ZIF-9. Therefore, considering the simple production process, low cost of raw materials, good adsorption capacity, strong adaptability, and good mechanical stability, the synthesized PVA/SA@ZIF-9 demonstrated its potential for some experimental heavy metal-containing wastewater treatment.

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Author Contributions  GZ: Experimentalize, Data collection, Writing-original draft. GY: Investigation, Aid with Synthesis and Preliminary Characterization. HC: Data curation, Formal analysis. HF: Supervision, Writing-review & editing.

Declarations

Conflict of Interest  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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