Facile fabrication of sodium carboxymethyl cellulose/reduced graphene oxide composite hydrogel and its application for Pb(II) removal

1 | INTRODUCTION

Heavy metals ions in water have attracted close attention due to their toxicity, non-biodegradability and carcinogenicity [1]. Because lead ions are more harmful to the human body and tend to accumulate in the body, their removal from wastewater is necessary [2]. Adsorption method was extensively used to remove/recover toxic metal ions, owing to its low cost, convenient operation, no secondary pollution and diversified nature [3–5]. Most conventional adsorbents are in powder form, which makes it difficult to collect after adsorption.

Graphene and its derivative have become widely used for functional materials [6, 7]. Graphene oxide (GO) with plenty of reactive functional groups including hydroxyl, carboxyl and epoxy groups is obtained by strong oxidation and stripping of graphite. Abundant oxygen-containing functional groups can be used as active sites to adsorb heavy metals. Therefore, GO can be widely used in the field of heavy metal adsorption [8, 9]. However, due to the presence of a large number of hydrophilic groups, GO has good hydrophilicity, which makes it difficult to be separated and recycled after adsorption [10, 11]. Therefore, it is necessary to further modify the GO. It is expected to assemble three-dimensional (3D) aerogels by combining GO with chain-like biomass molecules or polymers. Sodium carboxymethyl cellulose (CMC), a hydrosoluble anion linear biopolymer and semi-synthetic derivative of cellulose, is obtained by substituting the 2,3,6-hydroxyl groups of cellulose with a carboxymethyl moiety [12]. Because of its low cost, nontoxic, renewable, biodegradable and modifiable characteristics, CMC is considered a biocompatible material and can be used for drug delivery and tissue engineering. And the CMC aqueous solution still has high viscosity at low concentration, it is widely used as an adhesive in industry. It is also an effective adsorbent for removing metal ions because it contains many active functional groups, including hydroxyl and carboxyl groups that can chelate metal ions and interact with organic compounds. However, it has weak mechanical properties. Therefore, it is difficult to directly assemble GO and CMC to form aerogels with strong mechanical properties. Recent work has demonstrated that during AA reduction of graphene oxide, some oxygen-containing functional groups on the GO surface could be removed, which would lead to the aggregation of GO sheets and improve the mechanical strength on a macro scale [13, 14].

In this letter, the sodium carboxymethyl cellulose/reduced graphene oxide (rGO-CMC) composite hydrogel was prepared by one-step hydrothermal reduction with ascorbic acid. GO and CMC were cross-linked and entangled while GO was used as the structural substrate, CMC acted as the skeleton and the reduction process facilitated the formation of stable aerogels. The rGO-CMC composite hydrogel was used for adsorption of metal ions in aqueous solution. Compared with GO, rGO-CMC composite exhibited low hydrophilicity, avoided fracture and collapse, improved mechanical properties, and retained complete aerogels after freeze drying. This work will provide a convenient method for preparing rGO-CMC composite hydrogel adsorbents.

2 | EXPERIMENTAL PROCEDURES

Graphite power (100 mesh, purity > 99.5%) was obtained from Nontang Xianghai Carbon Product Co., Ltd. Sodium carboxymethyl cellulose (CMC, 800–1200 mpa s) was purchased from Shanghai Shanpu Carbon Product Co., Ltd. Metal salts including Pb(NO₃)₂, MnCl₂·4H₂O, K₂CrO₄, NiCl₂·6H₂O, Co(NO₃)₂·6H₂O and CuSO₄·5H₂O were supplied by Tianjin Kermel Chemical Reagent Factory. Ascorbic acid (AA, 99%) was provided by Aladdin Industrial Corporation. Sulfuric acid (H₂SO₄, 98%), hydrochloric acid (HCl, 37 wt%), phosphoric acid (H₃PO₄, 85%), potassium permanganate (KMnO₄) and hydrogen peroxide (H₂O₂, 30 wt%) were bought from Sinopharm Chemical Reagent Co., Ltd.

2.1 | Preparation of GO

Graphene oxide (GO) was synthesized by an improved hummers method [13]. Graphene oxide (GO) was synthesized by an improved hummers method. Firstly, the mixed acid of 36 mL H₂SO₄ and 4 mL H₃PO₄ was added into a mixture of 300 mg
of natural flake graphite powder and 1500 mg potassium permanganate powder in an ice bath. Next, the mixed system was stirred continuously at 50 °C in oil bath to full oxidation. Subsequently, the system was cooled to room temperature, and then 30% H₂O₂ was added to remove the residual KMnO₄ until the colour of suspension turned luminous yellow. After that, the dispersion was washed three times with 1 mol L⁻¹ HCl via centrifugation (10,000 rpm) to remove metal ions, and it was further washed with ultrapure water until the pH reached neutral. Finally, graphene oxide was made up to 60 mL with ultrapure water and sonicated for 30 min to obtain GO suspension (5 mg mL⁻¹).

2.2 Preparation of rGO and CMC/rGO aerogels

rGO and CMC/rGO aerogels were prepared by facile hydrothermal process (Figure 1). In a typical procedure, various amounts of sodium carboxymethyl cellulose (CMC) (0, 10, 20 and 30 mg) were added into 10 mL GO suspension (5 mg mL⁻¹), followed by stirring and ultrasonic for 20 min to disperse evenly. Next, 50 mg ascorbic acid (AA) was added, and the mixed solution was stirred for 10 min. The whole system was transferred into a 25 mL Teflon-lined autoclave and reacted at 80 °C for 4 h. The obtained CMC/rGO hydrogel was soaked in water overnight to remove the remaining AA and CMC, and then freeze-dried to obtain CMC/rGO aerogel. Composite materials with different mass ratios (GO:CMC = 5:0, 5:1, 5:2, 5:3) were defined as rGO, CMC/rGO-1, CMC/rGO-2 and CMC/rGO-3, respectively. When the content of CMC continued to increase, it caused the edge of the rGO/CMC composite to peel and scatter during the freeze-drying process. The effect of AA on the morphology of composites was also studied. When AA was not added, the composite did not form a columnar hydrogel.

2.3 Characterisation

The surface morphology of sample was studied by scanning electron microscopy (SEM, FSM-5600LV). The specific surface area (SSA) and pore size of materials were measured by Brunauer–Emmett–Teller (BET, Kubo X1000). Fourier transform infrared (FT-IR) spectroscopy was carried out using a Nicolet 6700 spectrometer. The elemental composition of materials was studied by X-ray photoelectron spectroscopy (XPS, Kubo X1000). The zeta potential of sample was analysed by the zeta potential analyser (ZS, MAL1042861).

2.4 Adsorption experiments

Batch adsorption experiments were carried out in sealed 50 mL conical flask which contained 5 mg of adsorbent and 25 mL of metal ion solution, and performed in a thermostatic oscillator. The adsorbed solution was filtered through a 0.45 μm filter membrane. The standard solutions of Pb(II), Cu(II), Ni(II), Mn(II), Co(II) and Cr(VI) were obtained by dissolving Pb(NO₃)₂, MnCl₂·4H₂O, K₂CrO₄, NiCl₂·6H₂O, Co(NO₃)₂·6H₂O and CuSO₄·5H₂O in ultrapure water, respectively. The adsorption kinetic was investigated by oscillating the lead ion solution (50 mg L⁻¹) and the rGO-CMC-3 adsorbent at 308 K with contact time ranging from 5 to 210 min. The adsorption isotherm was studied by oscillating the lead ion solution (10–100 mg L⁻¹) and the rGO-CMC-3 adsorbent at 298, 308 and 318 K. The effect of CMC content on the adsorption of different metal ions was studied. 0.1 M HNO₃ was used for regenerating adsorbent. HCl and NaOH solutions were used to adjust the pH of the solution. The initial and final concentrations of the metal ion solution were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The removal rate (Equation (1)) and adsorption capacity (Equation (2)) are calculated by the following equations:

$$R = \frac{C_0 - C_e}{C_0} \times 100\%$$

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

where $C_0$ (mg L⁻¹), $C_e$ (mg L⁻¹) and $C_t$ (mg L⁻¹) are the original concentration, the equilibrium concentration and instantaneous concentration of adsorbate. $q_e$ (mg g⁻¹) and $q_t$ (mg g⁻¹) represent adsorption capacity at equilibrium and at time $t$, $m$ (mg) and $V$ (mL) mean the mass and the volume of adsorbing material.
3 RESULT AND DISCUSSION

The morphologies of GO and CMC/rGO-3 were characterized by SEM in Figure 2. Obviously, GO has a significant gauzy lamellar structure and it has wrinkled surface, which is significant for its excellent adsorption property and good dispersion in water. However, the original GO is difficult to separate after adsorption and has poor mechanical properties. CMC/rGO-3 composite has the layer and pore structure. Compared with GO, the composite material forms thicker layered structures and rougher surfaces, which is beneficial to form a three dimensional rigid framework. Moreover, the composite material has larger pore junctions, which is more conducive to the rapid diffusion and adsorption of the adsorbate in the pore structure.

The zeta potential of samples rGO and CMC/rGO-3 were studied. It is obvious that the average zeta potential of rGO and the composite after introduction of CMC in water are $-34.9$ and $-37.1$ mV, respectively, which indicates that they are conducive to the adsorption of metal cations.

The N₂ adsorption–desorption isotherm, pore volume distribution and cumulative pore volume curves (inset) of the composite materials were shown in Figure 3. The BET specific surface areas (SSAs) of rGO, CMC/rGO-1, CMC/rGO-2 and CMC/rGO-3 are 38.69, 12.89, 22.19 and 24.02 m² g⁻¹, respectively. Compared with rGO, the SSAs of CMC/rGO composites reduce. It may be that after the introduction of CMC, the sites on GO are occupied [15]. However, with the increase of CMC content, the SSAs of composites tend to rise. rGO interlayer space is intercalated with more CMC, which can more effectively reduce interlayer accumulation, resulting in the increase of SSAs [16, 17]. The average pore sizes of rGO, CMC/rGO-1, CMC/rGO-2 and CMC/rGO-3 composites calculated by the Barrett–Joyner–Halenda method are 3.41, 8.31, 7.55 and 6.50 nm, which are mesoporous range. The pore size of composites material is larger than that of rGO, which is more conducive to the diffusion and adsorption of the adsorbate in the pore structure.

3.1 Effect of GO and CMC mass ratio on composite for adsorption of different metal ions

As displayed in Figure 4a, rGO-CMC-3 composite showed better adsorption capacities for metal cations (156.85, 35.70, 21.40, 20.85 and 15.80 mg g⁻¹ for Pb(II), Cu(II), Ni(II), Mn(II), Co(II)) than those of rGO, CMC/rGO-1 and CMC/rGO-2. Rich oxygen-containing functional groups, larger pore size and larger specific surface area are all conducive to adsorption. The abundant carboxylic acid groups on the CMC chain contribute to the efficient adsorption of metal cations. In addition, the SSA and average pore size of rGO-CMC-3 composite was larger than that of rGO-CMC-1 and rGO-CMC-2. The above reasons together led to the best effect of rGO-CMC-3 on the adsorption of Pb(II). In general, compared with other metal ions, the rich carboxyl functional groups on the surface of composites have higher affinity for lead ions [18], and the relative atomic mass of Pb(II) is larger, therefore, the adsorption capacity of the composite for Pb(II) is bigger than that of Cu(II), Ni(II), Mn(II) and Co(II). Cr₂O₇²⁻ is anion and has a weak interaction with the negatively charged CMC chains. Therefore, the increasing of CMC content in composite materials is not conducive to Cr(VI) adsorption. In the following experiments, the adsorption behaviour of rGO-CMC-3 composite on Pb(II) was studied in detail to further explore the adsorption mechanism.

3.2 Effect of time and adsorption kinetic

Batch of adsorption tests were carried out to study the adsorption performance of rGO-CMC-3 composite toward Pb(II). The adsorption capacity of rGO-CMC-3 toward Pb(II) increased with the increase of contact time in the first 2 h, and then remained stable with the further increasing of contact time (Figure 5(a)). The adsorption kinetic of Pb(II) onto rGO-CMC-3 was determined. The experimentally obtained adsorption data was fitted by pseudo-first-order, pseudo-second-order and
FIGURE 3  Nitrogen adsorption isotherm of (a) rGO, (b) CMC/rGO-1, (c) CMC/rGO-2 and (d) CMC/rGO-3; corresponding pore volume (blue curves) and pore volume distribution (black curves) of the composite materials (inset)

FIGURE 4  (a) Adsorption capacities of rGO-CMC composite for various metal ions; (b) effect of pH on adsorption of Pb(II) by rGO-CMC-3 composite in intraparticle diffusion model. The pseudo-first-order (Equation (3)), the pseudo-second-order (Equation (4)) and intraparticle diffusion (Equation (5)) equations are expressed as:

\[
\log(q_e - q_t) = \log q_e - k_1 t \\
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} = \frac{t}{q_e} \quad \text{(3)}
\]

\[
q_t = k_p t^{1/2} + c \\
\quad \text{(5)}
\]

where \(k_1 \, (\text{min}^{-1})\), \(k_2 \, (\text{g mg}^{-1} \text{min}^{-1})\) and \(k_p \, (\text{mg g}^{-1} \text{min}^{1/2})\) are the rate constants of pseudo-first-order, pseudo-second-order-kinetic models and intraparticle diffusion rate constant, respectively. The \(q_e \, (\text{mg g}^{-1})\) and \(q_t \, (\text{mg g}^{-1})\) refer to adsorption capacity of the adsorbent at equilibrium time and at time \(t\) (min), respectively. \(c\) is the particle diffusion equation constant.
Kinetic fitting results are shown in Figure 5 and Table 1. The adsorption of Pb(II) onto rGO-CMC-3 composite fitted better to the pseudo-second-order kinetic model, which means that the chemisorption is the rate-determining step. The intraparticle diffusion model is used to describe the diffusion process of heavy metal ions in the adsorbent. It can be seen from the fitting results that the adsorption process includes three stages. The first stage is the rapid diffusion process of heavy metal ions in the adsorbent boundary layer. The second stage is the rate-limiting diffusion process of heavy metal ions in the adsorbent. As the concentration of heavy metal ions in the aqueous solution decreases, internal diffusion begins to slow down and eventually reaches adsorption equilibrium. The fitting curve of the particle diffusion model is not linear in the entire time range, which indicates that the entire adsorption process is affected by multiple diffusion simultaneously.

### 3.3 Effect of concentration and adsorption isotherm

Figure 6(a) manifests the effect of initial concentration of Pb(II) on the adsorption capacity at different temperatures (298, 308, 318 K). The adsorption capacity of rGO-CMC-3 for Pb(II) increased as the Pb(II) concentration increased. The adsorption amount remained stable at higher initial ion concentration. This is mainly due to the limited active sites for adsorption of Pb(II), which gradually saturates with the increasing of adsorption concentration. As the temperature rose from 298 to 318 K, the adsorption capacity of the composite material for lead ions decreased slightly. Under experimental conditions, the maximum adsorption capacity of rGO-CMC-3 to Pb(II) was 184.9 mg g⁻¹. The experimental data was simulated by Langmuir (Equation (6)) and Freundlich (Equation (7)) isotherm models. The equations are presented as:
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FIGURE 6  (a) Effect of concentration on adsorption of Pb(II) by rGO-CMC-3 composite; (b) fitted curves by the Langmuir isotherm; (c) fitted curves by Freundlich isotherm; (d) liner curve of ln $k_d$ versus $1/T$ of Pb(II)

| TABLE 2  Fitted parameters of adsorption isotherm for Pb(II) on rGO-CMC-3 composite |
|-----------------|
| $T$ (K) | $R^2$ | $k_L$ | $q_m$ | $R^2$ | $k_F$ | $n$ |
|------|------|------|------|------|------|------|
| 298  | 0.9904 | 0.04727 | 222.72 | 0.8568 | 17.42 | 1.8415 |
| 308  | 0.9944 | 0.04938 | 214.59 | 0.8528 | 18.14 | 1.9023 |
| 318  | 0.9900 | 0.06132 | 196.08 | 0.8413 | 19.00 | 1.9862 |

where $q_e$, $q_m$ and $C_e$ are the equilibrium adsorption capacity (mg g$^{-1}$), the theoretical maximum monolayer adsorption capacity (mg g$^{-1}$) and the equilibrium concentration of heavy metal ions in solution (mg L$^{-1}$), respectively, $k_L$ is the Langmuir constant related to free energy of adsorption. Both $n$ and $k_F$ are the physical quantities of Freundlich isotherm related to adsorption capacity and strength, respectively.

The adsorption isotherm fitted curves and relevant parameters are exhibited in Figure 6 and Table 2. The coefficient of the Langmuir isotherm was found to be higher than that of Freundlich isotherm. The adsorption of rGO-CMC-3 toward Pb(II) was more consistent with the Langmuir isotherm model. This manifested that the adsorption process was primarily regarded as monolayer adsorption.

3.4 Adsorption thermodynamic

Adsorption thermodynamic parameters are used to investigate thermodynamic properties of adsorbent. The enthalpy ($\Delta H^\circ$, KJ mol$^{-1}$), entropy ($\Delta S^\circ$, J K$^{-1}$ mol$^{-1}$) and Gibbs free energy ($\Delta G^\circ$, KJ mol$^{-1}$) of the adsorption process were calculated by Equations (8)–(10):

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m}$$

$$\ln K_d = \frac{\Delta H^\circ}{R} - \frac{\Delta T \delta^\circ}{RT}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

where $C_0$ and $C_e$ (mg L$^{-1}$) are the initial and equilibrium concentration of Pb(II), $V$ (L) and $m$ (g) are the volume of the solution and the mass of adsorbent. $k_d$ means the adsorption distribution coefficient. $R$ (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ (K) are the
Table 3: Thermodynamic parameters for the adsorption of Pb(II) on rGO-CMC-3 composite

| T (K) | $\Delta G^\theta$, J mol\(^{-1}\) | $\Delta H^\theta$, KJ mol\(^{-1}\) | $\Delta S^\theta$, J K\(^{-1}\)mol\(^{-1}\) |
|-------|-------------------------------|-------------------------------|--------------------------------|
| 298   | −3.527                        | −5.460                        | −6.487                          |
| 308   | −3.462                        |                               |                                 |
| 318   | −3.397                        |                               |                                 |

The gas constant and the absolute temperature, respectively. $\Delta H^\theta$ and $\Delta S^\theta$ could be calculated from the slope and intercept of the plots of $\ln k_d$ versus $1/T$, respectively. Liner curve of $\ln k_d$ versus $1/T$ of Pb(II) is shown in Figure 6(d).

Thermodynamic parameters for the adsorption of Pb(II) on rGO-CMC-3 composite are shown Table 3. The negative value of $\Delta H^\theta$ indicated the adsorption process of Pb(II) was an exothermic process and the positive value of $\Delta S^\theta$ revealed an decreasing disorder and randomness at the solid–solution interface during the adsorption process. The negative values of $\Delta G^\theta$ confirm the spontaneous nature of adsorption process at different temperature. Adsorption thermodynamic parameters indicate that the adsorption is a spontaneous, exothermic, and solid–liquid system disorder reduction process.

3.5 Effect of pH

The pH value of solution is one of the governing factor for Pb(II) adsorption since it determines surface properties of adsorbents and adsorbates in the solution. Accordingly, a variety of adsorption studies were conducted under different pH conditions to study the effect of pH on the adsorption of Pb(II) (Figure 5(c)). When the initial pH value increased from 1 to 4, the adsorption amount Pb(II) increased from 6.60 to 164.45 mg L\(^{-1}\). After that, the adsorption amount of Pb(II) reached a platform. At lower pH conditions, the carboxylate groups on the surface of the composite are converted to carboxylic acid groups, and excess H\(^+\) also competes with Pb(II), which leads to a lower adsorption capacity. Pb(II) and carboxylate groups are more prone to bonding under near-neutral conditions. In addition, lead ions tend to precipitate at pH > 6 [19].

3.6 Adsorption mechanism

In order to further investigate the adsorption mechanism of rGO-CMC composite, the GO, CMC and rGO-CMC-3 before and after adsorption of Pb(II) were characterized by FT-IR and
XPS. As displayed in Figure 7(a), the adsorption peaks of GO at 3420, 1741, 1621 and 1109 cm$^{-1}$ can be attributed to the O H stretching vibration, the C O stretching mode, the stretching vibration of sp$^2$ carbon skeleton network and the alkoxy stretching vibration. In the spectrum of CMC, the peaks at 3444, 2928, 1616, 1442, 1329 and 1067 cm$^{-1}$ are assigned to the stretching vibration of O H groups, the C H stretching vibration, the stretching vibration of carboxylate groups, the CH$_2$ shear vibration, OH bending vibration and the stretching vibration of $>$CH O CH$_2$. Compared with GO, the O H adsorption peak of rGO-CMC-3 decreases significantly, indicating that GO is reduced. The peak of C C group shifts to 1632 cm$^{-1}$, indicating that π–π stacking occurs between GO layers. The adsorption band of C O stretching vibration shifts to 1731 cm$^{-1}$, showing that the strong hydrogen bonding interaction occurs between GO and CMC [20–25]. Compared with rGO-CMC-3, the adsorption peak strength of C O stretching vibration increases significantly after adsorption of Pb(II) by adsorbent, indicating that strong chelation interaction occurs between carboxyl groups and Pb(II) [10].

The XPS spectra of rGO-CMC-3 before and after adsorption of Pb(II) are shown in Figure 7(b,c). The peaks corresponding to C1s, O1s and Na1s could be seen in the spectra of rGO-CMC-3. The peaks of Pb(II) appear and the peaks of Na almost disappear after adsorption experiment. It indicates that Pb(II) is adsorbed on the adsorbent and ion exchange occurs. In comparison with rGO-CMC-3, the peak of O1s shifts from 533.02 to 532.94 eV and the binding energy of the peaks corresponding to O1s decreases, which is owing to bonding Pb(II) with oxygen atoms and increasing the electron density of oxygen atoms [26–29].

3.7 Regeneration performance of rGO-CMC composite

Reusability of adsorbents is an important factor for practical use. The reusability and regeneration performance of the rGO-CMC composite were investigated (Figure 7(d)). rGO-CMC composite adsorbed with lead ions can be regenerated by HNO$_3$ solution (0.1 mol L$^{-1}$). The adsorbent loaded with Pb(II) was immersed in 0.1 M HNO$_3$ solution for 0.5 h, then washed to neutral for the next round of adsorption. After five adsorption and desorption cycles, the removal rate retained above 90%. Based on the above results, rGO-CMC composite can be used as a potential adsorbent for heavy metal ions due to its good adsorption capacity and excellent regeneration performance.

4 CONCLUSION

In this study, the rGO-CMC composite was synthesized through a one-step hydrothermal reduction method using AA, and it was applied as reusable adsorbents for heavy metal removal in aqueous solution. The average pore size of rGO-CMC composite was mesoporous range, which is favourable for the diffusion and adsorption of the adsorbate in the pore structure. The maximum adsorption capacity of rGO-CMC-3 composite toward Pb(II) was 184.9 mg g$^{-1}$, and it possessed excellent regeneration performance and could maintain a removal rate of more than 90% after five cycles. The adsorption mechanism of composite materials was studied by series of adsorption tests and characterization. Ion exchange and chelation are beneficial to the adsorption process. Taken together, rGO-CMC composite could be used as a potential adsorbent to remove heavy metal ions in water purification.

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