



Ultra efficient removal of heavy-metal ions and dyes using a novel cellulose-based three-dimensional network

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Abstract Cellulose-based adsorbents have attracted extensive attention owing to their ecofriendly characteristics. However, most cellulose-based adsorbents possess inadequate adsorption capabilities for typical pollutants such as heavy-metal ions and dyes. Herein, we developed a cost-effective and robust cellulose-based adsorbent with a three-dimensional network structure based on hydrogen bonds and electrostatic interactions via the simple supramolecular self-assembly of carboxymethyl cellulose (CMC), cationic polyacrylamide (CPAM), and tannic acid (TA) (referred to as CMC–CPAM–TA). Benefiting from the abundant catechol/carboxyl groups and mesoporous/macroporous channels, CMC–CPAM–TA could trap Cu(II) ions and rhodamine B (RhB) (representing a typical heavy-metal ion and dye, respectively) by rapidly forming Cu–O coordination bonds and inducing electrostatic interactions. CMC–CPAM–TA exhibited high adsorption capacities for Cu(II) ions and RhB, which were 669.8 and 202.2 mg/g, respectively. These values are 1.3–23.6

and 1.1–72.2 times higher than those of commonly reported cellulose-based adsorbents, respectively. Furthermore, CMC–CPAM–TA showed high regenerative ability for Cu(II) ions and RhB after five cycles owing to its robust structure.

Keywords Cellulose · Adsorbent · Self-assembly

Introduction

Dyes and heavy-metal ions, which mainly result from printing, dyeing, and metal etching processes, are two of the most common sources of contamination in wastewater and may cause teratogenic, carcinogenic, and mutagenic effects in humans and aquatic organisms (Cai et al. 2021). Various methods have been employed to remove dyes and heavy-metal ions from water environments, including adsorption (Arora 2019; Yagub et al. 2014), ion exchange (Bashir et al. 2018), chemical precipitation (Chen et al. 2018), membrane separation (Li et al. 2019b), and reverse osmosis (Zhang et al. 2018), among which adsorption serves as one of the most effective and promising methods to address this serious environmental issue (Afroze and Sen 2018).

Among various adsorption materials developed till date, natural bio-based adsorbents have attracted extensive attention due to their cost-effectiveness, easy regeneration, widespread availability, and ecofriendly characteristics. In particular, cellulose, which

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is the most abundant natural polymer (Ayouch et al. 2021), has received considerable interest for chemical modification owing to the presence of abundant hydroxyl groups in its molecular chain (Marchessault 1983). This structural feature allows the grafting of different functional groups, such as amino, amide, carboxyl, and carbonyl sulfide groups, onto the surface of cellulose using various methods (Chen et al. 2019; Li et al. 2019a; Liu et al. 2015b; Wang et al. 2020), rendering modified cellulose suitable as an adsorbent to remove heavy metals or dyes via coordination bonds and electrostatic effects (Ren et al. 2016). However, the strong intermolecular and intramolecular hydrogen bonds in the hydroxyl groups tend to induce the aggregation of cellulose into bundles and the formation of highly crystalline structures with reduced porosity (Chen et al. 2019). These phenomena decrease the grafting rate of functional groups and negatively affect the mass transfer of an adsorbate in cellulose, reducing the adsorption capacity. Therefore, increasing the grafting rate of functional groups and modulating the molecular structure of materials are essential research targets to increase adsorption capacity and improve mass transfer rate of cellulose.

Sodium carboxymethyl cellulose (CMC) is an anionic ether polymer containing numerous carboxyl and hydroxyl groups in its macromolecular chain, which lead to its good solubility in aqueous media (French 2017; Lin et al. 2013; Wu et al. 2015). Therefore, as a precursor for preparing adsorbents, CMC can be expected to considerably improve the availability of natural cellulose (Ren et al. 2016). In recent years, many CMC-based adsorbents, such as CMC hydrogels (Wang et al. 2020), CMC-grafted graphene oxide/polyethylene glycol (Ayouch et al. 2021; Tohamy et al. 2020), and CMC-sulfonated graphene oxide composites (Liu et al. 2021; Sekine et al. 2020; Zhu et al. 2021), have been developed for the removal of heavy metals and dyes from wastewater. However, the practical applications of cellulose hydrogels and graphene oxide are restricted due to their complex production processes, lower mass transfer rates, and regeneration concerns (Afroze and Sen 2018). Therefore, addressing these issues by skillfully designing adsorption materials based on CMC constitutes an important yet challenging task.

Previous studies have reported that tannic acid (TA) can adsorb heavy metals and dyes owing to its

catechol structure (Liu et al. 2015a; Üçer et al. 2006; Yao et al. 2021; Zou et al. 2019); however, its solubility in aqueous media hinders its individual application for adsorption (Xia et al. 2021). Combining CMC and TA can be an effective approach to address the issue of regeneration because of the numerous carboxyl and hydroxyl groups of CMC and TA, which would lead to hydrogen bonds and electrostatic interactions with positively charged polymers. In addition, the carboxyl and hydroxyl groups in TA and CMC may function as adsorption sites to remove heavy metals and dyes.

As a proof of concept, herein, we report the use of CMC and TA as functional raw materials and cationic polyacrylamide (CPAM) as a crosslinking agent to obtain a self-assembled cellulose-based nanoporous adsorbent exhibiting a three-dimensional (3D) network (CMC–CPAM–TA) based on electrostatic interactions and hydrogen bonds (Fig. 1a–c). This nanoporous adsorbent can remove Cu(II) ions and rhodamine B (RhB) via the coordination between the catechol structure and Cu(II) ions and the electrostatic interaction between the hydroxyl/carboxyl groups and RhB (Fig. 1d, e). The adsorption capacities of CMC–CPAM–TA for Cu(II) ions and RhB reached 669.80 and 202.15 mg/g, respectively, outperforming most previously reported bio-based adsorbents. Its good recyclability and low cost render CMC–CPAM–TA suitable for wastewater purification via adsorption.

Experimental

Materials

Sodium carboxymethyl cellulose (CMC, Degree of substitution = 0.7, M_w = 90,000 g/mol) and Tannic acid (TA, AR) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Cationic polyacrylamide (CPAM, M_w = 8–10 million g/mol) and rhodamine B (RhB, AR) were purchased from Shanghai Macklin Biochemical Co., Ltd. Copper chloride (CuCl_2 , AR) and sodium hydroxide (NaOH, AR) were purchased from the Damao Chemical Reagent Factory. Absolute ethanol (AR) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Hydrochloric acid (HCl) was purchased from Yantai Far East Fine Chemical Co., Ltd.

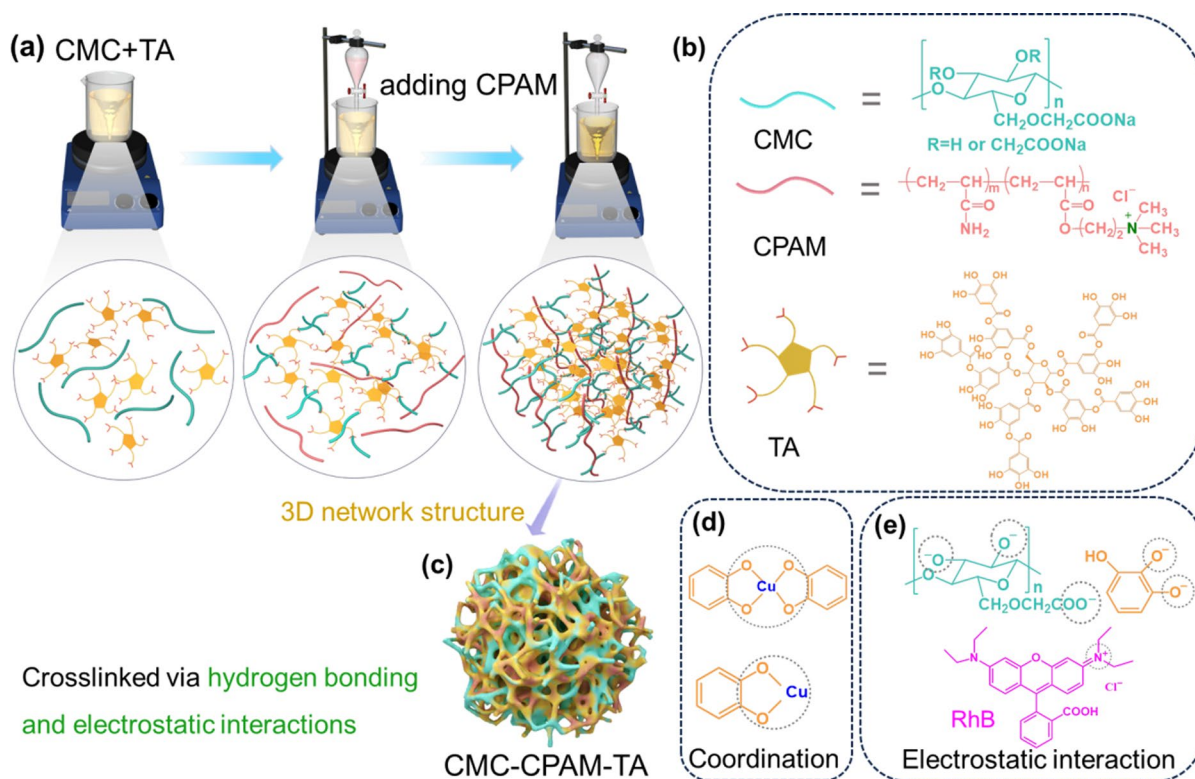


Fig. 1 Synthesis route for CMC–CPAM–TA and adsorption mechanism for Cu(II) ions and rhodamine B

Experimental methods

Preparation of the CMC–CPAM–TA adsorbent

First, TA, CMC, and CPAM solutions were prepared by dissolving 1 g of TA in 100 mL of distilled water at 40 °C, 2 g of CMC in 200 mL of distilled water at 70 °C, and 1 g of CPAM in 500 mL of 4 wt% ethanol solution at 70 °C, respectively, using a magnetic stirrer (700 r/min).

Then, the CMC solution was dropped into the TA solution at a rate of 5 mL/min under a stirring rate of 500 r/min. After titration, the CPAM solution was added to the mixed solution under the same conditions. In the reaction process, a large amount of sediment appeared. The reaction was considered to reach completion when no more sediment was formed. Finally, CMC–CPAM–TA was obtained by freeze drying for 48 h.

Adsorption of Cu(II) ions and RhB

Batch adsorption experiments were conducted in a 250 mL conical flask with a constant stirring rate of 150 r/min in a thermostatic oscillator. The effects of pH, initial concentration, amount of adsorbent, contact time, and temperature on the adsorption capacity for Cu(II) ions and RhB were investigated. The concentration of Cu(II) ions was determined via inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent 5110). The concentration of RhB was determined via ultraviolet–visible (UV–vis) spectrophotometry at a wavelength of 553 nm.

The adsorption capacities of CMC–CPAM–TA for Cu(II) ions and RhB were determined according to Eq. 1.

$$q = (c_0 - c_t)v/1000g \quad (1)$$

where q is the adsorption capacity (mg/g); c_0 and c_t are the concentrations of Cu(II) ions or RhB before and after adsorption, respectively (mg/L); v is the volume of the adsorption solution (mL); and g is the weight of CMC–CPAM–TA used (g).

The pseudo-first-order and pseudo-second-order kinetic models were used to explain the adsorption dynamics according to Eqs. 2 and 3 (He et al. 2021):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

$$q_t = k_2 q_e^2 t / (1 + k_2 q_e t) \quad (3)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t , respectively, and k_1 (min^{-1}) and k_2 ($\text{g/mg} \cdot \text{min}^{-1}$) represent the reaction rate constants corresponding to the pseudo-first-order and pseudo-second-order adsorption models, respectively.

The Langmuir and Freundlich isothermal models were used to evaluate the adsorption process between CMC–CPAM–TA and Cu(II) ions and RhB using Eqs. 4 and 5 (Cai et al. 2021):

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

where q_m is the maximum adsorption capacity (mg/g), c_e is the equilibrium concentration (mg/L), K_L is the Langmuir constant (L/mg), K_F is the Freundlich constant (mg/g), and n is the Freundlich linearity index.

Thermodynamic parameters of adsorption from solutions provide a great deal of information concerning the type and mechanism of the adsorption process. Thermodynamic parameters of Gibbs free energy (ΔG^0 , kJ/mol), enthalpy (ΔH^0 , kJ/mol) and entropy (ΔS^0 , kJ/mol/K) can be used to analyze the thermodynamics based on the following equations Eqs. 6 and 7 (Zhan et al. 2023):

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (6)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

where, R is 8.314 J/(mol K). K_d represented thermodynamic constant, the value of which was equal to that of the Langmuir equilibrium constant.

Regeneration

After the adsorption experiments, CMC–CPAM–TA was put into a conical flask containing 200 mL of distilled water and the pH value was adjusted to 2. Then, desorption was performed in a thermostatic oscillator for 2 h under stirring at 200 r/min at 25 °C. After desorption, the concentration of Cu(II) ions and RhB in the desorption solution was determined via ICP-OES and UV–vis spectroscopy, respectively. The desorption ratios were calculated using Eq. 8:

$$E(\%) = (C_t V_t / 1000 Q) \times 100\% \quad (8)$$

where C_t denotes the detected concentration of Cu(II) ions or RhB in the desorption solution (mg/L), V_t is the volume of the desorption solution (mL), and Q is the adsorption capacity of CMC–CPAM–TA for Cu(II) ions or RhB (mg/g).

Characterization

Fourier-transform infrared spectroscopy (FTIR; Bruker VERTEX70, Karlsruhe, Germany) was employed to investigate the changes in the functional groups of the materials before and after the self-assembly using the KBr pellet technique. The surface microstructure of the material before and after the self-assembly was observed via scanning electron microscopy (SEM; Gemini300, Carl Zeiss, Germany). Elemental mapping was performed during SEM analysis via energy-dispersive X-ray spectroscopy (EDS) using an Oxford X-MAX detector. The surface area and porous structure of CMC–CPAM–TA were observed using a specific surface analyzer (Maize 2460, Georgia, USA) using nitrogen as the adsorbate. All samples were degassed at 120 °C for more than 6 h before analysis. The thermal stability of CMC, CPAM, TA, and CMC–CPAM–TA was studied via thermogravimetric analysis (TGA; Mettler Toledo TGA/DSC 3+, Switzerland) under a nitrogen atmosphere at 30–800 °C with a heating rate of 10 °C/min. The zeta potentials of CMC, CPAM, TA, and CMC–CPAM–TA were determined using a Malvern Zetasizer Nano ZS90 instrument (Malvern, UK). The surface chemical compositions of the samples before and after adsorption was explored via X-ray photoelectron spectroscopy (XPS; Thermo

Fisher ESCALAB XI+, Waltham, MA, USA) with Al $K\alpha$ ($h\nu=1486.6$ eV) excitation, a passing energy of 50 eV for the full spectrum and 20 eV for the narrow spectra, and a step length of 0.05 eV. The concentrations of Cu(II) ions and RhB were analyzed via ICP-OES (Agilent 720ES, California USA) and UV-vis spectroscopy (Shimadzu UV-2600, Japan) at a wavelength of 553 nm, respectively.

Results and discussion

To prepare the three-dimensional network of the cellulose-based adsorbent, CMC and TA were first dissolved in water and slowly mixed; then, CPAM was slowly dropped into the resulting solution at a rate of 5 mL/min under a stirring rate of 500 r/min. The

formed precipitate was collected using a filter and vacuum freeze-dried to obtain the CMC-CPAM-TA adsorbent.

FTIR analysis was performed to investigate the structural changes in CMC, CPAM, and TA before and after the self-assembly. As shown in Fig. 2a, peaks corresponding to the $-NH_2/-NH-$ and $-OH$ groups of CMC-CPAM-TA were observed at $3200\text{--}3600\text{ cm}^{-1}$ (Gupta et al. 2018). The spectra of TA and CMC-CPAM-TA exhibited prominent absorption peaks at 1607 and 1533 cm^{-1} , which correspond to the vibrations of the benzene ring skeleton. Unlike in the case of TA, a new absorption peak at 1666 cm^{-1} was observed in the spectrum of CMC-CPAM-TA, possibly corresponding to the strong chemical interactions between the chemical groups connected to the benzene ring in

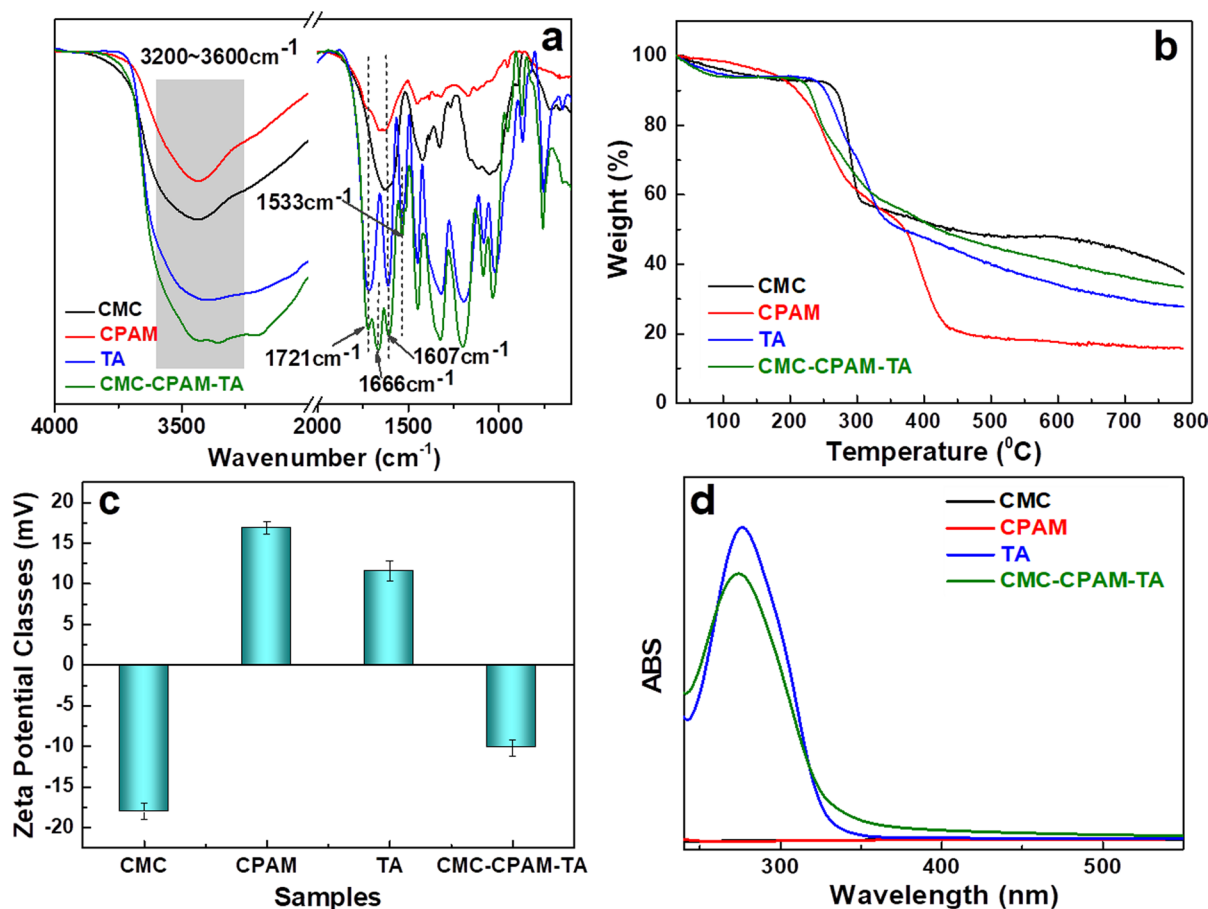


Fig. 2 Structural characterization results of CMC, CPAM, TA, and CMC-CPAM-TA. **a** FTIR spectra, **b** TGA results, **c** zeta potential measurement results, and **d** UV-vis spectra of the samples

TA and other chemical groups. In addition, the peak corresponding to the C=O stretching vibration was observed at 1721 cm^{-1} in the spectra of TA and CMC–CPAM–TA. Although CMC and CPAM contain C=O groups, no absorption peak attributable to this functional group was observed. Instead, an absorption peak was observed at 1666 cm^{-1} , which may be attributed the interactions between C=O in CMC, CPAM, and TA and different groups surrounding it. Moreover, the corresponding absorption peak of CMC–CPAM–TA may overlap with the absorption peak of the benzene ring skeleton. These results indicate the occurrence of the self-assembly of CMC and CPAM, followed by the occurrence of strong chemical interactions, which are most likely hydrogen bonding and electrostatic interactions according to the structural analysis of CMC, CPAM, and TA.

TGA was performed to investigate the thermal stability of the materials. Figure 2b shows that the thermal degradation of CMC, CPAM, and TA occurred at $295\text{ }^{\circ}\text{C}$ and $206\text{ }^{\circ}\text{C}$, $400\text{ }^{\circ}\text{C}$ and $280\text{ }^{\circ}\text{C}$, $310\text{ }^{\circ}\text{C}$, respectively. When the temperature reached $800\text{ }^{\circ}\text{C}$, the weight of CMC, CPAM, and TA decreased to 40.34%, 15.80%, and 27.73%, respectively. Meanwhile, the thermal degradation temperature of CMC–CPAM–TA was $250\text{ }^{\circ}\text{C}$ and its weight decreased to 38.80%, which was between that of CMC, CPAM, and TA and close to that of CMC. This indicates the presence of chemical bonds between CMC, CPAM, and TA in the material.

To study the mechanism of the self-assembly of the raw materials into CMC–CPAM–TA, the zeta potentials of the materials were analyzed before and after the self-assembly. As shown in Fig. 2c, the zeta potential of CMC was -18 mV , indicating its negative charge. In contrast, CPAM and TA were positively charged, with zeta potentials of 16.9 and 11.6 mV, respectively. This potential difference provided a strong driving force for the self-assembly. The zeta potential of CMC–CPAM–TA was -10.2 mV , which considerably differed from those of CMC, CPAM, and TA. This indicates the presence of electrostatic interactions between CMC, CPAM, and TA during self-assembly. Moreover, the negative charge of CMC–CPAM–TA implies that the negative carboxyl and phenoxy groups originating from CMC and TA tend to locate at the surface of CMC–CPAM–TA, which is beneficial for the removal of positive Cu(II)

ions and RhB via coordination and electrostatic effects, respectively.

UV–vis spectra shown in Fig. 2d show that CMC and CPAM exhibited no obvious absorption peaks in the range of 200–800 nm. Meanwhile, TA showed an absorption peak at 276 nm corresponding to the catechol group (Lee et al. 2023). After the self-assembly, this characteristic absorption peak was blue-shifted in the spectrum of CMC–CPAM–TA compared with that of TA, further confirming the self-assembly of CMC, CPAM, and TA. Thus, FTIR analysis results, zeta potential measurement results, and UV–vis spectra confirmed the successful self-assembly of the materials via hydrogen bonds or electrostatic interactions among the $-\text{OH}$, $-\text{COOH}$, and $-\text{NH}_2/-\text{NH}-$ groups.

To further explore the micromorphology of CMC–CPAM–TA, SEM analysis was performed. Fig. S1 shows that CMC, CPAM, and TA exhibited bulk morphologies with smooth surfaces. However, obvious interconnected nanoparticles were observed in CMC–CPAM–TA (Fig. 3a). The average size of the nanoparticles was determined to be ca. 44 nm using Gaussian function fitting (Fig. 3b). Moreover, the interconnection between the nanoparticles led to a mesoporous/macroporous structure, which was conducive to mass transfer and diffusion during the adsorption of Cu(II) ions and RhB. These observations indicate that the hydrogen bonds and electrostatic interactions between CMC, CPAM, and TA were the driving force for the supramolecular self-assembly.

The transmission electron microscopy (TEM) image presented in Fig. 3c shows the interconnected nanoparticles and apparent mesopores/macropores in CMC–CPAM–TA. The corresponding EDS mapping result revealed that C, N, and O were uniformly distributed in CMC–CPAM–TA (Fig. 3d). To determine the surface area and porous structure of CMC–CPAM–TA, which can be correlated to the number of adsorption sites available for the removal of Cu(II) ions and RhB, nitrogen adsorption–desorption measurements were performed. According to Fig. 3e, the surface area of CMC–CPAM–TA was $37.02\text{ m}^2/\text{g}$. A clear hysteresis loop in the relative pressure (p/p^0) range of 0.82–1.0 was observed in the nitrogen adsorption–desorption isotherm of CMC–CPAM–TA, indicating the presence of mesopores. Furthermore, when the p/p^0

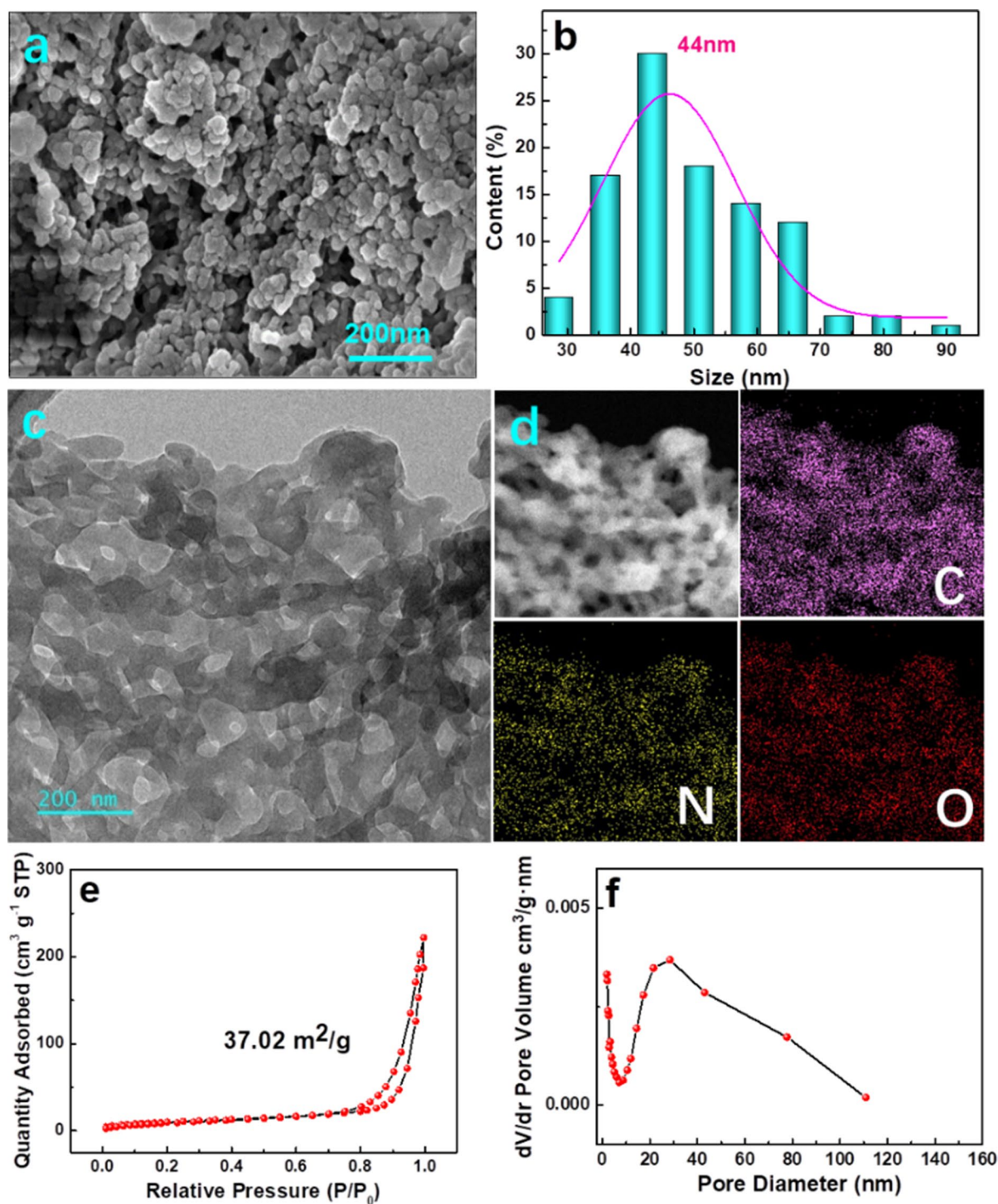


Fig. 3 Morphological and structural characterization of CMC-CPAM-TA. **a** SEM image, **b** particle size distribution, **c** TEM image, **d** EDS mapping, **e** nitrogen adsorption-desorption isotherms, and **f** pore size distribution

value approached 1.0, the nitrogen adsorption capacity drastically increased, indicating the presence of macropores in CMC–CPAM–TA. The mesoporous/macroporous structure of CMC–CPAM–TA was confirmed by pore size distribution, which was in the range of 10–110 nm (Fig. 3f). This result is in agreement with the SEM and TEM observations (Fig. 3a, c). The large surface area and mesoporous/macroporous supramolecular network structure of CMC–CPAM–TA are expected to improve the adsorption of Cu(II) ions and RhB by exposing more adsorption sites (i.e., catechol of TA and carboxyl groups of CMC) and enabling fast mass transport of Cu(II) ions and RhB from the solution to the adsorption sites.

Adsorption experiments using CMC–CPAM–TA

Effect of adsorbent dosage

Figure S2 shows the effect of adsorbent dosage on the adsorption capacity of CMC–CPAM–TA for Cu(II) ions and RhB determined using 200 mL of Cu(II)-ion and RhB solutions with an initial concentration of 200 mg/L at 25 °C for 120 min. The adsorption capacity of CMC–CPAM–TA for Cu(II) ions and RhB decreased with increasing adsorbent dosage because the contact probability between the adsorbent and Cu(II) ions or RhB decreased with increasing adsorbent dosage per unit volume.

Effect of pH

The pH of a solution affects the surface charge of CMC–CPAM–TA, which influences the adsorption capacity of CMC–CPAM–TA for Cu(II) ions and RhB. To evaluate the optimum pH for the removal of Cu(II) ions and RhB at 25 °C, the pH of the adsorption solution was controlled at 4–9. As shown in Fig. 4a, the adsorption capacity of CMC–CPAM–TA for Cu(II) ions increases as the pH rises from 3 to 6, which can be attributed to the protonation of the active carboxyl, phenoxy, and amino groups at low pH values. The presence of high concentration of H^+ at low pH values causes a competition between H^+ ions and Cu(II) for the adsorption sites of CMC–CPAM–TA (Teow et al. 2018; Zhang et al. 2021). When the pH increases, the surface sites of CMC–CPAM–TA are deprotonated, which promotes

the coordination and electrostatic interaction between Cu(II) ions and the adsorption sites (Gupta et al. 2018), enhancing the adsorption capacity. At $pH > 6$, a precipitate generated from the reaction of Cu(II) and OH^- is formed. For RhB, the adsorption capacity of CMC–CPAM–TA gradually increases with increasing pH, and the growth rate tends to stabilize at $pH > 5$. This is mainly due to the increase in the potential difference between CMC–CPAM–TA and RhB with increasing pH for $pH < 5$ (Fig. 4b), which increases the adsorption capacity for RhB by improving the electrostatic interaction between CMC–CPAM–TA and RhB (Liu et al. 2015a). At $pH > 5$, the adsorption capacity changes only slightly because the potential difference between CMC and RhB tends to stabilize (Fig. 4b). Thus, the pH values of 6 and 5 were selected as the optimal pH values for the adsorption of Cu(II) ions and RhB, respectively.

Effect of contact time and adsorption kinetics

To explore the equilibration time for the maximum adsorption capacity and adsorption kinetics of CMC–CPAM–TA, the adsorption capacity for Cu(II) ions and RhB was evaluated as a function of time. As shown in Fig. 4c, d, the adsorption capacity gradually increased with time. When the adsorption time for Cu(II) ions reached 60 min, the growth rate of the adsorption capacity decreased and reached equilibrium at 180 min. In the case of RhB, the turning point of the growth rate of the adsorption capacity was observed at 90 min and the equilibrium was reached at 240 min. This result was due not only to the presence of abundant adsorption sites but also to the macropores/mesopores and large surface area of CMC–CPAM–TA, which facilitated the exposure of adsorption sites and rapid mass transfer of Cu(II) ions and RhB from the solution to the adsorption sites within 60 and 90 min, respectively. The adsorption capacities of CMC–CPAM–TA for Cu(II) ions and RhB reached equilibrium at 180 and 240 min, respectively. Furthermore, the adsorption kinetics of CMC–CPAM–TA were studied using the pseudo-first-order and pseudo-second-order rate models. Figures 4c, d and Table S1 show that the pseudo-second-order rate model described the adsorption of Cu(II) ions and RhB by CMC–CPAM–TA better compared with the pseudo-first-order rate model due to its higher correlation

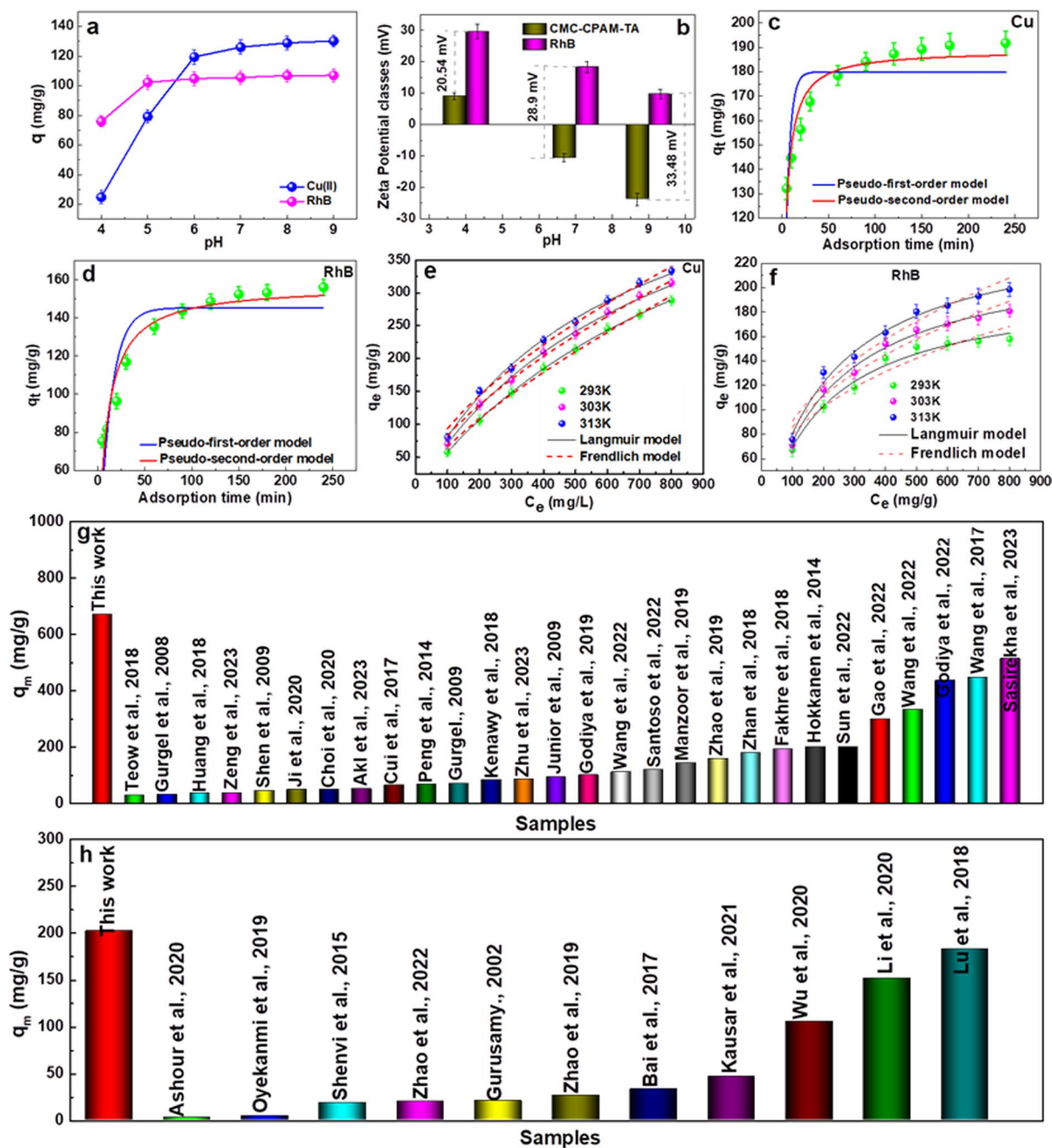


Fig. 4 Adsorption experiments of CMC-CPAM-TA. **a** Effect of pH on adsorption. **b** Potential difference between CMC-CPAM-TA and RhB. **c**, **d** Adsorption kinetics of CMC-CPAM-TA concerning Cu(II) ions and RhB. **e**, **f** Adsorption

isotherms of CMC-CPAM-TA concerning Cu(II) ions and RhB. **g**, **h** Comparison between the adsorption performance of CMC-CPAM-TA and reported adsorbents for Cu(II) ions and RhB

coefficient (R^2), which suggests that the removal of Cu(II) ions and RhB by CMC–CPAM–TA probably occurred via a chemical adsorption process.

Effect of initial Cu(II)-ion and RhB concentration and adsorption isotherms

Next, the effect of the initial concentrations of Cu(II) ions and RhB on the adsorption capacity was investigated. The corresponding adsorption isotherms are shown in Fig. 4e, f. As illustrated in Fig. 4f, the adsorption capacity of CMC–CPAM–TA increased with increasing initial concentrations of Cu(II) ions and RhB. In particular, when the RhB concentration exceeded 500 mg/L, the adsorption capacity stabilized, implying that the number of available adsorption sites became the limiting factor for the adsorption capacity. To further determine the maximum adsorption capacities of CMC–CPAM–TA for Cu(II) ions and RhB, Langmuir and Freundlich adsorption isotherm models were used. The fitting parameters are provided in Table S2, and the fitting curves are shown in Fig. 4e, f. The Langmuir model for Cu(II) and RhB yielded R^2 values of 0.9996 and 0.9808, respectively, which were higher than those obtained using the Freundlich model, demonstrating that the former described the adsorption behavior of CMC–CPAM–TA for Cu(II) ions and RhB better. These results indicate that CMC–CPAM–TA adsorbs Cu(II) ions and RhB in a monolayer adsorption mode. Moreover, the n values were greater than 1, indicating a high adsorption intensity and favorable adsorption of Cu(II) ions and RhB by CMC–CPAM–TA (Chen et al. 2019). According to the Langmuir model, the maximum adsorption capacity (q_m) values of CMC–CPAM–TA for Cu(II) ions and RhB were calculated to be 669.8 and 202.1 mg/g, respectively, which are 1.3–23.6 and 1.1–72.2 times higher than those of commonly reported cellulose-based adsorbents (Fig. 4g, h and Tables S3–S4).

Effect of temperature and thermodynamics

The effect of the temperature on the adsorption capacity of Cu(II) ions and RhB on the CMC–CPAM–TA was investigated. As shown in Fig. 4e, f, the adsorption capacities increased with increasing temperature. Heating is conducive to the Brownian motion of the molecules and free movement of the molecular

chains on the adsorbent, thus increasing the contact probability of the Cu(II) ions and RhB (Zhan et al. 2023). By changing the temperature, we further examined the absorption thermodynamic of CMC–CPAM–TA. According to the fitting results of Fig. 4e, f, CMC–CPAM–TA still followed the Langmuir isotherm model in the temperature range of 298–318 K. Based on this model and Eq. 6 and 7, we calculated Gibbs free energy (ΔG^0) and entropy (ΔS^0) (Fig S3 and Table S5). The positive values of ΔH^0 indicated the adsorption process was endothermic. The positive values of ΔS^0 reveal that the orderliness of the entire system decreases during adsorption. The absolute value of the Gibbs free energy increased, indicating that heating promoted the adsorption (Wang et al. 2023).

Effect of ionic strength

Here, NaCl was used to investigate the effect of ionic strength on the removal efficiency of Cu(II) ions and RhB. As shown in Fig. S4, the adsorption of Cu(II) ions and RhB on CMC–CPAM–TA decreased with increasing NaCl content from 0 to 1 mol/L in the Cu(II) ion and RhB solutions. This result was attributed to the following reasons: (1) the competition between the salt ions (Na^+ and Cl^-) and Cu(II) ions and RhB on the functional surface of the adsorbent ($-\text{COO}^-$, $-\text{N}^+$, and $-\text{OH}$). (2) NaCl is a strong electrolyte that exerts a salt effect on Cu(II) ions and RhB, hindering their contacts with the adsorbent. In this regard, how to modulate the selective adsorption capability of adsorbent is worth exploring in our future study.

Structural analysis of CMC–CPAM–TA after adsorption

According to the SEM images, the interconnected nanoparticle morphology of CMC–CPAM–TA was preserved after the adsorption of Cu(II) ions and RhB (Fig. 5a, b). The EDS mapping results obtained after the adsorption of Cu(II) ions revealed the presence of Cu(II) ions and a decrease in the C and O contents in CMC–CPAM–TA (Fig. 5c, d and Table S6), which indicates that a large amount of Cu(II) ions was adsorbed on CMC–CPAM–TA. After RhB adsorption, the EDS mapping revealed an increase in the C content and a decrease in the O content in

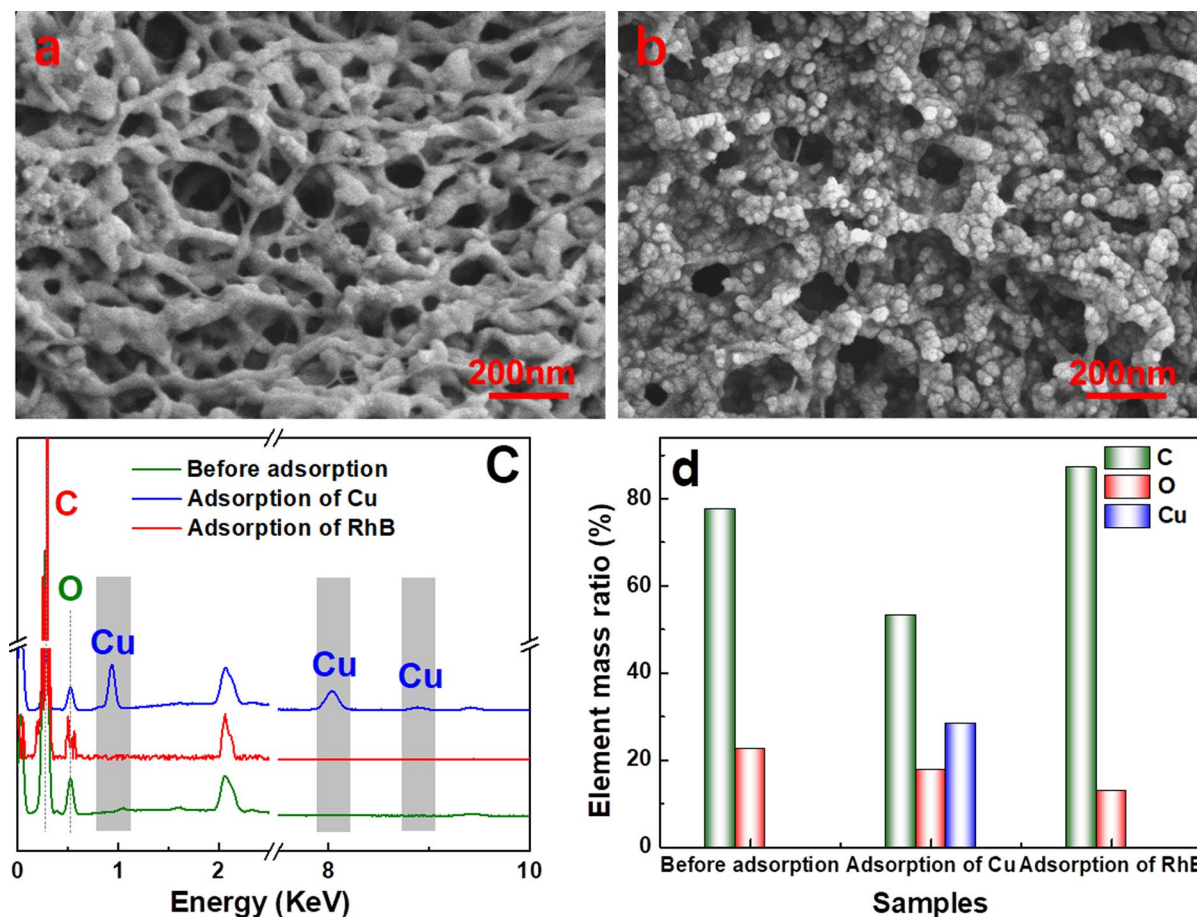


Fig. 5 Structural analysis of CMC-CPAM-TA after adsorption. **a, b** SEM images after adsorbing Cu(II) ions and RhB, respectively. **c** EDS curves. **d** Elemental analysis results after adsorption

CMC-CPAM-TA, which is consistent with the mass ratio of C and O in RhB (Table S6), indicating that a large amount of RhB was adsorbed on CMC-CPAM-TA.

Next, XPS analysis was performed to investigate the interaction between the adsorption sites and Cu(II) ions and RhB. As shown in Fig. 6a, an obvious Cu2p peak appeared in the XPS Cu2p spectrum of CMC-CPAM-TA after adsorption of Cu(II) ions, suggesting its efficient adsorption capability for Cu(II) ions. As RhB contains no other elements except C, O, and N, no new peak appeared after adsorption of RhB.

Before adsorption, the O1s XPS spectrum of CMC-CPAM-TA showed two peaks at 532.5 and 531.0 eV, which can be assigned to C=O and C–O bonds (Xia et al. 2023), respectively (Fig. 6b).

However, upon adsorption of Cu(II) ions, the C–O peak shifted from 531.0 to 531.25 eV (Fig. 6d), which indicates that the C–O bond of catechol in TA coordinated with Cu(II). Further, after adsorption, no remarkable change in the peak at 399.25 eV attributed to the C–N group in CPAM was observed in the N1s XPS spectrum (Fig. 6c, e). These findings indicate that adsorption by CMC-CPAM-TA proceeds via the formation of Cu–O coordination bonds, highlighting the role of the catechol groups in the removal of Cu(II) ions. Meanwhile, the N1s XPS spectrum of RhB showed two peaks at 401.25 and 399.35 eV; the former, which corresponds to protonated N, shifted to 402.35 eV after adsorption (Fig. 6g, h). Similarly, the O1s XPS spectrum of RhB showed a peak at 531.75 eV and another at 533.55 eV, which is attributed to –C=O and shifted to 532.35 eV after

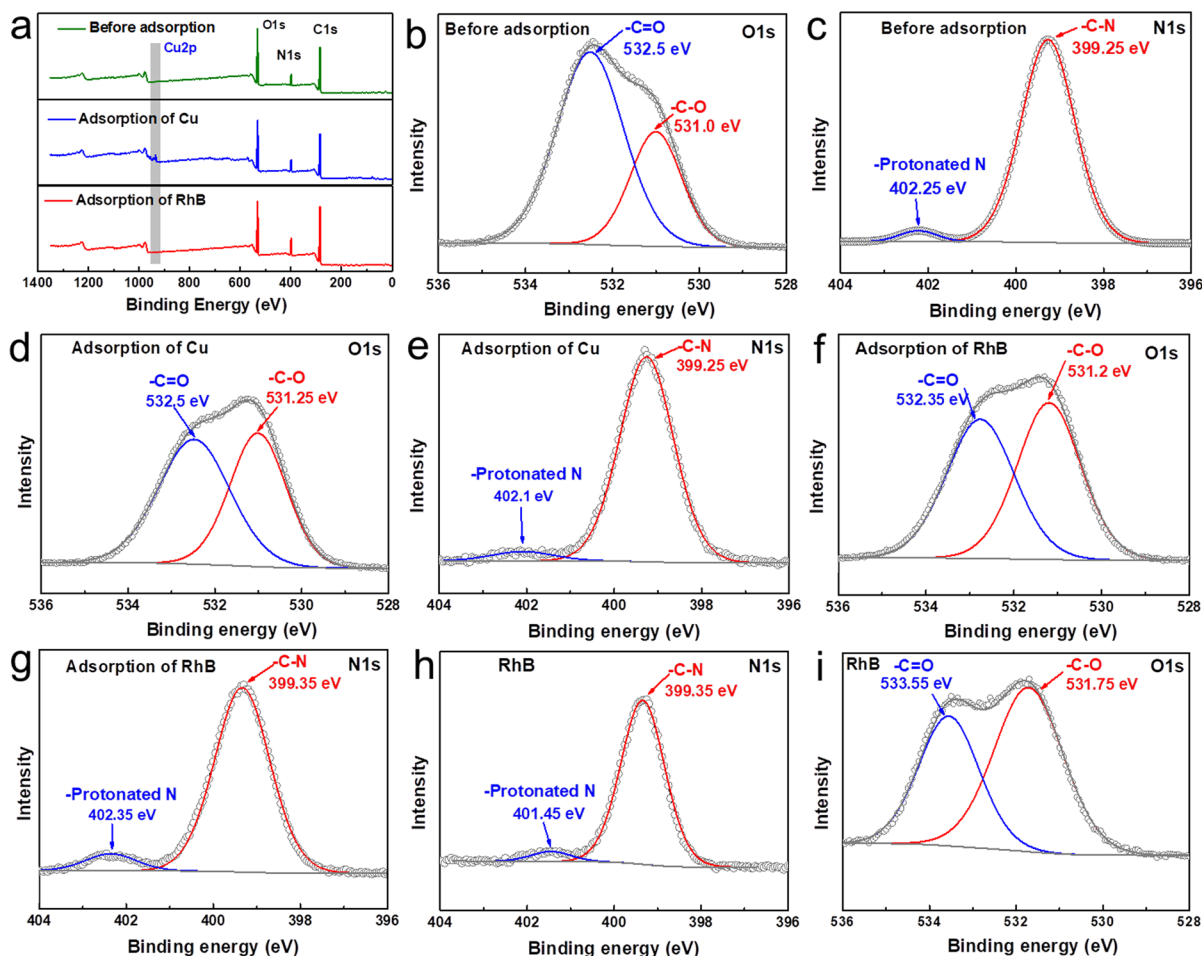


Fig. 6 XPS spectra of CMC-CPAM-TA before and after adsorption. **a** Full XPS spectra, **b**, **c** O1s and N1s XPS spectra before adsorption, **d**, **e** O1s and N1s XPS spectra after adsorption of Cu(II) ions, **f**, **g** O1s and N1s XPS spectra after adsorption of RhB, and **h**, **i** O1s and N1s XPS spectra of RhB

adsorption (Fig. 6f, i). These results suggest that the adsorption of RhB on CMC-CPAM-TA occurred via electrostatic interactions between N^+ and $-C=O$ in RhB and $-C=O$ and N^+ in CMC-CPAM-TA, respectively.

Regeneration performance

To evaluate the regeneration, stability, and reusability of CMC-CPAM-TA, desorption experiments were conducted using distilled water as the desorption solvent. After adsorption, the Cu- and RhB-loaded CMC-CPAM-TA adsorbents were immersed in distilled water for 30 min and the pH of the solution was adjusted to three. Next, the spent CMC-CPAM-TA

was freeze-dried and reused. The adsorption performance of CMC-CPAM-TA for Cu(II) ions and RhB was evaluated in 200 mL of Cu(II) and RhB solutions (200 mg/L) for 60 min at pH values of 6 and 5, respectively, at 25 °C. As shown in Fig. 7a, d, CMC-CPAM-TA retained 79% and 63% of the initial adsorption capacity for Cu(II) ions and RhB, respectively, after five cycles. The SEM image obtained after regeneration showed that CMC-CPAM-TA still exhibited the interconnected nanoparticle morphology of the pristine sample (Fig. 7b, e). Furthermore, the corresponding EDS mapping revealed that the signal corresponding to the Cu element considerably decreased when CMC-CPAM-TA was regenerated (Fig. 7c–f and Table S7). These data indicate that

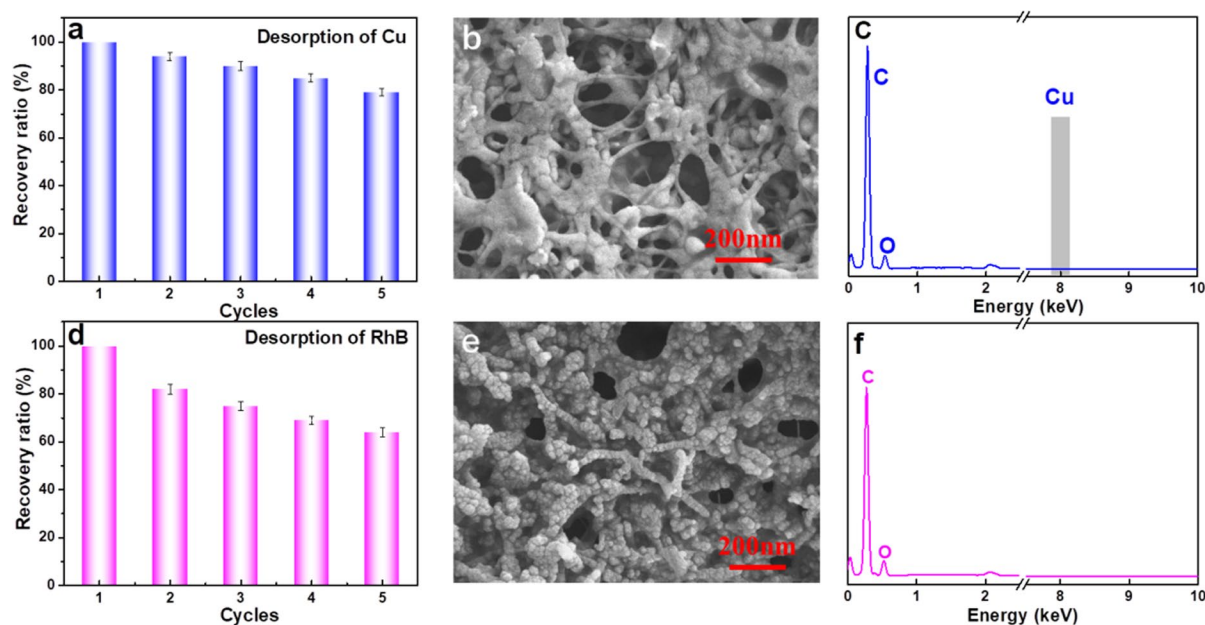


Fig. 7 Regeneration performance of CMC-CPAM-TA. **a** Desorption capacity of CMC-CPAM-TA for Cu(II) ions. **b** SEM image and **c** EDS curve of CMC-CPAM-TA after

desorption of Cu(II) ions. **d** Desorption capacity of CMC-CPAM-TA for RhB. **e** SEM image and **f** EDS curve of CMC-CPAM-TA after desorption of RhB

the regeneration performance of CMC-CPAM-TA decreased after five cycles. In this sense, it is worth exploring how to improve the regenerative ability in our future, which would promote this adsorbent to move towards application for large-scale wastewater treatment.

Conclusion

Herein, we developed an efficient cellulose-based adsorbent (CMC-CPAM-TA) using a facile, environmentally friendly, and economical method based on the formation of hydrogen bonds and electrostatic interactions between the catechol, carboxyl, and amino groups in CMC, CPAM, and TA, respectively. This cellulose-based adsorbent exhibited a clear 3D mesoporous/macroporous network structure and large surface area (37.02 m²/g), enabling the exposure of abundant adsorption sites and fast mass transfer of Cu(II) ions and RhB during adsorption. The adsorption capacity of CMC-CPAM-TA for Cu(II) ions and RhB was 669.8 and 202.15 mg/g, respectively. The investigation of the adsorption mechanism revealed that the removal of Cu(II) ions proceeded via the

formation of Cu–O coordination bonds between the Cu(II) ions and catechol groups, whereas that of RhB proceeded via the occurrence of electrostatic interactions between the hydroxyl/carboxyl groups and RhB, which followed the Langmuir isotherm adsorption model. Regeneration experiments revealed that CMC-CPAM-TA maintained high adsorption capacity for Cu(II) ions and RhB after five cycles due to its robust structure. The high adsorption capacity and regenerative ability of CMC-CPAM-TA render this low-cost bio-based adsorbent potentially useful for application in wastewater purification and environmental remediation.

Author contributions All authors contributed to the study conception and design. Material preparation and data collection and analysis were performed by NNX, QW, and SLB. The first draft of the manuscript was written by NNX and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

Ethical approval This study did not involve human or animal subjects, and thus, no ethical approval was required. The study protocol adhered to the guidelines established by the *cellulose*.

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