

Hydrogel Beads Based on Carboxymethyl Cellulose for Removal Heavy Metal Ions

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ABSTRACT: Environment-friendly carboxymethyl cellulose (CMC) hydrogel beads were successfully prepared using epichlorohydrin (ECH) as a crosslinking agent in the suspension of fluid wax. There was an ether linkage formed between ECH and CMC, which was identified from bands in FTIR spectra of the prepared hydrogel. The prepared hydrogel beads with diameters about 4 mm were apparently spherical and fully transparent. The X-ray diffraction (XRD) spectra indicated that the adsorption of metal ion onto the oxygen atom of carboxyl group led to change in crystallinity patterns of hydrogels. The scanning electron microscope (SEM) images clearly showed that the hydrogels had an internal porous structure. The adsorption capacity increased as initial concentrations of metal

ions and the pH value of metal ion solution increased. Freundlich and Langmuir isotherm models were employed to analyze the data from batch adsorption experiments. There are very good correlation coefficients of linearized equations for Langmuir model, which indicated that the sorption isotherm of the hydrogel beads for metal ions can be fitted to the Langmuir model. The maximum adsorption amount of hydrogel beads for metal ions is 6.49, 4.06, and 5.15 mmol/g for Cu(II), Ni(II), and Pb(II), respectively. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1204–1210, 2011

Key words: carboxymethyl cellulose; hydrogel; beads; adsorption; heavy metal ions

INTRODUCTION

Owing to nonbiodegradable and accumulation in the food chain, heavy metal ions from industrial effluents are seriously threatening the environment and public health even at very low concentrations.^{1–3} It is very significant to remove heavy metal ions from wastewater before draining.

Over the past decades, increasing effort has been concentrated on developing various methods that can effectively remove heavy metal ions from aqueous environments. Some prevalent methods for removing heavy metals include chemical precipitation,⁴ membrane filtration,⁵ ion exchange,⁶ liquid extraction,⁷ reverse osmosis,⁸ activated carbon adsorption,⁹ and biopolymer adsorbents.¹⁰ Adsorption based on biopolymer possesses a number of advantages including renewable, biodegradable and modifiable, etc,^{11–13} and was thus regarded as one of the most popular, economic and effective measures for the removal of heavy metals from wastewater.

Cellulose is regarded as the most abundant and renewable biopolymer in nature, and can be chemically modified for enhanced metal binding ability via graft¹⁴ or copolymerization,¹⁵ etc. Because there is much crystalline region in raw or modified cellulose,^{16,17} the adsorption of metal ions can only take place at the amorphous region.¹⁸ As a result, raw or modified cellulose has low adsorption capacity for heavy metal ions.¹⁹

Hydrogel is a three-dimensionally crosslinked networks polymer, and can encompass a wide range of chemical compositions. It has inherently hydrophilic network, but not dissolve in aqueous solution. It was reported that hydrogels have high adsorption capacity for heavy metal ions by reducing the crystallinity through the gel formation process.²⁰ Furthermore, hydrogels can be synthesized in bead form via inverse suspension crosslinking.²¹ Owing to its chemical stabilities, good mechanical strength, the relatively large surface area and uniform particle size and shape,^{22,23} hydrogel beads are the most promising materials which can be used to remove heavy metal ions.

Carboxymethyl cellulose (CMC) is an ionic polysaccharide that contains carboxyl groups and can be used to prepare heavy metal adsorption materials.²⁴ In this article, we successfully prepared a novel kind of hydrogel beads based on CMC using epichlorohydrin (ECH) as crosslinker by inverse suspension

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crosslinking. The adsorption behavior of the hydrogel beads were examined with Pb^{2+} , Ni^{2+} , and Cu^{2+} aqueous solutions as model wastewater.

EXPERIMENTAL

Materials

CMC was purchased from Aladdin-Reagent (Shanghai, China). The molecular weight and total degree of substitution of CMC were 250,000 and 1.2, respectively. All other reagents (analytical grade) used in this study were supplied from Aladdin-Reagent and were used without further purification.

Hydrogel beads synthesis

The CMC hydrogel beads were synthesized by inverse suspension crosslinking. In the experiment, the 5 wt % CMC solutions were prepared by directly mixing 5 g solid NaOH and 5 g CMC with 90 mL deionized water. Then 10 mL ECH was added to 90 mL CMC solutions under stirring (400/rpm) for 20 min. The mixtures were dispersed in a continuous phase of 1000 mL fluid wax (Density: 0.87–0.895; Flash point: 226.5°C). The reaction was held under stirring (300/rpm) at 0°C for 48 h. The resulting beads were washed with deionized water and acetone until the unreacted substance and fluid wax were completely removed. The obtained hydrogel beads were frozen for 8 h in ultra low temperature freezer (U410-86, England) at –70°C. The frozen hydrogels were dried in freeze dryer (ALPHA1-2/LDplus, German) under vacuum (RZ6, German).

Adsorption experiments

The freeze-dried hydrogel beads (1 g) were soaked in various concentrations of aqueous metal ions (1 L) for 72 h at room temperature. Adsorption amount of metal ions can therefore be calculated from the difference between initial and final concentration using atomic absorption spectrophotometer (Hitachi Z-5000, Japan). The amount of metal ions adsorbed at adsorption equilibrium was calculated according to the following eq. (1), whereas the ratio of metal ions adsorbed to initial metal ions was calculated according to the following eq. (2):

$$Q_e = (C_0 - C_e)V/W \quad (1)$$

$$R_m = (1 - C_e/C_0) \times 100 \quad (2)$$

Where C_0 and C_e are the initial and equilibrium metal ions concentrations (mol/L), respectively. V is the volume of the solution (L) and W is the weight of the dried hydrogel beads (g).

Characterization

FTIR spectroscopy analysis

The freeze-dried samples were compressed into KBr pellets. FTIR spectra of the samples were recorded with FTIR spectrometer (Bruker Vector 33, German) from 4000 to 500 cm^{-1} .

Wide-angle X-ray diffraction pattern

The dried samples were compressed into the disks, and then measured with an X-ray diffractometer (WAXD, Rigaku D/max-III A, Japan) with $\text{Cu } \alpha$ at 40 kV and 30 mA in the region of 2θ from 4 to 60°.

Morphology observation of hydrogels

The swollen equilibrium hydrogel samples were frozen to –70°C and then freeze-dried under a vacuum until all water was sublimed. The freeze-dried samples were fractured carefully in liquid nitrogen, and then fixed on tubs with sputter coated with gold before observation. Morphology of external and fractured surface of samples was observed by scanning electron microscope (Nova NanoSEM 430, Fei Company) with 5 kV.

RESULTS AND DISCUSSION

Preparation of CMC/ECH beads

CMC/ECH hydrogel beads were synthesized using a suspension crosslinking technique with epichlorohydrin as crosslinking agent in aqueous alkaline conditions. The proposed reaction mechanism of ECH with CMC is shown in Figure 1. ECH was widely used as a crosslinker to react with the hydroxyl groups of polysaccharide.^{25–30} In alkaline conditions, the hydroxyl groups of CMC become alcoholate anion. The alcoholate anion attacks the epoxy groups of ECH to form a monoether of chloropropanediol.^{25,26} A new epoxy group will yield by chloride displacement rearranges of the chloropropanediol monoether.³⁰ When the new epoxy groups react with the hydroxyl groups of another CMC, the crosslinking reaction occurs between ECH and CMC. In the reaction, there may be some side reactions, for example, some ECH molecules may only react with one hydroxyl group of CMC and some unreacted ECH hydrolyzes to glycerol.^{27,30}

Analysis of FTIR

FTIR spectra of the CMC and the CMC hydrogel are shown in Figure 2. An obvious difference is observed between the spectrum of the CMC and the spectrum of the CMC hydrogel. The bands at 1422, 1608, 2931 cm^{-1} , and 3420 cm^{-1} are assigned to the

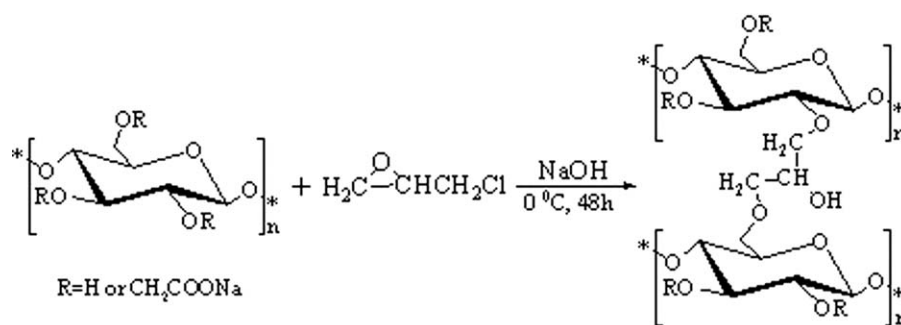


Figure 1 Preparation of the CMC hydrogel particles with ECH as crosslinker.

stretching vibration of COO⁻ (symmetric), COO⁻ (asymmetric), C—H (aliphatic), and O—H, respectively.^{26,31} The bands observed at 1608 and 1422 cm⁻¹ in the spectrum of CMC/ECH hydrogel indicate that the carboxyl groups of CMC exist in the hydrogels after crosslinking. It can be seen from the spectrum of CMC/ECH hydrogels that some typical peaks appear at 1327, 1262, and 1064 cm⁻¹. The peaks at 1327 and 1262 cm⁻¹ belong to stretching vibration of new bond C—O—C and C—C stretching vibration from the components of the reacted ECH with CMC, respectively.³² whereas the band appeared at 1064 cm⁻¹ is characteristic for bending vibration of —OH group. The results show that a crosslinking reaction occurs between ECH and the hydroxyl groups of CMC.

X-ray diffraction patterns

As shown in Figure 3, there are several very sharp and clear diffraction signals at $2\theta = 15, 17.8,$ and 22.8° in the X-ray diffraction (XRD) diffractogram of CMC, which are the characteristic diffraction of cellulose.³³ However, these diffraction signals at $2\theta =$

$15, 17.8,$ and 22.8° were not observed in the XRD diffractogram of CMC/ECH hydrogels, which suggests that the chemical crosslinking between the CMC and ECH could destroy the crystallization of the CMC and increase the amorphous region in the CMC/ECH hydrogel.²⁰ These results indicated that the metal ions could more easily penetrate into the hydrogel beads due to reducing the crystallinity during the gel formation. Therefore, the CMC/ECH hydrogel beads have higher adsorption capacity for heavy metal ions. The XRD patterns of the metal ions-loaded hydrogel beads show distinct and complex peaks. The intensity of peak at 31.6° decreased, however, the diffraction peaks at 45.3 and 56.3° have completely vanished, instead there were some diffraction peaks at $24.6, 33.8,$ and 38° in Figure 3(C–E). It is, thus, reasonable to assume that metal ions adsorbed on hydrogel beads formed coordination bonds with the oxygen atoms in the carboxyl groups of hydrogel beads.^{34–37}

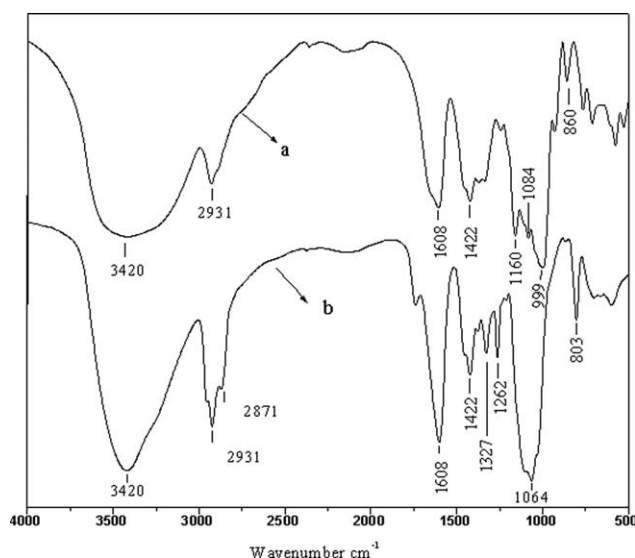


Figure 2 IR spectra of (a) CMC and (b) CMC/ECH hydrogel.

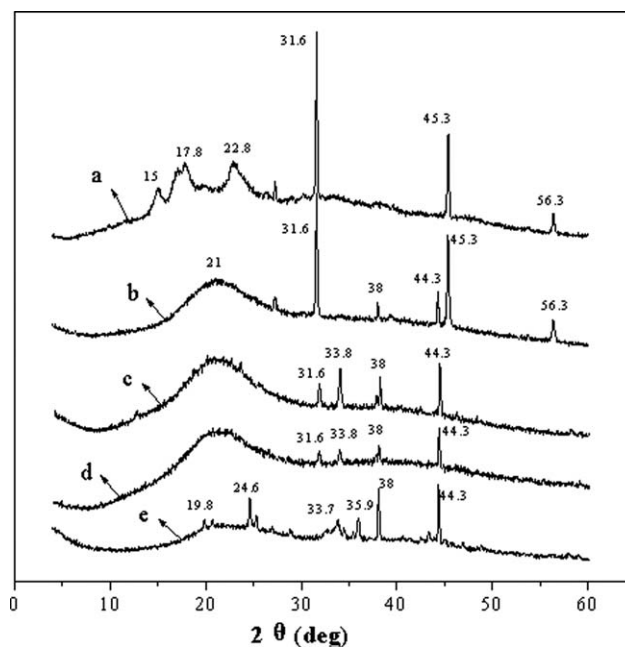


Figure 3 XRD patterns of (a) CMC, (b) CMC/ECH hydrogel, (c) Hydrogel-Cu²⁺, (d) Hydrogel-Ni²⁺, and (e) Hydrogel-Pb²⁺.



Figure 4 Photographs of hydrogel beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Morphology of hydrogels

The prepared hydrogel beads were apparently spherical and fully transparent (Fig. 4). The diameters of these beads are about 4 mm (Fig. 4). The SEM images clearly show that the hydrogels show a porous structure in the internal [Fig. 5(a)]. There are numerous carboxylate anions (COO^-) in network of hydrogel beads. The electrostatic repulsions among the carboxylate anions (COO^-) resulted in the expansion of the hydrogel network and the increase in the amount and size of pore.^{38,39} As a result of numerous small pores in the hydrogel network, metal ions can easily diffuse in and out. Therefore, hydrogel beads have high adsorption capacity. After adsorbing metal ions,

the SEM micrograph of hydrogel is shown in Figure 5(b). The morphological difference is obviously observed between the unload hydrogel and the load hydrogel. The pore size of the load hydrogel decreases because the electrostatic repulsions decline in the network of hydrogels after the anion hydrogels absorbed the cationic metal ions.

Effect of the initial pH

There are many carboxylic groups in the CMC/ECH hydrogels. The pH of metal ion solutions will affect the protonation of the carboxylic groups in the CMC/ECH hydrogels. Hence, it is important to examine the effect of solution pH on adsorption performance of hydrogels. As shown in Figure 6, the adsorption ratio (R_m) increases with the increase of the solution pH values for the CMC/ECH hydrogels. Michie suggested that sorption of copper from solution by cellulose is due entirely to the action of acidic groups in the cellulose molecules.⁴⁰ With increasing the pH from 2 to 7, deprotonation is occurred and resulting in ionization of more carboxylic groups ($-\text{COOH}$) that can be transferred to the carboxylate ions (COO^-) participated in the hydrogel matrix.⁴¹ The carboxyl ions have the stronger electrostatic attraction to the metal ions adsorbed than the carboxyl groups.⁴² As a result, the adsorption capacity of metal ions increases rapidly. Because the pK_a of the carboxylic groups is 4.6, the hydrogel is highly ionized when the pH of solution is the higher than 4.6. The result is that the slow increase is observed at $\text{pH} > 4.6$.

Effect of the initial metal concentration

To study the effect of the metal ion concentration on the adsorption amount and ratio, a series of freshly

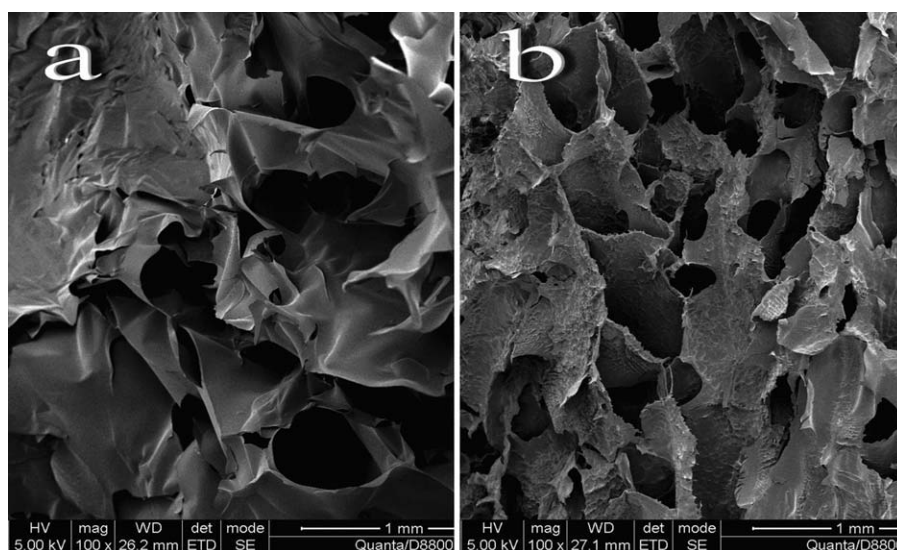


Figure 5 SEM photographs of hydrogels cross-sections: (a) before absorption metal ions (magnification $\times 100$) and (b) after absorption metal ions (magnification $\times 100$).

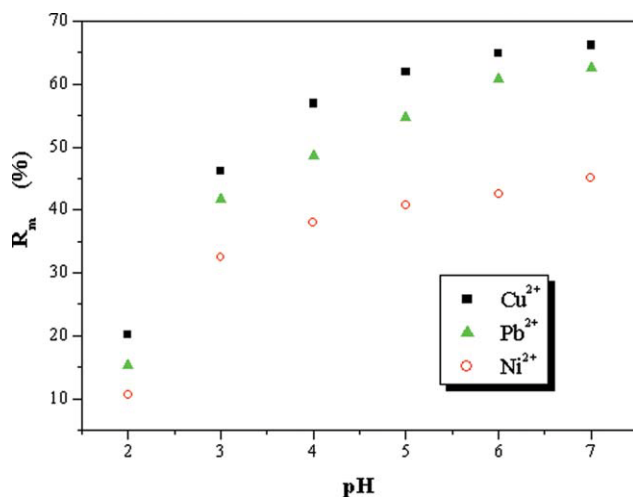


Figure 6 Effects of pH on the metal ion adsorption ratios of CMC/ECH hydrogel (■) Cu²⁺, (▲) Pb²⁺, and (○) Ni²⁺. Adsorption condition: initial concentration of metal ions 3 mmol L⁻¹, room temperature, 48 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

prepared metal ion solutions were used. Figure 7 shows the effect of metal ion concentration on the adsorption of the different metal ions. The amount of metal ions adsorbed increases with an increasing concentration. The maximum amount of metal ions adsorbed exceeds to 6.23, 3.02, and 4.82 mmol/g for Cu(II), Ni(II), and Pb(II), respectively. The reason for absorption amount of copper ion over others is that copper ion has a stronger attraction to the lone pair of electrons in the oxygen atoms of carboxyl groups, which causes to form more stable complexes with Cu(II) than Ni(II) or Pb(II).³⁷ As shown in Figure 8,

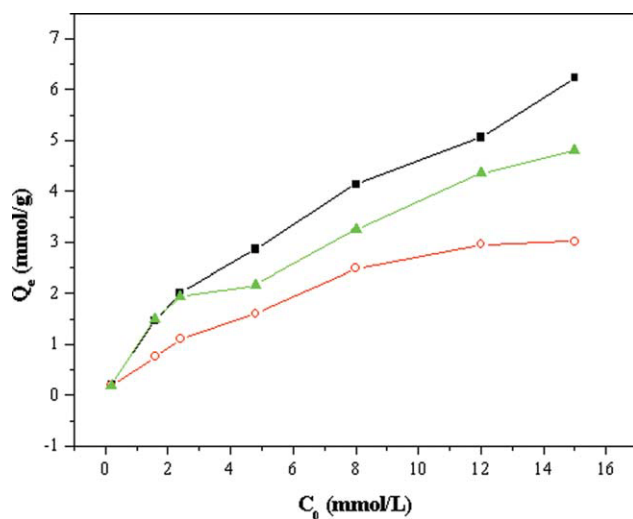


Figure 7 Effect of the initial concentration on the adsorption behavior of metal ions on CMC/ECH hydrogel beads (■) Cu²⁺, (▲) Pb²⁺, and (○) Ni²⁺. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

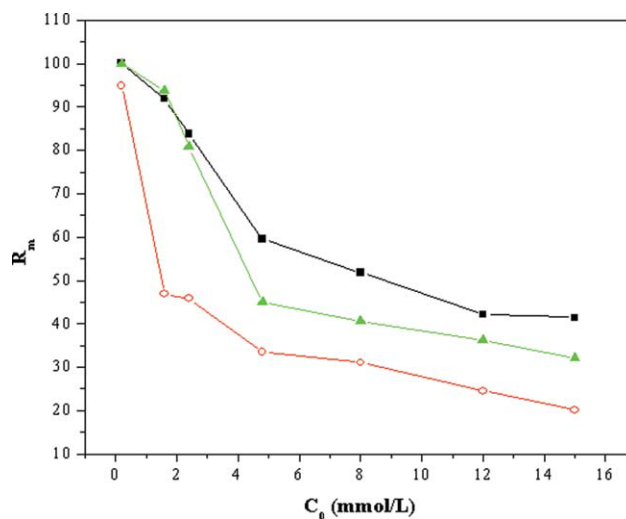


Figure 8 Metal ion adsorption ratio profiles of CMC/ECH hydrogels at room temperature (■) Cu²⁺, (▲) Pb²⁺, and (○) Ni²⁺. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the absorption ratio for Cu²⁺ and Pb²⁺ is higher than 99%, the absorption ratio for Ni²⁺ exceeds to 95% when the metal ion concentration is lower than 0.2 mmol/L. The ratio of adsorption decreases with increasing concentration, but hydrogel beads show a better adsorption capacity for the studied metals. As compared with these adsorbents outlined in Table I, the CMC/ECH hydrogel beads have the larger adsorption capacity. Therefore, the hydrogel beads were studied to recover heavy metal from metal solution.

TABLE I
Comparison of Maximum Adsorption Capacity of Cellulose Material

Cellulose materials	Maximum adsorption capacity (mmol L ⁻¹)	References
CMC/ECH hydrogel bead	Cu(II): 6.49; Ni(II): 4.06; Pb(II): 5.15	In this work
Mercerized sugarcane bagasse chemically modified with succinic anhydride	Cu(II): 2.89; Pb(II): 2.42	43
Cellulose-g-GMA-Imidazole	Ni(II): 0.84	44
Carboxymethylated-bacterial cellulose	Cu(II): 0.20; Pb(II): 0.29	24
Succinylated mercerized cellulose modified with triethylenetetramine	Cu(II): 1.08; Pb(II): 0.93	45
Cellulosic fibers modified by β-cyclodextrin	Cu(II): 0.10	46
Chitosan entrapped CM-cellulose hydrogels	Cu(II): 2.65	42
Diethylenetriamine-bacterial cellulose	Cu(II): 0.99; Pb(II): 0.42	47

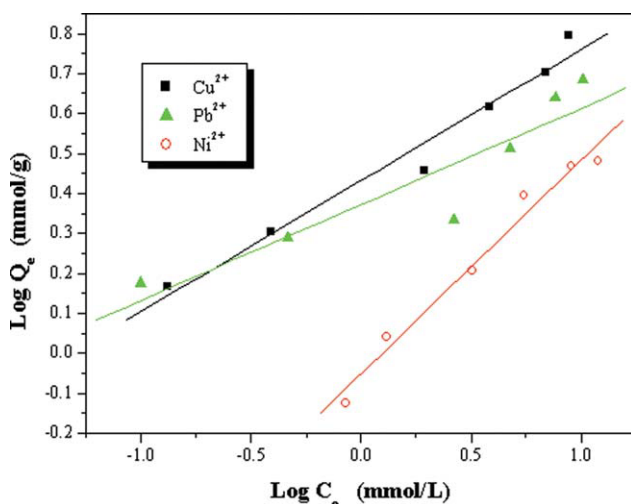


Figure 9 Linearized adsorption isotherm of Freundlich at room temperature (■) Cu²⁺, (▲) Pb²⁺, and (○) Ni²⁺. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

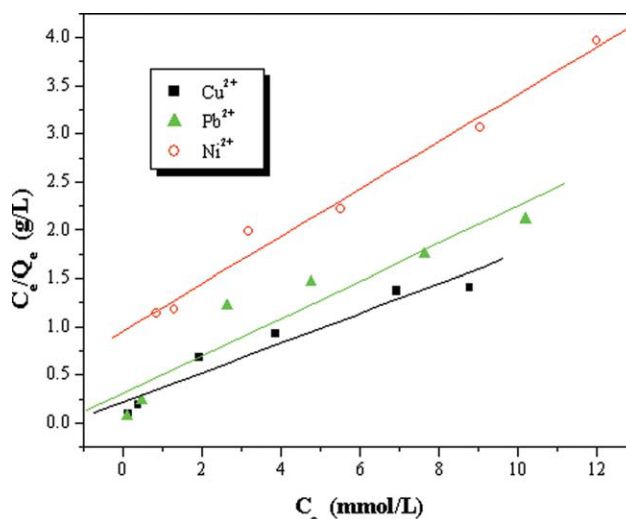


Figure 10 Linearized adsorption isotherm of Langmuir at room temperature (■) Cu²⁺, (▲) Pb²⁺, and (○) Ni²⁺. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Adsorption isotherms

Two empirical adsorption models, Freundlich and Langmuir, are often used to study the adsorption behavior. In this work, the experimental data obtained at pH 7 are analyzed with the Freundlich and Langmuir equations. The Freundlich and langmuir isotherms are given by eq. (3) and (4), respectively:

$$\log Q_e = \log K_F + 1/n \log C_e \tag{3}$$

Where K_F and n are the Freundlich constants related to adsorption capacity and intensity, respectively. C_e is the equilibrium concentration of metal ion in the solution.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{bQ_{\max}} \tag{4}$$

Where Q_{\max} and b are the Langmuir constants related to maximum monolayer adsorption capacity and adsorption energy, respectively.

Figure 9 shows the Freundlich isotherm obtained by plotting $\log Q_e$ and $\log C_e$, and the values of K_f , n , and R^2 are listed in Table II. The Langmuir sorption

isotherm is shown in Figure 10. The adsorption equations and parameters are presented in Table III. Based on these coefficients obtained, it can be concluded that the Langmuir equation ($R^2 > 0.90$) gives a better fit to the experimental data of lead and nickel ions than the Freundlich equation ($R^2 > 0.85$).^{48,49} Therefore, it is suggested that this sorption process takes place at the functional groups/binding sites on the surface of the CMC/ECH hydrogel beads, which is considered as monolayer adsorption. The correlation coefficients from copper ion reveal that the Freundlich equation ($R^2 = 0.971$) gives a better fit to the experimental data than the Langmuir equation ($R^2 = 0.936$). The results show that the sorption behavior of hydrogels is very complicated and might be affected by many factors.

CONCLUSION

Superabsorbent hydrogel beads based on CMC were prepared by suspension crosslinking method and were characterized by FTIR, XRD, and SEM. The presence of absorption bands around 1327, 1266, and 1064 cm^{-1} confirms that a new bond C—O—C between ECH and CMC was formed. XRD spectra

TABLE II
Freundlich Equation-Fitted Parameters

Metal ions	Freundlich equation	K_F	n	R^2
Copper	$\log Q_e = 0.433 + 0.327 \log C_e$	2.71	3.06	0.971
Lead	$\log Q_e = 0.373 + 0.240 \log C_e$	2.36	4.17	0.858
Nickel	$\log Q_e = -0.0506 + 0.533 \log C_e$	0.89	1.88	0.977

TABLE III
Langmuir Equation-Fitted Parameters

Metal ions	Langmuir equation	Q_{\max}	b	R^2
Copper	$C_e/Q_e = 0.154C_e + 0.213$	6.49	0.723	0.936
Lead	$C_e/Q_e = 0.194C_e + 0.308$	5.15	0.630	0.900
Nickel	$C_e/Q_e = 0.246C_e + 0.951$	4.06	0.259	0.984

revealed that the crystallinity of hydrogel beads was lower than that of pure CMC. It is reasonable to assume that metal ions adsorbed on hydrogel beads formed coordination bonds with the oxygen atoms in the carboxyl groups of hydrogel beads. The prepared hydrogel beads showed good adsorption ability for heavy metal ions. The maximum amount of adsorbed metal ions from the data of Langmuir model is 6.49, 4.06, and 5.15 mmol/g for Cu(II), Ni(II), and Pb(II), respectively, at pH 7. The studies of adsorption demonstrate that the hydrogel beads have a potential application in removal and recovery of heavy metal ions from wastewater.

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