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Journal of Hazardous Materials B136 (2006) 930–937

Journal of Hazardous Materials

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Adsorption properties of crosslinked carboxymethyl-chitosan resin with Pb(II) as template ions

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Received 13 October 2005; received in revised form 8 December 2005; accepted 16 January 2006

Abstract

In the current study, we attempt to find a new adsorbent material based on chitosan to improve adsorption selectivity for heavy metals, so that the crosslinked *N*,*O*-carboxymethyl-chitosan resin with Pb(II) as template ions (crosslinked CMC template) were synthesized by using CMC adsorbed Pb(II) ions crosslinked with glutaraldehyde. The effects on adsorption capacities such as amount of crosslinking agent, degree of substitution of CMC, pH value of the initial solution and adsorption time were investigated. The adsorption experiments demonstrated the crosslinked CMC template has high adsorption selectivity for Pb(II) ions in solution containing single metal ions or coexistence of three metals ions of Cu(II), Zn(II) and Pb(II). Furthermore, it was investigated that the crosslinked CMC template has a good reusability and stability as compared to CMC. Finally, we studied the adsorption mechanism by FTIR spectra and XPS analysis. The results reveal that the adsorption of crosslinked CMC template and CMC for Pb(II) is a chelation process.

Keywords: Adsorption; *N*,*O*-carboxymethyl-chitosan; Crosslinked; Lead; Template

1. Introduction

Today, environmental conservation is of increasing social and economic importance. A particularly intractable pollution problem is that of the contamination of waters by heavy metals [1]. Traditional treatment methods such as chemical precipitation as metal hydroxide, electro deposition, ion exchange, and membrane separation have been applied. Adsorption seems to be a good alternative, and many adsorbents have been tested for the adsorption of various heavy metals.

Chitosan has undoubtedly been one of the most popular adsorbents for the removal of metal ions from aqueous solution and is widely used in waster treatment applications [2–5]. In spite of its prolific use, the adsorption ability of chitosan has not been realized to a satisfying level. In recent years, attention has been focused on various adsorbents that have metal-binding capacities and high selectivity to remove unwanted heavy metals from contaminated water [6,7].

Further chemical modifications of chitosan have been made to improve the selectivity and the capacities for metal ions [8]. Carboxymethylation was prepared and regarded as a simple and effective process to facilitate the adsorption ability of chitosan with heavy metals [9,10]. Carboxymethyl-chitosan has many reactive functional groups, amino group, carboxyl group, as well as both primary and secondary hydroxyl groups at the C-3, C-6 positions, respectively. This special structure makes it exhibit chelation with various metal ions [11]. However, carboxymethyl-chitosan can dissolve in acidic solution and water, so the template resin has been developed to reinforce the adsorption selectivity of chitosan by using a metal cation as template. And the crosslinked carboxymethyl-chitosan templates also provide the potential for regeneration and reuse after metal adsorption.

The main purpose of this study was to investigate the adsorption properties of the crosslinked *N*,*O*-carboxymethyl-chitosan (CMC) resin with Pb(II) as template. The study included the preparation of the crosslinked CMC resin with Pb(II) as template, which has been performed through the observation of the influence of pH, degree of substitute (DS) of CMC and the crosslinking agent dosage, and the examination of the adsorption

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doi:10.1016/j.jhazmat.2006.01.033

behaviors of the crosslinked CMC resin with Pb(II) as template for single metal ions and the mixed solution of three metal ions. Furthermore, the adsorption mechanism of the crosslinked CMC resin with Pb(II) as template for Pb(II) ions in acetate solution was investigated via characterization of Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Materials

Chitosan with 40 mesh, 90% degree of deacetylation (DD) and molecular weight of 6×10^5 was purchased from Yuhuan Ocean Biology Company (Zhejiang, China), chloroacetic acid and all the other reagents used in this experiment were of analytical grade.

2.2. Preparation of CMC

Preparation of CMC and determination of the DS were similar to those methods found in the literature [12,13], and a series of CMC samples with different DS were obtained by given different reaction time and temperature.

2.3. Preparation of the crosslinked CMC resin with Pb(II) as template ion

A 5.00 g of CMC with DS of 0.85 was added to a 500 mL beaker flask containing 450 mL of Lead acetate solution (initial concentration 0.02 mol/L, pH 5.9), and then the beaker flask was placed in a thermostated shaker (THZ-98A) for 24 h with a shake of 120 rpm at 25 °C. The product was filtered under reduced pressure, and the residue was washed with distilled water until no Pb(II) ion in the filtrate was detected by Na_2S, and then was washed with ethanol and ether in turn, dried in vacuum, thus the product of CMC after Pb(II) adsorption was obtained.

A 1.00 g of the product was swelled in 30.00 mL of distilled water, a certain volume of glutaraldehyde (1 wt.%) was added with stirring for 5 h at 50 °C, and then the crosslinked product was filtered and washed with distilled water until pH 7.0. The obtained product was dipped into 0.1 mol/L HCl stirring for 1 h at room temperature, and filtered. The process was repeated until Pb(II) ions were removed completely. The template resin was treated with 0.1 mol/L NaOH for 5–8 h in order to activate amino group, then it was filtered and washed with water, ethanol and ether in turn. The crosslinked CMC resins with Pb(II) as template ion, denoted as the crosslinked CMC template, were obtained. The preparation process is shown in Scheme 1.

2.4. Adsorption experiments

2.4.1. Single metal ions adsorption experiment

A 0.10 g of CMC with a certain DS or the crosslinked CMC template was added to 25.00 mL of acetate solution (initial M^{2+} concentration 0.02 mol/L) with a given pH adjusted with 0.1 mol/L CH_3COOH or $NH_3 \cdot H_2O$, shaking 24 h at 25 °C, then filtered and dried. The adsorption capacities of metal ions were obtained from the initial and the final concentration of metal ions in the acetate solution determined by atomic adsorption spectrophotometer and the mass of adsorbent used.

2.4.2. Three metals ions co-adsorption experiment

A 0.10 g of CMC or the crosslinked CMC template was added to 25.00 mL of acetate solution containing Cu(II), Zn(II) and Pb(II) ions (initial concentration of single species 0.02 mol/L) at pH 6.2, shaking 24 h at 25 °C, then filtered and dried. The contents of M(II) ions were determined by atomic adsorption spectrophotometer and then the adsorption capacities were calculated by mass of adsorbent used.

2.4.3. Reusability experiment

The crosslinked CMC template adsorbed Pb(II) ions was dipped into 0.1 mol/L HCl stirring for 1 h at room temperature to remove Pb^{2+}, and then was treated with 0.1 mol/L NaOH for 5–8 h. Finally it was filtered and washed with water, ethanol and ether in turn. The crosslinked CMC template obtained was used in adsorption experiment, and the process was repeated 10 times.

2.5. Characterization

The Fourier transform infrared (FTIR) spectra of CMC and the crosslinked CMC template before and after Pb(II) adsorption were obtained with a Perkin–Elmer FTIR 1600 series spectrometer and all samples were prepared as potassium bromide pellets.

X-ray photoelectron spectroscopy of CMC and the crosslinked CMC template before and after Pb(II) adsorption were recorded by using an X-ray photoelectron spectrometer (VG Scientific Escalab 210-UK) equipped with a twin anode (Mg Kα/Al Kα) source.

3. Results and discussion

3.1. Preparation of the crosslinked CMC template

3.1.1. Influence of DS of CMC

In order to obtain a perfect crosslinked CMC resin with Pb(II) as template ion, it is necessary to investigate the influence factors on the adsorption capacity for Pb(II). In our previous work, adequate studies suggested that the adsorption capacities of the crosslinked chitosan resin with metal ions as template for metal ions are dependent on the reaction time, the reaction temperature, the pH in the solution, the metal species, the degree of deacetylation of chitosan and the dosage of crosslinking agent [14,15]. It also revealed that the adsorption capacities do not depend on the physical form of the polymer (either as a film, powder or in solution) and that the selectivity does not depend on the size and hardness of considered ions [16]. However, the properties of adsorbent are important factors for metal ions. So herein the effects of DS of CMC was investigated.

Fig. 1 shows the influence of DS of CMC on adsorption capacity for Pb(II) ion at the pH value of 5.9. It is observed that the adsorption capacities of Pb(II) ions increase with increasing the DS of CMC at the range of 0.62–1.25. Considering the

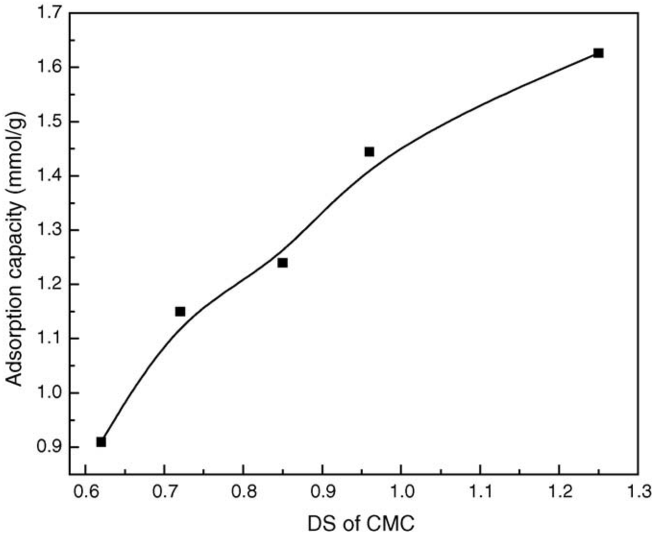
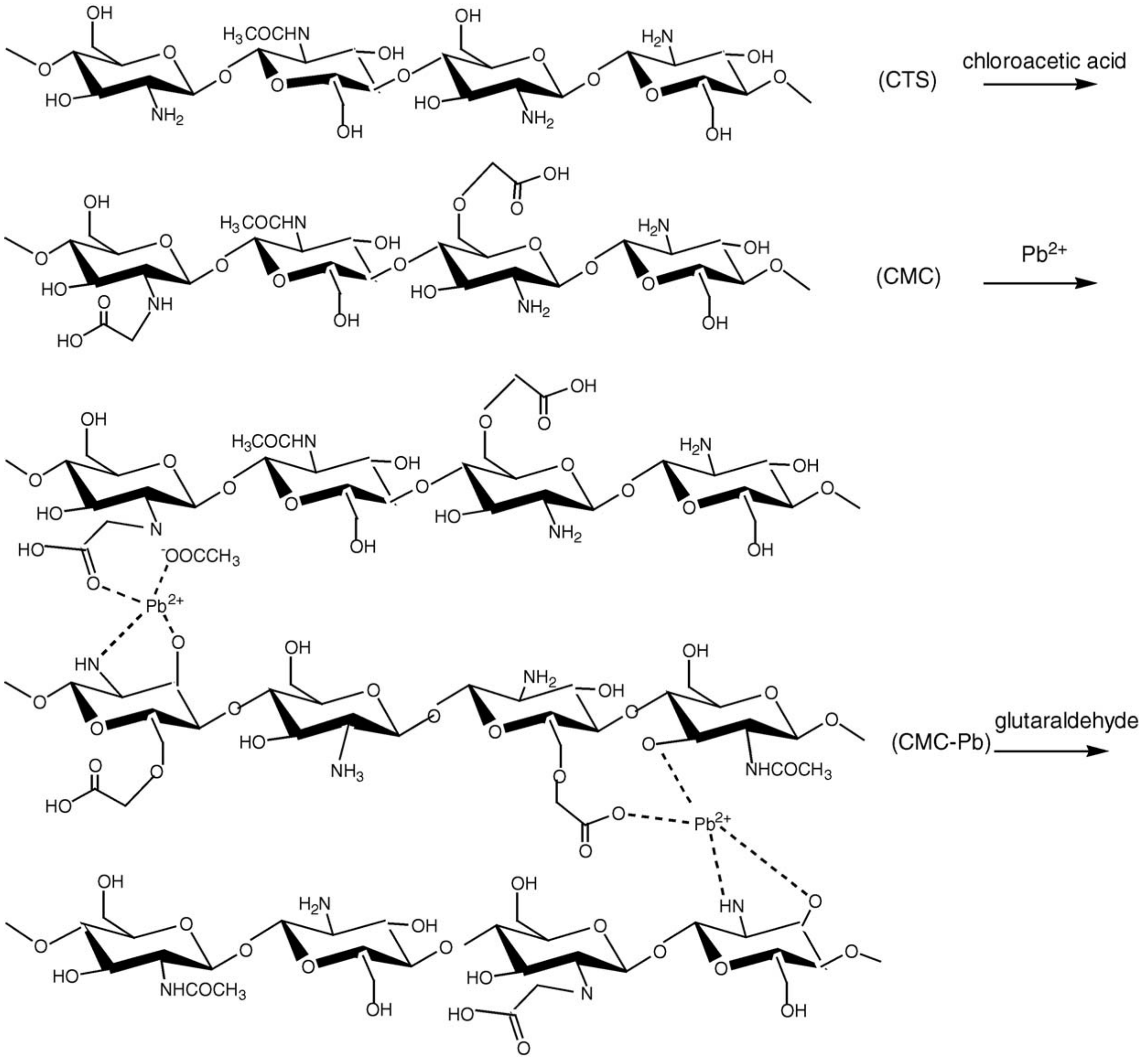


Fig. 1. Relationship between the DS of CMC and adsorption capacity of CMC for Pb(II) ions (0.10 g of CMC, pH = 5.9, shaking 24 h at 25 °C).

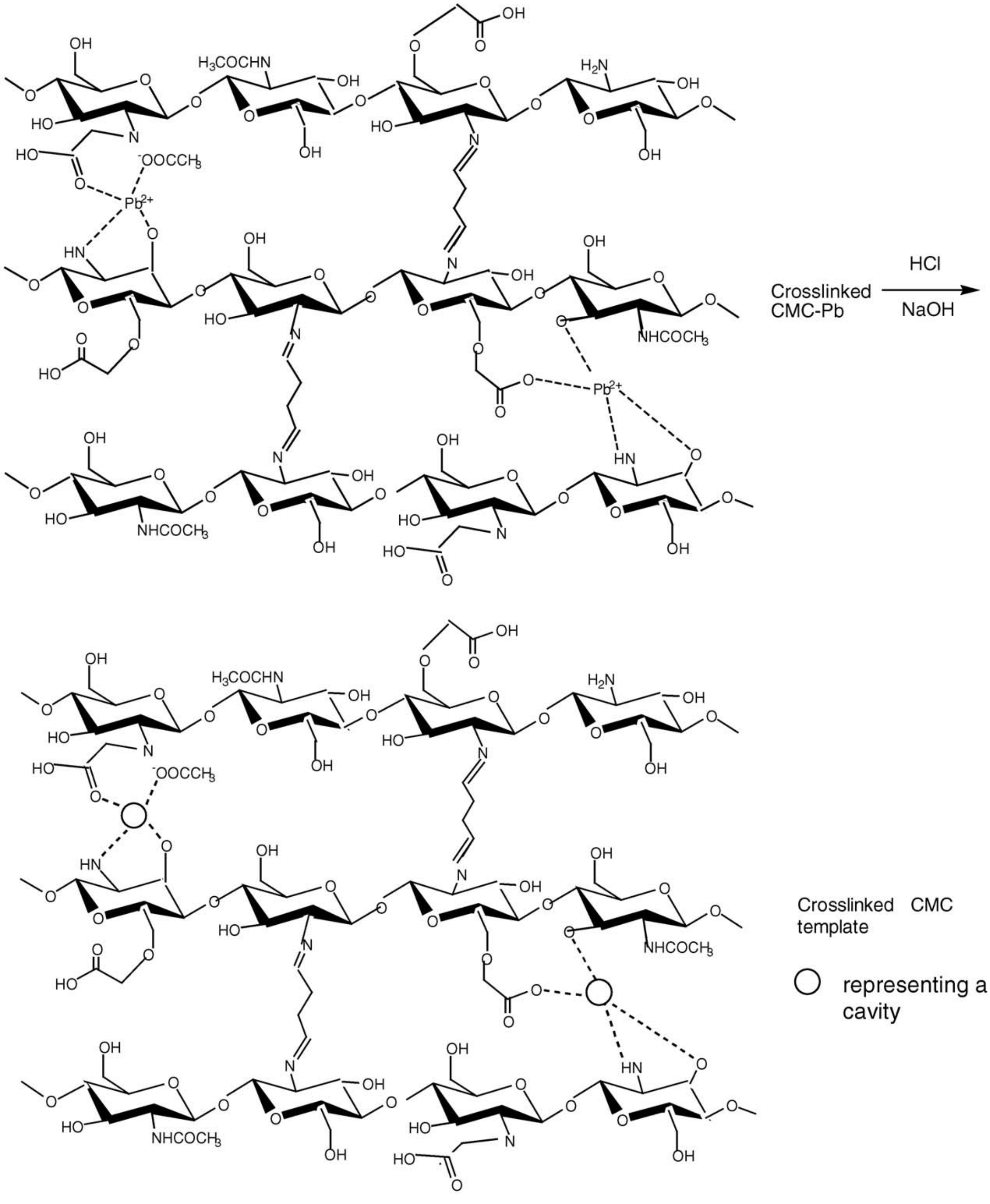
carboxymethyl substituting for hydrogen atom of the $-NH_2$, the amount of amino group decrease, whereas the adsorption capacity of Pb(II) in acetate solution increases apparently with an increase of DS between 0.62 and 1.25. This phenomenon suggests that the amount of carboxymethyl groups affect the adsorption capacities of Pb(II) ions directly and the main adsorption sites of CMC for Pb(II) ions are on the carboxymethyl group.

3.1.2. Influence of crosslinking agent dosage

Similarly, it is also necessary to investigate the effect of the dosage of crosslinking agent tests, which is the basic work of preparing the crosslinked CMC template. Fig. 2 shows that the formation of crosslinking between the amino group and aldehyde group improve the adsorption capacity up to a maximum before a decrease in adsorption capacity occur as the dosage of glutaraldehyde increases. The increase in adsorption capacity at dosage of aldehyde group between 0.31 and 0.51 mol, may be attributed to the low level of crosslinking, which prevent the formation of closely packed chain arrangements without a



Scheme 1. Preparation process of the crosslinked CMC template.



Scheme 1. (*Continued*).

significant decrease in the swelling capacity. As increasing the dosage of crosslinking agent, an optimum crosslinking network is formed in an appropriate aldehyde/amino ratio (0.51 mol of aldehyde corresponding to 1 mol of amino group) for Pb(II) adsorption. In addition, it cannot only reduces the opening of polymer network by supplementary linkages between polymer chains, but also the expansion of the polymer network results in a reduction of steric hindrance effect and a significant increase of adsorption capacity for Pb(II) ions. Beyond the point of 0.51 mol, the declining swelling and decreasing accessibility of the higher crosslinking polymer are due to a more extensive three-dimensional network and an increase in the hydrophobic character, thus resulting in the decrease of adsorption capacity. As a consequence of Schiff's base reaction, the glutaraldehyde crosslinking amino group involved in chemical linkages is not available for adsorption, and thus the adsorption capacity should

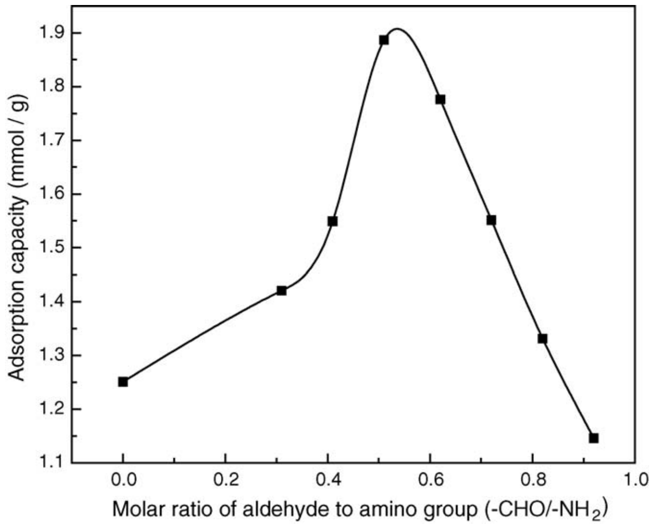


Fig. 2. Effect of the dosage of crosslinking agent on the adsorption capacity of the crosslinked CMC template for Pb(II) ions (0.10 g of the crosslinked CMC template, pH = 5.9, shaking 24 h at 25 °C).

decrease, if the main adsorption sites occur on amino group. However, it is noticeable that the adsorption capacities of the samples selected in the experiment for Pb(II) ions are larger than that of CMC, which further suggests that the main adsorption sites should be on the carboxymethyl group rather than amino groups of CMC.

3.2. *Adsorption properties of the crosslinked CMC template*

3.2.1. *Adsorption of Pb(II) ions*

3.2.1.1. Influence of pH value. Fig. 3 shows the relationship between pH value of the original solution and adsorption capacities of CMC and the crosslinked CMC template for Pb(II) ions. As seen from Fig. 3, it is observed that the adsorption capacity of Pb(II) ions increase with increasing the pH value of the solution and then decreases with further increase pH value. In addition, the better adsorption of CMC for Pb(II) ions in acetate solution appears at the pH of 5–6. A similar result is observed in the curve of the crosslinked CMC template. These experimental results suggest that adsorption properties of both CMC and the crosslinked CMC template in aqueous media are controlled by pH value. It is also observed that the adsorption capacities for Pb(II) ions of crosslinked CMC template always had greater than those of CMC in the pH range studied, which further suggests that the formation of three dimensional structure is better fit for Pb(II) adsorption.

The lower adsorption capacity of Pb(II) ions at $pH < 3.5$, is due to the weaker electrostatic repulsion between the Pb(II) cations and protonated amino and carboxymethyl group of CMC. With the increase of pH value, the carboxymethyl and amino groups are free from the protonation, the adsorption mechanism may be partially replaced by a chelation mechanism, and so the adsorption capacity increases. However, the precipitation occurrence for Pb(II) ions could lead to the decrease of the adsorption capacity. Interestingly, the CMC dissolved at pH lower than 2.5, while the crosslinked CMC template did not occurred the phenomena at the pH ranging from 2 to 7.5. The experimental results suggest that crosslinking reaction is able to improve the chemical stability of the CMC and enhance the adsorption range of pH value.

3.2.1.2. Influence of adsorption time. The experimental results of Pb(II) adsorption on CMC and the crosslinked CMC template versus time are shown in Fig. 4. The adsorption kinetics of the crosslinked CMC template was faster than CMC. The adsorption equilibrium was reached at about 15 h for the crosslinked CMC template, while took about 20 h for CMC. The fast adsorption rate of the crosslinked CMC template may probably be due to its special structure with the volumetric space for Pb(II) adsorption.

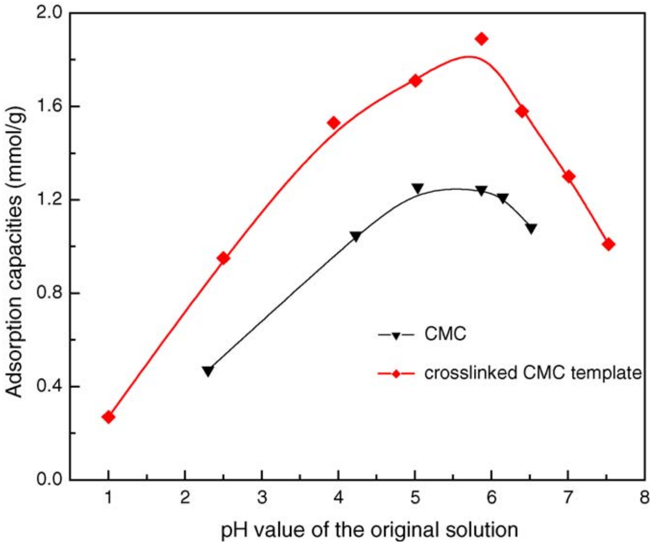


Fig. 3. Relationship between pH value of original solution and adsorption capacities of CMC and the crosslinked CMC template for Pb(II) ions (0.10 g of CMC with DS of 0.85 or crosslinked CMC template with the $-CHO/-NH_2$ ratio of 0.51, shaking 24 h at 25 °C).

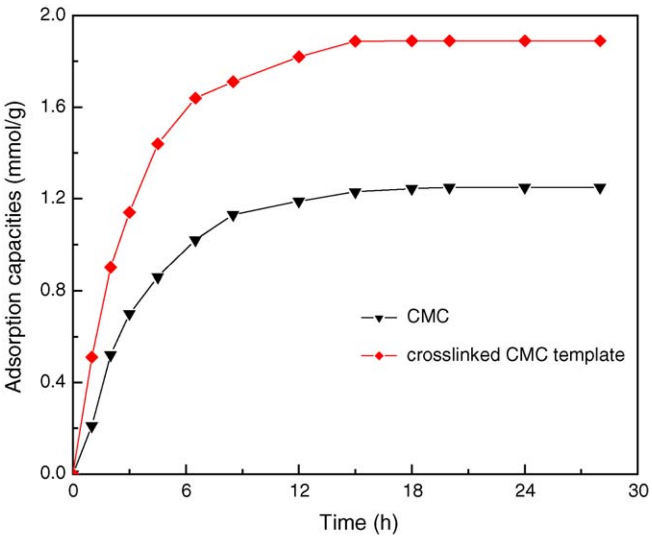


Fig. 4. Effect of the adsorption time on the adsorption capacities of CMC and the crosslinked CMC template for Pb(II) ions (0.10 g of CMC with DS of 0.85 or crosslinked CMC template with the $-CHO/-NH_2$ ratio of 0.51, pH 5.9 at 25 °C).

Table 1
Adsorption capacities of CMC with DS of 0.85 (a) and the crosslinked CMC template with the –CHO/–NH_2 ratio of 0.51 (b) for single metal ions

Adsorbents	Adsorption capacities (mmol/g)				
	Cu(II)	Co(II)	Ni(II)	Zn(II)	Pb(II)
a	1.95	1.48	1.93	1.50	1.24
b	1.82	1.17	0.78	0.74	1.89

3.2.2. Adsorption of the other single metal ions

Table 1 summarizes up the adsorption capacities for metal ions onto CMC and the crosslinked CMC template. As seen from Table 1, the adsorption capacities of the crosslinked CMC template for Cu(II), Co(II), Ni(II), and Zn(II) decreased significantly compared to those of CMC. On the one hand, this may be attributed to the extent of crosslinking and the decrease of amount of amino group, which are expected to play a great part in the adsorption control [17]. On the other hand, this is attributed to that the three-dimensional network of the crosslinked CMC template, provides a cavity tailored to the volumetric space of Pb(II) ions to adsorption(which is shown in Scheme 1). On the contrary, the formation of crosslinked CMC template leads to some restriction of new interchain linkages in the polymer network and the loss of the chain flexibility, resulting in a decrease of the accessibility and a descent of adsorption capacities for other metal ions. Furthermore, it is noticeable that although the account of adsorption for Cu(II) ions decreased as compared to CMC, the crosslinked CMC template could act as effective for Cu(II) ions. A similar result was obtained by crosslinking chitosan with chloromethyl oxirane and template ions reported by Ohga et al. [18]. It also can be seen that the crosslinked CMC template has a better adsorption capacity for Pb(II) ions, which further suggests that the crosslinked CMC template can selectively adsorb Pb(II) ions.

3.2.3. Co-adsorption of three metal ions

The selective adsorption of the two adsorbents for Cu(II)–Zn(II)–Pb(II) from the acetate mixture solution is shown in Table 2. By comparing the selectivity of the crosslinked CMC template for Cu(II), Zn(II) and Pb(II) with those of CMC, it can be found that the adsorption of the crosslinked CMC template for Pb(II) is prior to Cu(II), while only Cu(II) ions was adsorbed selectively on CMC at pH 6 in acetate solution. From the results of selectivity coefficient (K), it can be seen that $K_{\mathrm{Pb}^{2+}/\mathrm{Cu}^{2+}}$ and $K_{\mathrm{Pb}^{2+}/\mathrm{Zn}^{2+}}$ of CMC has been improved 15- and 41-fold, respectively, after treated. In addition, both CMC and the crosslinked CMC template have a good adsorption capacity for Cu(II) ions, on the contrary, hardly adsorb Zn(II) ions. The results further suggest that the crosslinked CMC template can selectively recognize Pb(II) ions, and it is concluded that a selective separation of Cu(II), Zn(II) and Pb(II) could be affected by using an appropriate adsorbent.

Table 2
Adsorption selectivity of CMC with DS of 0.85 (a) and the crosslinked CMC template with the –CHO/–NH_2 ratio of 0.51 (b) for Pb(II)–Cu(II)–Zn(II) acetate solution

Adsorbents	Adsorption capacities (mmol/g)			Selectivity coefficient (K)	
	Cu(II)	Zn(II)	Pb(II)	$K_{\mathrm{Pb}^{2+}/\mathrm{Cu}^{2+}}$	$K_{\mathrm{Pb}^{2+}/\mathrm{Zn}^{2+}}$
a	1.88	0.30	0.15	0.08	0.5
b	1.69	0.10	2.08	1.23	20.8

3.2.4. Reusability

The reusability of the crosslinked CMC template in Pb(II) adsorption is also investigated in this study (the data of adsorption capacities after reuse for 10 times are shown in Fig. 5). It is observed that the adsorption capacities of Pb(II) ions decrease slightly from 1.89 to 1.71 mmol/g with increasing the times of the reuse, and the adsorption capacity for Pb(II) ions is quite higher after reuse for 10 times, which indicates that the crosskinked CMC template has a good reusability.

3.3. Adsorption mechanism of the crosslinked CMC template for Pb(II) ions

3.3.1. FTIR analysis

The FTIR spectra of CMC with DS of 0.85 (a) and the crosslinked CMC template (b) before and after Pb(II) adsorption are shown in Fig. 6. In general, from Fig. 6a and b, it is observed that the changes of the crosslinked CMC template before and after Pb(II) adsorption are quite similar with those of CMC before and after Pb(II) adsorption, indicating that the mechanisms for Pb(II) of the two types of adsorbents are essentially the same. The major alterations are: (1) The absorb bands of C=O stretching vibration disappear, and the bands of the N–H bending vibration shift to 1588 cm^{-1}, resulting from a steric effect for bending vibration of the N–H bond after coordinating. (2) The absorb bands at 1411 cm^{-1}, corresponding to the stretching vibration of –COO, strengthen and shift to lower wave number, which suggest that the carboxymethyl group of the polymers participate in the coordination. (3) The absorb bands at 1070 cm^{-1}, associated with the stretching of the secondary –C–OH, have a

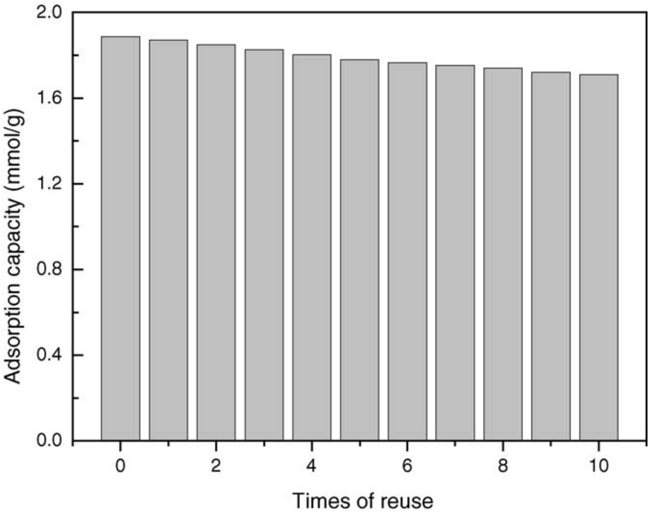


Fig. 5. Relationship between the times of reuse and adsorption capacity of the crosslinked CMC template for Pb(II) ions (0.10 g of crosslinked CMC template with the –CHO/–NH_2 ratio of 0.51, pH 5.9, shaking 24 h at 25 °C).

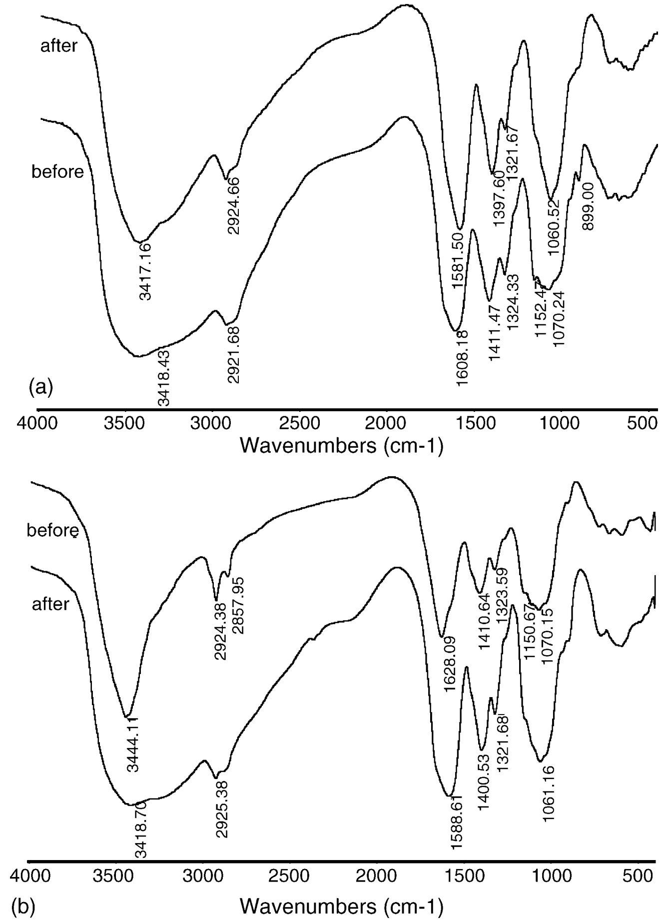


Fig. 6. FTIR spectra of CMC with DS of 0.85 (a) and the crosslinked CMC template with the –CHO/–NH_2 ratio of 0.51 (b) before and after Pb(II) adsorption.

Table 3
Binding energies (BE) of O 1s, N 1s, Pb $4f_{5/2}$ and Pb $4f_{7/2}$ obtained from the XPS spectra of CMC with DS of 0.85 before (a) and after (b) Pb(II) adsorption, the crosslinked CMC template with the –CHO/–NH_2 ratio of 0.51 before (c) and after (d) Pb(II) adsorption

Samples	Binding energies (BE)			
	Pb $4f_{7/2}$	Pb $4f_{5/2}$	O 1s	N 1s
a	–	–	531.1	398.1
b	137.5	142.5	531.4	398.4
c	–	–	532.0	398.7
d	137.6	142.7	531.7	398.6
$Pb(Ac)_2{\cdot}H_2O$	138.5	143.2	531.3	–

significantly downward shift, and the intensity become stronger. (4) The absorb bands at 1152 cm^{-1} corresponding to the stretching of C–N bond weaken and shifted to higher wave number, which indicates the formation of N–Pb bond in the adsorption process. These results indicate that the O and N atoms in the crosslinked CMC template or CMC participated in coordination with Pb(II).

Moreover, it is can be seen that after CMC adsorbed Pb(II) ions, the wide peaks at 3418 cm^{-1}, corresponding to the stretching vibration of –NH_2 group and –OH group, narrowed significantly, and the bands at 2922 and 2857 cm^{-1} strengthened (Fig. 6a). In contrast, after the crosslinked CMC template adsorbed Pb(II) ions, these peaks widened and weakened evidently (Fig. 6b). This obvious difference in the FTIR spectra between CMC and the crosslinked CMC template before and after Pb(II) adsorption is due to the crosslinking reaction. From the FTIR spectra analysis, it can be concluded that the carboxymethyl group, amino group, and the secondary hydroxyl group participate in the adsorption process.

3.3.2. XPS analysis

To further verify the findings from the FTIR spectra, XPS were employed. Table 3 shows the XPS data of O 1s, N 1s, Pb $4f_{7/2}$ and Pb $4f_{5/2}$ of CMC with DS of 0.85 and the crosslinked CMC template before and after Pb(II) adsorption. Comparison of the Pb 4f XPS data of b and d with that of $Pb(Ac)_2$ indicates that the BEs of Pb $4f_{7/2,5/2}$ electron shifted from 138.5 and 143.2 eV to 137.5 and 142.5 eV, 137.6 and 142.7 eV, respectively. It is noticeable that the BEs of Pb $4f_{7/2,5/2}$ electron had quite a large shift towards to the lower energy region, which is 1.0 and 0.7 eV, 0.9 and 0.5 eV, respectively. These downward shifts may be explained as the increase in the electronic density around Pb(II) resulting from the electron receiving from the other atoms in the crosslinked CMC template or CMC units, which provides evidence to the chelation between the crosslinked CMC template or CMC and Pb(II) ions during the adsorption process as well.

After CMC adsorbed Pb(II) ions, the BEs of O 1s and N 1s electron were found to be 0.3 and 0.3 eV higher than those of O 1s and N 1s electron before adsorption, respectively. Accordingly, these upward shifts may be explained as the decreases in the electronic density around O and N atoms resulting from the electron draining to Pb(II) [19]. XPS results indicate that the Pb(II)–O and Pb(II)–N coordinate bonds were formed in Pb(II) adsorption onto CMC, which is in good agreement with the FTIR results. On the contrary, after the crosslinked CMC template adsorbed Pb(II) ions, the BEs of O 1s and N 1s electron were found to be 0.3 and 0.1 eV lower than those of O 1s and N 1s electron before adsorption, respectively. The reason is unknown, but it is sure that the phenomena is related to the crosslinked reaction and the formation of cavity tailored to volumetric space of Pb(II) ions.

4. Conclusions

As a result of preparation of the crosslinked CMC template using CMC with DS of 0.85, it was found that the optimum pH value 5.0–6.0, the appropriate ratio of aldehyde/amino of 0.51 to obtained maximum adsorption capacities for Pb(II) ions. In the study of the adsorption properties, it was found the crosslinked CMC template has high adsorption capacities for Pb(II) ions in solution containing single metal ions or three metals ions. Furthermore, although the adsorption capacities for Cu(II), Co(II), Ni(II), Zn(II) decreased as compared to those of CMC, the selectivity was greatly increased, and the crosslinked CMC template selectively adsorb Pb(II) ions from the mixture solution of Pb(II)–Cu(II)–Zn(II), which provides an effective way to separate Cu(II), Zn(II) and Pb(II) ions selectively. It was also found that the crosslinked CMC template has good reusability and adsorption capacities for Pb(II) ions after reuse of 10 times. The FTIR spectra and XPS data revealed that the sorption of CMC and the crosslinked CMC template for Pb(II) was a chelate process through both oxygen and nitrogen atoms coordinated with Pb(II) in the polymer chain.

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