Adsorption of lead using a novel xanthated carboxymethyl chitosan

Qingping Song, Chongxia Wang, Ze Zhang and Jiangang Gao

ABSTRACT

Adsorption of Pb(II) was studied using a novel xanthated carboxymethyl chitosan (XCC). The XCC was synthesized using the xanthation reaction of N-carboxymethyl chitosan (NCMC). The chemical structure of XCC was characterized by UV-visible spectra. The effects of initial pH value of the solutions, contact time and adsorption isotherms on adsorption of Pb(II) were investigated. Moreover, the possible adsorption mechanism was identified using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The experimental results showed XCC experienced a high adsorption capacity. The adsorption isotherm followed the Langmuir model. The maximum adsorption capacity obtained from the Langmuir model was 520.8 mg/g. Thermodynamic studies revealed a spontaneous and exothermic adsorption process. FTIR and XPS studies showed that the carboxyl groups, nitrogen atoms and sulfur atoms participated in the adsorption of Pb(II).

Key words | adsorption, chitosan, lead, xanthated chitosan

INTRODUCTION

Many industries discharge heavy metals such as lead, cadmium and nickel in their waste waters. Among the heavy metal ions, lead ion is one of the most toxic heavy metals and it is widespread in air, water and soil. Today, several methods have been developed for removing heavy metal in aqueous solution including chemical precipitation, adsorption, and ion-exchange method. Among the applicable methods, adsorption is now recognized as an effective, efficient and economic method for heavy metal removal from wastewater (Demirbas 2008).

In particular, chitosan (CTS) has received a lot of attention for heavy metals removal because of its excellent metal-binding capacities and low cost. Chitosan is the N-deacetylated derivative of chitin, which is widely spread in crustaceous shells, insects, and fungal cell walls. Chitosan has many hydroxyl and amino groups that can chelate heavy metal ions. Therefore, CTS presents as a very promising starting material for chelating metals (Varma et al. 2004). In addition, the amino and two hydroxyl groups on each glucosamine in the repeating unit of CTS can act as reactive site for chemical modification. In order to increase the adsorption ability of CTS and to improve the adsorption selectivity of metal ions, a great number of CTS derivatives has been obtained by introducing new functional groups on the CTS backbone (Jayakumar et al. 2010). Among all the CTS derivatives, N-carboxymethyl chitosan (NCMC) was reported to enhance heavy metal adsorption capacity compared to CTS (An et al. 2009). The structure of NCMC may also be related to the well-known chelating agent EDTA (ethylenediaminetetraacetic acid); the sequence of N-C-C-O permits formation of a stable pentaatomic rings with heavy metals (Wang & Song 2012).

Sulfur compounds are very efficient at chelating metals because sulfur has a very strong affinity for most heavy metals. Xanthation of carbohydrate materials, particularly CTS, has been reported for removal of metals from aqueous solutions (Chauhan et al. 2012). Xanthated CTS derivative was prepared by reaction of CTS with CS₂ under alkaline conditions in a heterogeneous reaction (Sankararamakrishnan & Sanghi 2006). This material has strong metal chelating capability due to presence of the xanthate groups in the CTS chain (Chauhan & Sankararamakrishnan 2008; Sankararamakrishnan et al. 2007). However, xanthation of CTS was prepared in heterogeneous reaction because CTS is insoluble in water; therefore reaction times of 24 h were required for complete reaction due to low activity.

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In this paper, a novel xanthated carboxymethyl chitosan (XCC) was synthesized by reaction of water-soluble NCMC derivatives and CS$_2$ via a homogeneous reaction. Using this method, the reaction time of xanthation was greatly shortened. Since the carboxyl group and xanthate groups were both introduced into the bone of CTS, the adsorption ability of XCC towards heavy metals was greatly improved. Its chemical structure was characterized by UV–visible (UV–vis) spectra and a series of batch adsorption experiments were conducted to evaluate the adsorption performance of lead ions onto the XCC. In addition, the possible adsorption mechanism was identified using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

**MATERIALS AND METHODS**

**Materials**

Chitosan (93% deacetylated) was obtained from Jinhu Biochemistry Co. Ltd (Shandong, China). All other chemicals and reagents were of analytical grade and used without purification. Metal ion solutions were prepared from analytical-grade metal salt of Pb(NO$_3$)$_2$ with distilled water.

**Synthesis of XCC**

The synthesis of XCC was composed of two steps, and the reaction can be represented in Figure 1. The first step was preparation of NCMC and the second step was the introduction of the xanthate group to the NCMC through a chemical reaction with CS$_2$ in basic conditions. The NCMC derivative was synthesized according to previous work (Song et al. 2014). Briefly, chloroacetic acid (8.0 g) was dissolved in 70 mL distilled water and the solution was adjusted to pH 7.0 with NaOH (3.17 g) dissolved in 30 mL distilled water, then CTS (2.0 g) was introduced into the solution. The reaction mixture was heated to 90°C with vigorous stirring and maintained for 4 h to react. During this process, the pH value of the reactant system was controlled at 7.0 by dropping in 20% Na$_2$CO$_3$ to neutralize HCl with an interval of 30 min. After, the solution was cooled to room temperature and 95% ethyl alcohol (200 mL) was added to precipitate out the product. The precipitate was filtered, sequentially washed with 90% ethyl alcohol twice and 100% ethyl alcohol once. This product is referred to as NCMC.

NCMC was added into 50 mL of 14% NaOH solution to swell and alkalize at room temperature for 1 h. Further, 2 mL of CS$_2$ was added into the reaction and stirred at room temperature for 3 h. The solution was adjusted to pH 8.0 by addition of HOAc, then stopped by adding 70% ethyl alcohol (200 mL). The solid was filtered and rinsed in 70–100% ethyl alcohol to desalt and dewater, and vacuum dried at room temperature for 24 h to give the final yellow product.

**Characterization of xanthated carboxymethyl CTS**

The UV–vis spectra of the samples were obtained on a UV–vis spectrophotometer (UV-2550, Shimadzu). FTIR spectroscopy for the XCC was carried out using the KBr disk technique using an FTIR spectrometer, model Equinox55 (Bruke). X-ray photoelectron spectra of XCC before and after Pb(II) adsorption were obtained by using an Escalab 250 XPS spectrometer (Thermo-VG Scientific).

**Adsorption experiments**

Adsorption experiments were conducted in a 50 mL conical flask. One hundred milligrams of adsorbent was added into 50 mL of an aqueous solution containing Pb(II) (0.01 mol/L). After stirring at a defined time (5–180 min), the mixture was filtered. The final metal ion concentrations were measured on a Ruili WFX-110 atomic absorption spectrophotometer. The adsorption capacity of adsorbent was calculated according to the following equation:

$$q = \frac{V(C_0 - C_f)}{m}$$  \hspace{1cm} (1)

where $q$ is the adsorption capacity (mg/g), $C_0$ and $C_f$ are the initial and final concentrations of Pb(II) (mg/L) respectively.
$V$ is the volume of the Pb(II) solution (L) and $m$ is the mass of adsorbent (g).

The effect of initial pH on the adsorption capacity of XCC for Pb(II) was studied by varying pH value from 2.0 to 5.5 at the sorbent dosage of 100 mg/50 mL at 25°C for 60 min. The pH of the initial 50 mL solution of Pb(II) was adjusted to the required pH value using appropriate concentrations of HCl or NaOH solutions. Different contact times (5–180 min) were studied using different Pb(II) concentrations (0.006, 0.008 and 0.01 mol/L) with 100 mg XCC. The experiments were controlled at pH 5.5 and room temperature.

Adsorption isotherm studies were conducted for 180 min with shaking to reach adsorption equilibrium by varying the initial Pb(II) concentration from 0.005 to 0.01 mol/L. The initial pH value was adjusted to 5.5 and the adsorption temperature varied from 298 to 318 K.

RESULTS AND DISCUSSION

Characterization of adsorbent

The structure of XCC was confirmed by UV–vis spectra of the samples. Figure 2 shows the UV–vis spectra of CTS in 0.01 M hydrochloric acid solution and XCC derivative. In the UV spectrum of CTS, an absorption band appeared at 207 nm, which showed the presence of acetyl groups (Wu & Zivanovic 2013). However, in the UV spectrum of XCC in aqueous solution, two new absorption bands appeared at 256 and 297 nm, which were attributed to $\pi-\pi^*$ of C=S and $n-\pi^*$ S=C=S respectively, indicating that the xanthate groups were introduced onto the CTS bone. Additionally, these two new absorption bands disappeared in the UV spectrum of XCC in 0.01 M hydrochloric acid solution, indicating that the xanthate group is known to be unstable in acid solution. This was consistent with previous results (Kim et al. 1999).

Effect of pH

The effect of initial solution pH on Pb(II) removal by XCC is shown in Figure 3(a). As indicated in Figure 3(a), the pH of the aqueous solution was clearly an important parameter that controlled the adsorption process. Within the range of pH values from 2.0 to 3.0, the adsorption capacity significantly increased from 352.3 to 486.9 mg/g. With further increase of pH (3.0–5.5), the adsorption capacity of Pb(II) gradually reached the maximum of 517.9 mg/g at pH 5.5.

In acidic medium, adsorption capacity of XCC decreased due to the protonation of amino group, carboxyl group and xanthate group, which inhibits the chelating interaction between Pb(II) and functional groups. Moreover, the number of positively charged surface sites in XCC increased, which did not favor the adsorption of positively charged metal cations, due to electrostatic repulsion (Zhang & Wang 2010). With increase in pH, the surface functional groups of XCC will be deprotonated to some extent and will tend to suppress the positive charging or even transfer.

Figure 3 | (a) Effects of pH and (b) contact time on adsorption of Pb(II) on XCC.

Figure 2 | UV-vis spectra of chitosan and XCC.
to the negatively charged state, which will be helpful for the electrical attraction and uptake for the lead cation (Huang & Zhu 2012).

Effect of contact time

The effect of contact time on the adsorption of XCC for Pb(II) was investigated at different initial solute concentrations and the results are shown in Figure 3(b). The rates of adsorption of Pb(II) on XCC were seen to increase markedly during the first 60 min and to gradually approach the limiting adsorption after 180 min.

Adsorption isotherms

The adsorption isotherm model describes the interaction of adsorbate with adsorbents and is important for predicting adsorption performance of the adsorbent. Two of the most commonly used isotherm theories have been adopted in this work, namely Langmuir and Freundlich. The linear form of the Langmuir isotherm is given by:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \]  
where \( q_e \) and \( C_e \) are the amount adsorbed (mg/g) and the adsorbate concentration on solution (mg/L), both at equilibrium; \( K_L \) (L/mg) is the Langmuir constant related to the energy of adsorption; and \( q_m \) (mg/g) is the maximum adsorption capacity for monolayer formation on adsorbent.

The linearized Freundlich form is:

\[ \ln q_e = \frac{1}{n} \ln C_e + \ln K_F \]
where \( K_F \) and \( n \) are the Freundlich constants, which are related to adsorption capacity and intensity (mg/g), respectively. Values of \( K_F \) and \( n \) can be calculated from a linear plot of \( \ln q_e \) versus \( \ln C_e \).

The adsorption isotherms of Pb(II) onto XCC at different temperatures ranging from 298 to 318 K are illustrated in Figure 4. It is obviously seen that the increase in temperature from 298 to 318 K decreases the adsorption. These results confirm the exothermic nature of the adsorption process. The model parameters obtained by applying Langmuir and Freundlich models to the experimental data are given in Table 1. Comparing their linear correlation coefficients, it can be concluded that the Langmuir isotherm represents a better fit of experimental data than the Freundlich model. In addition, the Langmuir constant \( K_L \) indicates the adsorption affinity of the metal ions for the adsorbent. High value of \( K_L \) indicates a much stronger affinity of metal ion adsorption. It is obvious that XCC had the highest \( K_L \) values at 298 K, which is consistent with the \( q_m \) obtained by Langmuir model.

| Table 1 | Parameters for Pb(II) adsorption according to the Langmuir and Freundlich isotherms |
|---------|---------------------------------|---------------------------------|-------------------------------|-------------------------------|-----------------|
|        | Langmuir                        | Freundlich                      |                               |                               |                 |
| \( T \) (K) | \( Q_m \) (mg/g) | \( K_L \) (L/mg) | \( R^2 \) | \( K_F \) (mg/g) | \( n \) | \( R^2 \) |
| 298     | 520.8                           | 0.06092                         | 0.999                         | 423.9                         | 36.7            | 0.866        |
| 308     | 518.1                           | 0.05463                         | 0.999                         | 399.2                         | 28.5            | 0.950        |
| 318     | 507.6                           | 0.05091                         | 0.999                         | 396.3                         | 30.5            | 0.887        |

Thermodynamic study

The free energy change (\( \Delta G^\circ \)), enthalpy change (\( \Delta H^\circ \)) and entropy change (\( \Delta S^\circ \)) for the adsorption process were calculated using the following equations (Liu 2009; Wang & Wang 2010):

\[ \Delta G^\circ = -RT \ln K_L \]

[4]

\[ \ln K_L = - \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]

[5]

where \( \Delta H^\circ \) (J mol\(^{-1}\)) and \( \Delta S^\circ \) (J mol\(^{-1}\) K\(^{-1}\)) are enthalpy and entropy changes, respectively, \( R \) is the universal gas constant.
constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \(T\) is the absolute temperature (K). Plotting \(\ln K_c\) against \(1/T\) gives a straight line with slope and intercept equal to \(-\Delta H / R\) and \(\Delta S / R\), respectively. The values of these parameters are summarized in Table 2. The negative values for the Gibbs free energy confirmed the process of the adsorption was spontaneous in nature. The negative value of \(\Delta H\) (\(-7.103\) kJ mol\(^{-1}\)) indicated that the adsorption was an exothermic process. The reason can be attributed to the formation of stable covalent bonding between XCC and Pb(II). Further, the positive value of \(\Delta S\) reflects good affinity of the XCC towards Pb(II) ions and the increasing randomness at the solid–solution interface during the adsorption process (Liu et al. 2012).

### Adsorption mechanism of Pb(II) on XCC

To elucidate the mechanism, the surface interactions involved in the adsorption process were examined. FTIR spectra have been a useful tool in identifying the existence of functional groups in a molecule as each specific chemical bond often shows a unique energy absorption band. Figure 5 shows the FTIR spectra of XCC before and after Pb(II) adsorption. After adsorption, the absorption bands at 1,601 and 1,406 cm\(^{-1}\) assigned to the asymmetric and symmetric stretching of COO\(^-\) groups in XCC decreased to 1,583 and 1,385 cm\(^{-1}\), respectively (Lv et al. 2009; Wang & Song 2012). Such shifts indicate that the COO\(^-\) groups of XCC are involved in the co-ordination with Pb(II). The adsorption bands of 3,450 and 1,317 cm\(^{-1}\) corresponding to the N–H stretching vibration and C–N stretching vibration (Li & Bai 2005), respectively, shifted to 3,425 cm\(^{-1}\) and disappeared completely, which indicated that the amino groups were involved in the adsorption. Moreover, the absorption band at 1,063 cm\(^{-1}\) attributed to C–S and S–C–S symmetric stretching (Sankararamakrishnan & Sanghi 2006), which was overlapped with C–OH stretching vibration, shifted to 1,045 cm\(^{-1}\) after adsorption, indicating that the xanthate groups of XCC participate in the adsorption process.

To verify the findings from the FTIR spectra, XPS analysis was used to determine the chemical states of the functional groups on the XCC surface before and after Pb(II) adsorption. The XPS spectra of C 1s and O1s before and after adsorption of Pb(II) did not show any noticeable change after Pb(II) adsorption, indicating that these atoms are not involved in the chemical adsorption of Pb(II). But the computer deconvolution XPS spectra of N 1s and S 2p showed significant changes, which are shown in Figure 6.

The computer deconvolution XPS spectrum of S 2p showed two peaks before Pb(II) adsorption at the binding energy of 161.5 and 167.9 eV, corresponding to C–S and C = S, respectively (Chen & Wang 2012). However, after adsorption, two peaks at 162.4 and 168.2 eV were observed for Pb(II), respectively. Chemical shifts are considered significant when they exceed 0.5 eV (Hasan et al. 2006). This phenomenon can be attributed to the formation of S = C–S–Pb(II) complexes, in which a lone pair of electrons in the sulfur atom was donated to the shared bond between the S and Pb(II) (Liang et al. 2009). So the XPS spectra provided evidence of metal binding to sulfur atoms.

The computer deconvolution XPS spectrum of N 1s showed binding energy increased from 399.2 eV to 399.9 eV after adsorption of Pb(II), suggesting the formation of a –NH\(_2\)–Pb(II) complex in which a lone pair of electrons in the nitrogen atom is shared between the N and Pb(II).

Therefore, the FTIR and XPS of XCC spectra before and after adsorption of Pb(II) provided evidence that the mechanism of Pb(II) adsorption is mainly through the formation of coordination bonds with the COO\(^-\) groups, nitrogen atoms and sulfur atoms in XCC. The complexation adsorption of Pb(II) on XCC can be described as follows (Figure 7).

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Thermodynamic parameters for the adsorption of Pb(II) ions by XCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(K)</td>
<td>(\Delta G) (kJ mol(^{-1}))</td>
</tr>
<tr>
<td>298</td>
<td>(-23.392)</td>
</tr>
<tr>
<td>308</td>
<td>(-23.901)</td>
</tr>
<tr>
<td>318</td>
<td>(-24.487)</td>
</tr>
</tbody>
</table>

Figure 5 | FTIR spectra of XCC before and after adsorption of Pb(II).
CONCLUSIONS

An efficient and novel chelating agent with xanthate groups and carboxyl groups in CTS has been successfully synthesized via two common reactions. The ability of XCC to remove Pb(II) was studied. The data demonstrated that the biomaterials can be effective adsorbents for the removal of Pb(II) from aqueous solution. The equilibrium data were well described by the Langmuir isotherm equations. FTIR and XPS spectral analysis inferred that the COO⁻ groups, and nitrogen and sulfur atoms on XCC were involved in complexation with Pb(II).

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