Investigation of adsorption capacity of \textit{N}-carboxymethyl chitosan for Pb(II) ions

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ABSTRACT

\textit{N}-carboxymethyl chitosan (NCMC) was prepared by reacting chitosan (CTS) with chloroacetic acid and characterized by $^{13}$C-NMR spectroscopy to confirm that carboxymethylation occurred only in the amino groups. The adsorption properties of CTS, NCMC and O-carboxymethyl chitosan (OCMC) towards Pb(II) ions were evaluated and the order of the adsorption capacity was as follows: NCMC > OCMC > CTS. The effects of initial pH value (2.0–5.5) of the solutions and contact time (5–120 min) on adsorption of Pb(II) were investigated and the kinetic data were evaluated using the pseudo-first-order and pseudo-second-order models. Kinetics study showed that the adsorption process followed second-order kinetics rather than the first-order one. Furthermore, the experimental equilibrium data of Pb(II) on the NCMC were analyzed using the Langmuir and Freundlich isotherm models and the results indicated that the Langmuir model gave a better fit than the Freundlich equation and the maximum adsorption capacity obtained from the Langmuir model was 421.9 mg $g^{-1}$.

Key words | adsorption, isotherm, kinetics, lead(II) ions, \textit{N}-carboxymethyl chitosan

INTRODUCTION

Chitosan (CTS) is a nitrogenous polysaccharide obtained by deacetylating chitin. Since it has hydroxyl and amino groups that can serve as chelating sites, chitosan was widely used in wastewater treatment especially to remove heavy metal ions (Varma et al. 2004; Guibal et al. 2006). However, the adsorption ability of chitosan has not been realized to a satisfying level. In recent years, attention has been focused on the modification of chitosan to improve its adsorption ability and there are various types of modified methods such as xanthated chitosan (Chauhan & Sankararamakrishnan 2008), chitosan composites and crosslinked chitosan (Wang & Wang 2010; Li et al. 2012).

Among the various chitosan derivatives, carboxymethyl chitosan (CMC) is the most important kind due to its better solubility in water. According to the substitution position of carboxymethyl groups, CMC can be divided into \textit{O}-carboxymethyl chitosan (OCMC), \textit{N}, \textit{O}-carboxymethyl chitosan (N, O-CMC) and \textit{N}-carboxymethyl chitosan (NCMC). OCMC and N, O-CMC can be prepared by reacting chitosan with chloroacetic acid in isopropyl alcohol as a solvent (Wasikiewicz et al. 2005; Sun et al. 2006b). However, the traditional method for the preparation of NCMC consists of reacting free amino groups of chitosan with glyoxylic acid to produce a soluble aldimine and then reduction of the aldimine product with sodium borohydride (Jayakumar et al. 2010). This method, however, involves using a relatively expensive reagent of glyoxylic acid and a two-step reaction, which may restrict the applications of NCMC to some extent. In our previous work (Song et al. 2011), NCMC could be achieved directly from chitosan with chloroacetic acid instead of expensive glyoxylic acid. The method is relatively simple and the process control is easy. Although there are a few literatures concerning the application of NCMC in adsorption fields (Muzzarelli et al. 1982; Ngah & Liang 1999; Wang & Song 2002), few publications focus on the Pb(II) adsorption on NCMC or comparing the adsorption ability of NCMC and OCMC to the best of our knowledge.

In this study NCMC was prepared for the removal of Pb(II) metal ions from aqueous solutions. The adsorption properties of Pb(II) on CTS, OCMC and NCMC were determined, compared with each other and the influence of experimental parameters was subsequently studied. At last, the possible adsorption mechanism was identified using Fourier transform infrared spectroscopy (FTIR).
MATERIALS AND METHODS

Materials

Chitosan, with a degree of deacetylation (DD) calculated to be 93% by $^1$H-NMR, was purchased from Qingdao Jinhu Biochemistry Co., Ltd (Shandong Province, China). Pb(II) ions solutions were prepared from analytical grade metal salts [Pb(NO$_3$)$_2$] with distilled water; other chemicals were analytical grade and directly used without further purification.

Preparation of NCMC and OCMC

The NCMC derivatives were synthesized according to our method with some modification (Song et al. 2011). Briefly, NaOH (3.17 g) was dissolved in 30 mL of distilled water to be used as a pH adjuster. Chloroacetic acid (7.5 g) was dissolved in 70 mL of distilled water and the pH value of the resulting solution was adjusted to 7.0 with the above solution of NaOH. Then chitosan (1.5 g) was introduced into the above resulting solution. The reaction mixture was heated to 90 °C with vigorous stirring and maintained for 4 h to react. During this process, pH value of the reactant system was controlled at 7.0 by dropping 20% Na$_2$CO$_3$ to absorb HCl with an interval of 60 min. After the reaction was stopped by adding 200 mL of 95% ethanol, the desired product was precipitated and filtered, desalted and dewatered twice by rinsing with 90% ethanol and absolute ethanol, and then dried under vacuum. Therefore, the NCMC products exist in the form of sodium salt. To compare the adsorption ability of NCMC and OCMC, OCMC was prepared following the method described in the literature (Chen & Park 2003).

Characterization of samples

$^{13}$C-NMR spectrum of NCMC was recorded on a Bruker Avance-300 NMR spectrometer using D$_2$O as solvent. FTIR spectra were obtained with a Bruker Equinox55 FT-IR spectrophotometer in KBr pellets to characterize the NCMC samples before and after Pb(II) adsorption.

Adsorption experiments

To determine the adsorption abilities of NCMC toward Pb(II) ions, 100 mg of adsorbent was added into 50 mL of an aqueous solution containing Pb(II) (0.01 mol L$^{-1}$) then stirred for a given time and filtered. The temperature was controlled to 25 °C and the final metal ion concentrations were determined by atomic absorption spectrophotometer. The adsorption capacity of adsorbent was calculated according to the following equation:

$$ Q = \frac{V(C_0 - C_f)}{m} $$

where $Q$ is the adsorption capacity (mg g$^{-1}$), $C_0$ and $C_f$ are the initial and final concentrations of Pb(II) (mg L$^{-1}$) respectively, $V$ is the volume of the Pb(II) solution (L) and $m$ is the mass of adsorbent (g).

In order to compare the adsorption properties of different adsorbents for Pb(II), experiments were performed by placing 100 mg of CTS, OCMC or NCMC into flasks containing 50 mL of Pb(II) solution (0.01 mol L$^{-1}$). The flasks were then agitated on a shaker at 250 rpm for different contact times (5–120 min) while keeping the temperature at 25 °C.

To analyze the effect of pH value on adsorption of Pb(II), the pH of initial Pb(II) solutions was adjusted to different values of 2.0, 3.0, 4.0, 4.6, 5.0, and 5.5 with aqueous solution of HCl (0.1 mol L$^{-1}$) and NaOH (0.1 mol L$^{-1}$), whereafter 100 mg of adsorbent NCMC was added into 50 mL of the above Pb(II) solutions (0.01 mol L$^{-1}$), then the mixtures were all filtered after stirring for 30 min at 25 °C.

The adsorption kinetics was studied by shaking a mixture of 100 mg of adsorbent and 50 mL of Pb(II) solution (pH 5.5) at 25 °C. The initial concentration of Pb(II) ion solution was 0.01 mol L$^{-1}$. At different time intervals, the precipitates of adsorbent and ions were filtrated and the residual Pb(II) ion concentrations were determined.

Adsorption isotherm studies were conducted for 120 min with shaking to reach adsorption equilibrium at six different initial Pb(II) ion concentrations, viz: 0.005, 0.006, 0.007, 0.008, 0.009, 0.01 mol/L. The initial pH value was adjusted to 5.5 and the adsorption temperature varied from 25 to 45 °C.

RESULTS AND DISCUSSION

Characterization of NCMC

Actually, NCMC could hardly be obtained from the direct alkylation of chitosan with chloroacetic acid under strong basic conditions, which would be attributed to low alkylation reaction selectivity between amino and hydroxyl groups. Specifically, since the reactivity of hydroxyl groups (–OH) is higher than that of amino groups (–NH$_2$) in a strong basic environment, the product would be a mixture.
of N, OCMC derivatives with substitution on both the –OH groups of C\textsubscript{6} and C\textsubscript{3} and the –NH\textsubscript{2} groups (Chen & Park 2003). However, in mild alkaline medium, the reaction activity of –NH\textsubscript{2} is significantly higher than that of –OH; therefore carboxymethylation will only take place on –NH\textsubscript{2} groups by controlling reaction conditions.

\(^{13}\text{C}\)-NMR data of NCMC reveal the successful carboxymethylation substituted only on NH\textsubscript{2} groups (Figure 1). The \(^{13}\text{C}\) resonances of NCMC are as follows: C\textsubscript{1} (99.62 ppm), C\textsubscript{2} (60.53 ppm), C\textsubscript{3} (69.99 ppm), C\textsubscript{4} (77.29 ppm), C\textsubscript{5} (74.66 ppm), C\textsubscript{6} (66.99 ppm). In particular, the C7 (–C\textsubscript{a}H\textsubscript{2}COOD) and C8 (–C\textsubscript{a}OOD) signals can be found at 56.19 and 178.9 ppm respectively, which confirms that carboxymethylation occurred on the amino groups (Chen et al. 2003; Miranda et al. 2006; Felicio et al. 2008). That is to say, there are only two peaks of –CH\textsubscript{2}COOD in NCMC, whereas there are five peaks of –CH\textsubscript{2}COOD in N, O-CMC due to three sites (OH-C\textsubscript{3}, OH-C\textsubscript{6}, NH\textsubscript{2}-C\textsubscript{2}) for carboxymethylation.

Adsorption abilities of CTS, OCMC and NCMC toward Pb\textsuperscript{II}]

The adsorption capacity of CTS, OCMC and NCMC was found out by varying contact time in the range of 5–120 min shown in Figure 2. It is clear from Figure 2 that all the adsorbents reached saturated adsorption after 120 min. The maximum adsorption capacities of CTS, OCMC, and NCMC were found to be 111.7, 343.6 and 404.8 mg g\textsuperscript{-1}, respectively. Among the adsorbents, NCMC has a higher adsorption capacity than OCMC, which in turn is higher than that of CTS.

To understand the nature of lead adsorption and identify the possible sites of lead binding to NCMC, FTIR spectra were obtained for NCMC before and after lead adsorption in Figure 3. After adsorption, the asymmetric and symmetric stretching vibrations of carboxylic anions (–COO\textsuperscript{−}) in NCMC shift from 1,591 and 1,408 cm\textsuperscript{-1} to 1,582 and 1,400 cm\textsuperscript{-1}, respectively (Sun et al. 2006a; Patel & Sinha 2009; Lv et al. 2009), which indicates that carboxyl groups are main chelating functional groups for Pb\textsuperscript{II} ions. Although there is the possibility of overlapping between the N-H and the O-H stretching vibrations, the strong broad band at 3,412 cm\textsuperscript{-1} is characteristic of the N-H stretching vibration (Jin & Bai 2002). The significant change from 3,412 to 3,399 cm\textsuperscript{-1} after lead adsorption indicates that the N-H vibration was affected due to lead adsorption. Furthermore, absorption bands at 1,325 and 733 cm\textsuperscript{-1} correspond to –C–N stretching vibration and N-H rocking bands were shifted to 1,329 and 739 cm\textsuperscript{-1} after adsorption (Jin & Bai 2002) indicating that nitrogen atoms are also the main adsorption sites for lead adsorption on NCMC.

In addition, NCMC has a higher adsorption capacity than OCMC; the reason can probably be attributed to the similar molecular structures of NCMC and EDTA, which permit forming a stable penta-atomic ring of metal chelates (see below).
The suggested structure of NCMC after adsorption of Pb(II) ions.

**Effects of pH value on Pb(II) adsorption**

Figure 4 shows the relationship between initial pH value of Pb(II) solutions and the corresponding adsorption capacity of NCMC. As seen from Figure 4, with the pH value of Pb(II) solution increasing from 2.0 to 3.0, the adsorption capacity of NCMC sharply increased from 95.8 to 359.3 mg g\(^{-1}\)/C\(_0\) and then slowly increased from 359.3 to 397.1 mg g\(^{-1}\)/C\(_0\) following a further increase of pH from 3.0 to 5.5. Additionally, the maximum adsorption capacity of 397.1 mg g\(^{-1}\)/C\(_0\) was obtained when initial pH value of solution was 5.5.

The reason for the above tendency may be due to the existence of different forms of NCMC in different pH solutions. In acidic solutions, the carboxyl groups and secondary amino groups will be all protonated, which reduces the number of binding sites available and the forming possibilities of penta-atomic rings for the adsorption. When at a comparatively high pH value, the carboxyl groups exist as –COO\(^-\) anions, which exert a stronger electrostatic attraction for Pb(II). Considering that the metal ions might precipitate as hydroxide, Pb(II) ions start precipitating when the pH value is higher than 5.5 based on the \(K_{sp}\) of Pb(OH)\(_2\) (1.43 \(\times\) 10\(^{-15}\)) (Hao et al. 2012), which will cause inaccurate interpretation of adsorption (Ngah et al. 2002; Xu et al. 2005), so pH value of 5.5 was chosen for further experiments.

**Adsorption kinetics**

The influence of contact time on Pb(II) adsorption on NCMC can be seen from Figure 5(a). The adsorption capacity of NCMC increased rapidly within 5 min, whereas a slight increase from 374.0 to 407.3 mg g\(^{-1}\)/C\(_0\) was noted from 5 to 120 min, meaning that the adsorption almost reached equilibrium. In a word, fast kinetics is the characteristic in adsorption of Pb(II) in the first 5 min and there are two possible explanations. On one hand, the adsorption rate is usually dependent upon the number of available adsorption sites on the adsorbent, and the fast adsorption rate reflects good accessibility of the binding sites to metal ions (Jin & Bai 2002). NCMC possesses lots of functional groups such as amino, hydroxyl and carboxyl groups. On the other hand, the nitrogen atoms in amino groups and –COO\(^-\) groups may have synergistic chelate combinations with Pb(II) ion, which are beneficial to form a stable five-membered chelate ring.

In order to evaluate the mechanism of the adsorption kinetics, two kinds of kinetic models, such as pseudo-first-order and pseudo-second-order models, had been exploited to analyze the experimental data and find out the adsorption mechanism (Kumar et al. 2006). The equations of the two kinetic models are expressed as:

\[
\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t
\]

\[
\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{t}{Q_e}
\]

where \(k_1\) is the pseudo-first-order adsorption rate constant (min\(^{-1}\)) and \(k_2\) is the constant of pseudo-second-order adsorption (g min\(^{-1}\) mg\(^{-1}\)), \(Q_e\) and \(Q_t\) are the amounts of
metal ions adsorbed at equilibrium (mg g\(^{-1}\)) and any time \(t\) (min), respectively. The rate constant \(k_1\) and correlation coefficients were determined by plotting the log(\(Q_e - Q_t\)) against \(t\) and the straight-line plots of \(t/Q_t\) versus \(t\) were used to calculate the rate constant \(k_2\) and other kinetic parameters similarly.

In contrast to the pseudo-first-order model, the pseudo-second-order kinetic model provided a better correlation \((R^2 = 0.999)\) for the Pb(II) adsorption onto NCMC. The linearized form of the pseudo-second-order model is presented in Figure 5(b) and this model provided a rate constant \(k_2\) of 2.92 \(\times 10^{-3}\) g min\(^{-1}\) mg\(^{-1}\). Besides, the \(Q_e\) value was obtained to be 409.8 mg g\(^{-1}\) from the slope of the linear plot of \(t/Q_t\) versus \(t\), and this value was in excellent agreement with the experimental \(Q_e\) value of 407.3 mg g\(^{-1}\), with only a 0.61% deviation. However, the value of \(R^2\) for the pseudo-first-order is low at 0.969. Therefore, these results suggest that the adsorption behavior of NCMC toward Pb(II) can be well described by the pseudo-second-order kinetic model equation. In addition, the results suggest a chemical adsorption mechanism. It is more likely to predict that the adsorption behavior may involve valence forces through sharing of electrons between Pb(II) and adsorbent (Kumar et al. 2006).

Equilibrium adsorption isotherms and thermodynamic study

Equilibrium isotherms can be used to describe the adsorption characteristics and determine the adsorption capacities of metal ions. Two well-known and most commonly used ones are Langmuir and Freundlich isotherms (Liu et al. 2012). In this study, both Langmuir and Freundlich models were used to study the adsorption equilibrium and they can be represented by the following equations:

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_{\text{max}}} + \frac{1}{K_L Q_{\text{max}}}
\]

\[
\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F
\]

where \(C_e\) is the equilibrium concentration (mg L\(^{-1}\)), \(Q_e\) is the adsorbed amount of metal ions (mg g\(^{-1}\)), \(Q_{\text{max}}\) is the maximum adsorption capacity corresponding to complete monolayer coverage (mg g\(^{-1}\)), \(K_L\) is a constant related to the affinity of the binding sites (L mg\(^{-1}\)). The plot of \(C_e/Q_e\) against \(C_e\) gives a straight line with a slope of 1/\(Q_{\text{max}}\) and an intercept of 1/(\(K_L Q_{\text{max}}\)). \(K_F\) and \(n\) are the Freundlich
constants which are related to adsorption capacity and intensity (mg g$^{-1}$), respectively. Freundlich constants $K_F$ and $n$ can be determined from a linear plot of $\ln Q_e$ versus $\ln C_e$.

The calculated results of the Langmuir and Freundlich isotherm constants are listed in Table 1. It was found that the adsorption of Pb(II) on NCMC was well correlated with the Langmuir equation, indicating that the adsorption process was mainly monolayer adsorption. The values of $Q_{\text{max}}$ obtained from the Langmuir isotherm decreased from 421.9 to 406.5 mg g$^{-1}$ when the temperature increased from 298 to 318 K while the values of $K_L$ decreased from 0.01185 to 0.01090 L mg$^{-1}$. This indicates that the Pb(II) adsorption process is exothermic in nature.

The free energy change ($\Delta G$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$) for the desorption process were calculated using the following equations (Liu 2009):

$$\Delta G = -RT \ln K_L$$

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where $\Delta H$ (J mol$^{-1}$) and $\Delta S$ (J mol$^{-1}$ K$^{-1}$) are enthalpy and entropy changes, respectively, $R$ is the universal gas constant (8.314 J mol$^{-1}$ K) and $T$ is the absolute temperature (K). Plotting $\ln K_L$ against $1/T$ gives a straight line with slope and intercept equal to $-\Delta H / R$ and $\Delta S / R$, respectively. The results are also listed in Table 1. The small negative $\Delta H$ (in absolute value) indicates that the adsorption is an exothermic adsorption process with a low heat exchange. The positive value of $\Delta S$ reflects good affinity of the NCMC towards Pb(II) ions and the increasing randomness at the solid-solution interface during the adsorption process (Liu et al. 2012). The increasing randomness also probably arises from the releasing of protons or sodium ions by occupied complexation sites. Thus, the negative values of $\Delta G$ (close to $-20$ kJ/mol) suggest that the process is spontaneous and a chemical adsorption mechanism (Bessbousse et al. 2022). The Langmuir and Freundlich adsorption isotherms of the NCMC towards Pb(II) ions are provided in the Supplementary Material (available online at http://www.iwaponline.com/wst/068/438.pdf).

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