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Effect of carboxyethylation degree on the adsorption capacity of Cu(II) by *N*-(2-carboxyethyl)chitosan from squid pens

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ABSTRACT

Chitosan was prepared by *N*-deacetylation of squid pens β-chitin, and *N*-carboxyethylated chitosan (*N*-CECS) with different degrees of substitution (DS) were synthesized. DS values of *N*-CECS derivatives calculated by ^{1}H nuclear magnetic resonance (NMR) spectroscopy were 0.60, 1.02 and 1.46, respectively. The adsorption capacity of Cu(II) by *N*-CECS correlated well with the DS and pH ranging from 3.2 to 5.8. The maximum Cu(II) adsorption capacity (q_m) of all three *N*-CECS at pH 5.4 was 207.5 mg g^{-1}, which was 1.4-fold higher than that of chitosan. The adsorption equilibrium process was better described by the Langmuir than Freundlich isotherm model. Adsorption of Cu(II) ion onto *N*-CECS followed a pseudo-second order mechanism with chemisorption as the rate-limiting step. In a ternary adsorption system, the adsorption capacity of Cu(II) by *N*-CECS also presented high values, and q_m for Cu(II), Cd(II), and Pb(II) were 150.2, 28.8, and 187.9 mg g^{-1}, respectively.

1. Introduction

Water pollution has become a serious global problem. Contamination of water by heavy metal ions is a serious global ecological and health problem because of the non-biodegradability and toxicity of these ions (Kandile, Mohamed, & Mohamed, 2015; Liu & Bai, 2014; Vieira & Beppu, 2006). For example, high concentrations of copper, used extensively in electrical power plants, cause harmful, acute, and even fatal effects on human beings, other animals, and plants (Mi, Wu, & Lin, 2015; Sun & Wang, 2006; Wu, Liou, Yeh, Mi, & Lin, 2013).

A number of technologies have been investigated for removing heavy metal ions from wastewaters, including chemical precipitation (Fu, Xie, Tang, Wang, & Jiang, 2012), ion exchange (Li, Wang, Yuan, & Fu, 2014), electrodialysis treatment (Gherasim, Křivčíkb, & Mikulášek, 2014), adsorption procedures (Ahmad et al., 2015; Kandile et al., 2015), or a combination of these processes. Comparatively, adsorption is recognized as an extensively used process due to convenience, ease of operation and simplicity of design (Faust & Aly, 1987). Adsorbents can be regenerated for multiple reuses during adsorption process. Conventional activated carbon has been widely used for the removal of heavy metal from wastewater, but is sometimes restricted due to its higher cost (Bansal & Goyal, 2005). In recent years an increasing interest has been focused on biosorbents such as chitosan (Liu & Bai, 2014; Liu, Li, Zhu, Lia, & Kumar, 2014; Mi et al., 2015) and date palm (Ahmad et al., 2012; Ahmad, Rafatullah, Ghazali, Sulaiman, & Hashim, 2011; Vakili, Rafatullah, Salamatinia, et al., 2014) for the treatment of heavy metal removal due to their nontoxicity, biodegradability, and potentially low cost.

Chitin, a linear homopolysaccharide composed of partly deacetylated 2-acetamide-2-deoxy-β-D-glucopyranose units linked by β-(1→4) bonds, occurs abundantly in the biomass (Mathur & Narang, 1990; Muzzarelli, 1988). Most natural chitins have the α-type crystal structure, while the β-type chitin with weak intermolecular hydrogen bonding is mainly present in squid pens (Muzzarelli, 1977). Chitosan (poly-β-1,4-linked glucosamine) is a cationic polysaccharide obtained from alkaline *N*-deacetylation of chitin. Comparing the two, chitosan has more efficient adsorption ability than chitin due to the presence of a large number of free amine ($-NH_2$) functional groups (Vieira & Beppu, 2006).

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Numerous studies have demonstrated chitosan prepared from β-chitin exhibited higher reactivity compared to that of α-chitin (Huang et al., 2015; Kurita, Ishii, Tomita, Nishimura, & Shimoda, 1994). These results suggest that chitosan derived from β-chitin may have potential as a novel functional biopolymer for heavy metal removal.

Various attempts have been made to increase the adsorption performance of chitosan (Monier, Ayad, Wei, & Sarhan, 2010; Nishad, Bhaskarapillai, Velmurugan, & Narasimhan, 2012; Vakili, Rafatullah, Ibrahim, et al., 2014; Varma, Deshpande, & Kennedy, 2004). Carboxyalkylation of chitosan is perhaps the simplest way to allow an enhanced ability for removal of heavy metal ions (Bratskaya, Pestov, Yatluk, & Avramenko, 2009; Zhang et al., 2014). According to their different substitution positions on the carboxyethyl group, carboxyethyl chitosan (CECS) can be divided into three types: *O*-CECS, *N*-CECS, and *N*,*O*-CECS. The number of carboxyethyl groups and substitution positions in the chitosan chain will directly affect the properties of carboxyethyl chitosan (CECS). It was found that CECS could be used as a flocculant in water treatment applications (Bratskaya et al., 2009; Zhang et al., 2014). Other researchers' work using CECS were mainly focused on the structure of the metal complex with CECS, its biological activity, and preparation of biomaterials for medical and pharmaceutical applications (Huang et al., 2015; Skorik et al., 2005; Weng, Romanov, Rooney, & Chen, 2008). *N*-(2-carboxyethyl)chitosan (*N*-CECS), a derivative produced by selective nucleophilic substitution, can be synthesized via a Michael-type 1,4-conjugate addition, or alkylation by halocarboxylic acids in neutral or mild alkaline conditions (Huang et al., 2015). However, to the best of our knowledge, there have been no attempts to evaluate the relationship between the adsorption of heavy metal ions on *N*-CECS and their degrees of carboxyethyl substitution.

In this paper, chitosan was prepared by alkaline *N*-deacetylation of squid pen β-chitin. Three *N*-CECSs with different degrees of substitution (DS) were synthesized to investigate the effect of substituent groups on the ability of *N*-CECS to adsorb Cu(II). Adsorption kinetics and various isotherm models were also evaluated to better understand the adsorption process.

2. Materials and methods

2.1. Chemicals

Squid pens were obtained from Hangzhou Baokai Biochemical Co., Ltd. (Hangzhou, China). 3-Chloropropionic acid, sodium bicarbonate, copper(II) sulfate pentahydrate, cadmium(II) nitrate tetrahydrate, lead(II) nitrate, acetic acid, sodium acetate trihydrate, and glycine were purchased from Aladdin-reagent Co., Ltd. (Shanghai, China). All other chemicals were analytical grade and used without further purification. All water used in extraction and analysis was distilled and deionized.

2.2. Preparation of chitosan from squid pens

The preparation of chitosan from squid pens was carried out using the method described by Huang, Zhao, Hu, Mao, and Mei (2011). Chitosan with >90% degree of deacetylation was prepared from squid pens with a viscosity average-molecular weight of 6.5×10^5 Da.

2.3. Preparation of N-CECS

N-CECS with different DS values was prepared by slightly modifying the method of Huang et al. (2015) and Skorik et al. (2003). Synthesis process of *N*-CECS was shown in Fig. 1. According to Fig. 1, chitosan (2 g) was dissolved in water (140 mL) containing a prescribed amount of 3-chloropropionic acid for 1 h. An equivalent amount of $NaHCO_3$ was added to the dissolved chitosan samples, which were stirred adequately to remove excess CO_2 (pH ~6.5). After stirring at 60 °C for 5–6 h, $NaHCO_3$ (6 g) was added to alkalize the solution and the system was allowed to react until completion. When the reaction was complete, the product was filtered and precipitated in ethanol. The precipitant was subsequently dissolved in water (20 mg mL^{-1}). The product was then dialyzed using a regenerated cellulose tube (Mw cut-off 3500) against distilled water for 3 days, and lyophilized to get purified *N*-CECS. The sample was kept for long storage in a freezer at −20 °C.

2.4. Characterization of N-CECS derivatives

^{1}H nuclear magnetic resonance (NMR) spectra of *N*-CECS were recorded on a Bruker AVANCE III 500 MHz using D_2O as the solvent operating at 25 °C. The DS values were estimated by the integrals of $\delta(-CH_2COOH)$ in the amino group using Eq. (1).

$$\mathrm{DS} = \frac{y + 2z}{x + y + z} \qquad (1)$$

where x corresponds to the mole fraction of glucosamine units, y is the mole fraction of mono-carboxyethylated glucosamine units, and z is the mole fraction of di-carboxyethylated glucosamine units.

Fourier transform infrared (FT-IR) spectra of *N*-CECS and the complex formed by *N*-CECS and Cu(II) after adsorption were obtained using a Bruker FT-IR spectrometer (vertex 70, Bruker Optik GmbH, Ettlingen, Germany).

2.5. Adsorption experiments

To study the adsorption properties, *N*-CECS was shaken with a metal ion solution for 3 h at 200 rpm at 25 °C. The adsorption system contained 40 mmol L^{-1} acetate–acetate buffer solution at pH 5.4, 0.5 g L^{-1} *N*-CECS, and 10 mmol L^{-1} metal ions. After complete adsorption, the adsorbed mixture was separated from its suspension by centrifugation. Metal salts used were copper sulfate for Cu(II), lead nitrate for Pb(II), and cadmium nitrate for Cd(II). The concentrations of Cu(II), Pb(II) and Cd(II) in the supernatant was determined by flame atomic absorption spectroscopy (AAS) (SHIMADZU, AA-6300) at wavelengths of 324.7, 283.3, and 357.9 nm, respectively. Competitive adsorption was investigated with each metal ion at a concentration of 5 mmol L^{-1}.

The effect of pH on the adsorption capacity for Cu(II) was tested by varying the adsorption pH value with a glycine–HCl buffer (pH 2.5) and an acetate–acetate buffer (pH 3.2–5.8). The kinetic adsorption and adsorption equilibrium isotherms were tested at pH 5.4 by varying the adsorption time (0–90 min), initial concentration of metal ions (0–20 mmol L^{-1}). Adsorption capacity was calculated using Eq. (2)

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

where q_e represents the adsorption capacity (mg g^{-1}), C_0 and C_e are the initial and equilibrium Cu(II) concentrations (mg L^{-1}) in solution, respectively, V is the volume of Cu(II) solution (L), and m is the mass (g) of the adsorbent used.

In the adsorption equilibrium isotherm, the Langmuir isotherm model is expressed according to Eq. (3) (Liu et al., 2014; Petrova, Neudachina, Mekhaev, & Pestov, 2014).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (3)$$

where K_L is the Langmuir constant (L mg^{-1}), C_e (mg L^{-1}) is the Cu(II) concentration at equilibrium, q_e is the amount of Cu(II) adsorbed at