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Removal of cadmium from aqueous solution using low molecular weight chitosan derivative

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ABSTRACT

A 2^3 factorial design was used to examine the sorption of Cd^{2+} onto cross-linked low molecular weight chitosan pyruvic acid derivative. Three factors and two levels of solution pH (A) (6.0 or 10.0), temperature (B) (45 or 70 °C) and Cd(II) concentration (C) (1 or 3 mg/L) were considered. Batch mode system was employed with 0.05 g of the sorbent and 25 mL of Cd(II) solution. The efficiency of cadmium removal during an exposition time of 4 h was then evaluated. The factors and their interaction effect on the cadmium removal efficiency followed the order: Cd(II) concentration > solution pH > interaction between solution pH and Cd(II) concentration > interaction between solution pH, temperature and Cd(II) concentration. Langmuir isotherm model was the best isotherm model. The Pseudo second order fitted well the kinetic data. The thermodynamic studies revealed the nature of the cadmium sorption.

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1. Introduction

Water pollution by cadmium is a challenge to environmentalist because of the toxic effect to living organisms. The main sources of cadmium discharge into the environment by waste streams are electroplating, smelting and alloy manufacturing, pigments, plastics, battery mining and refining processes (Benguella & Benaissa, 2002). Cd(II) has been well documented for its harmful effect on living systems (Huang et al., 2013). Cd(II) is known to lead into bone lesions, hypertension, renal disturbances, cancer and lung insufficiency in humans (Sharma, 1995). The main methods for the elimination of cadmium from an aqueous environment include adsorption, chemical precipitation, reverse osmosis and ion exchange, *etc.* (An, Park, & Kim, 2001; Bailey, Olin, Bricka, & Adrian, 1999). Among the aforementioned methods, adsorption has been identified to be simple, effective and economical alternative for elimination of traces of metal, because of the ease and efficiency with which it can be applied for the treatment of wastewater containing heavy metal (Goel, Kadirvelu, Rajagopal, & Garg, 2006; Zhao, Repo, Yin, & Sillanpää, 2013). Chitosan (CS) is one of the most accepted materials for heavy metal removal (Babel & Kurniawan, 2003; Chu, 2002). Regardless of its inexhaustible utilization, the sorption capacity of CS has not been fully appreciated. Currently, the spotlight is on different sorbents with high selectivity and capacities for heavy metals (Rêgo, Cadaval, Dotto, & Pinto, 2013). Chemical modifications of chitosan with carboxylic groups will achieve the aforementioned objectives (Gandhi, Kousalya, Viswanathan, & Meenakshi, 2011; Ravi Kumar, 2000). Carboxymethylation has been acknowledged to be the way forward to improve the sorption capacity of CS for metals (Chen & Park, 2003; Jeon & Höll, 2003; Sun, Wang, & Wang, 2006). Carboxymethylation of chitosan (CMCS) is an approach where carboxyl groups such as glyoxylic acid, levulinic acid, among others is introduced through a Schiff reaction and then reduced with NBH_3CN or $NaBH_4$ (Delben, Stefancich, & Muzzarelli, 1992). *N*-Carboxymethyl chitosan (NCMC) is also known as glycine glucan (Muzzarelli, Tanfani, Emanuelli, & Bolognini, 1985) and is recognized to increase cobalt, copper, nickel, cadmium and lead ions chelation capacity in relation to pristine chitosan as a result of the high content of COOH in the glycine of NCMC (Delben et al., 1992; Muzzarelli, 1986). CMCS has numerous functional groups such as an amino group, a carboxyl group and hydroxyl groups. This enables it to show chelation with various metal ions (Hon & Tang, 2000; Sun et al., 2006). On the other hand, carboxymethyl-chitosan can dissolve in pH ≤ 7, so

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it is imperative to cross-link it with glutaraldehyde to enhance the mechanical strength and chemical resistance (Ngah & Fatinathan, 2008; Wan Ngah, Endud, & Mayanar, 2002).

In our previous work (Boamah et al., 2014), chitosan was degraded into two kinds of low molecular weight chitosan (CS_8 and CS_{11}), modified with pyruvic acid (PA) and then cross-linked with glutaraldehyde (GLA) to obtain CS_8PA-GLA and CS_{11}PA-GLA. The adsorbents were characterized with FTIR. Factorial design was used to evaluate the effect of adsorbent dosage, adsorbent type and lead(II) concentration on the adsorption capacity of CS_8PA-GLA and CS_{11}PA-GLA. The findings indicated that it was easy to modify chitosan with pyruvic acid when molecular weight decreases. Also, CS_8PA-GLA was better than CS_{11}PA-GLA for lead sorption. In this present study, chitosan was degraded into low molecular weight chitosan (CS_8), modified with pyruvic acid (PA) and then cross-linked with glutaraldehyde (GLA) to obtain cross-linked low molecular weight chitosan pyruvic acid derivative (CS_8PA-GLA) for the removal of cadmium. The prepared sorbent was characterized with FTIR, SEM, TG/DSC, XRD and BET methods. Factorial design was used to explore the important parameters such as pH of the solution, temperature (°C) and Cd(II) concentration that affect cadmium sorption. Specifically, full factorial design (2^3) was used to limit the number of actual experiments performed as well as to probe possible interaction between the aforementioned parameters and their effect on the removal of cadmium.

2. Materials and methods

2.1. Materials

Low molecular weight chitosan (CS_8) which is an oligomeric polymerization molecular with 8° of glucosamines (degree of polymerization is 8, polydispersity index (M_w/M_n) is 1.31 and the average Mr is *ca.* 1401 Da) was prepared in accordance with the literature described previously (Boamah et al., 2014; Zhang, 2009), pyruvic acid (PA), glutaraldehyde (GLA) and all other chemicals and reagents were of analytical grade. Distilled water was used to prepare solutions.

2.2. Preparation of low molecular weight chitosan pyruvic acid derivative

CS_8 (1 g) was placed in a flask, and 20 mL of 0.20 M acetic acid was added. Ten drops of acetic acid (99.5%) and 70 mL of methanol were added. Pyruvic acid (2.825 g) dissolved in 10 mL of methanol was added over a period of 5 min at 35 °C. The slurry was stirred for 1 h after which the pH was attuned to 4.5 using NaOH (2 M). $NaBH_4$ (1.5 g) was dropped slowly, and the solution was mechanically stirred for 24 h. Hydrochloric acid (2 M) was used to attune the pH to 4.5. It was evaporated and then filtered by adding anhydrous methanol. Low molecular weight chitosan pyruvic acid derivative was vacuum dried at 30 °C.

2.3. Preparation of cross-linked low molecular weight chitosan pyruvic acid derivative

0.5 g of water-soluble low molecular weight chitosan pyruvic acid derivative was swelled in 20 mL of methanol and 5 drops of acetic acid (99.5%) were added. Glutaraldehyde (GLA) (0.537 g) was dropped slowly and was agitated at 25 °C for a day. The rationale for the cross-link of water-soluble low molecular weight chitosan pyruvic acid derivative with glutaraldehyde was to enhance the resistance of the product against acid, alkali and chemical (Ngah & Fatinathan, 2008; Wan Ngah et al., 2002). Methanol was used to wash the prepared cross-linked low molecular weight chitosan derivative particles through filtration. The cross-linked low molecular weight chitosan pyruvic acid derivative in the form of particles was vacuum dried at 30 °C. The cross-linking of low molecular weight chitosan pyruvic acid derivative with glutaraldehyde is shown in Fig. 1A.

2.4. Characterization

2.4.1. Gel filtration chromatography (GFC)

Changes of molecular weight of chitosan were determined through gel filtration chromatography (GFC) using an RI K-2301 refractive index detector and TSK-GEL G4000 PWXL column (30 cm × 7.5 mm). The solute was eluted with HAc/NH_4Ac buffer solution (pH 4.5) at a flow rate of 0.43 mL/min.

2.4.2. Fourier transform infrared spectroscopy (FTIR)

FTIR (Nicolet Nexus 470) was also used to characterize low molecular weight chitosan (CS_8), low molecular weight chitosan pyruvic acid derivative and cross-linked low molecular weight chitosan pyruvic acid derivative before and after sorption of cadmium. Dried samples were grinded with potassium bromide (KBr) powder and then pressed into pellets for FTIR measurement.

2.4.3. Scanning electron microscope (SEM)

SEM image of cross-linked low molecular weight chitosan pyruvic acid derivative prior to sorption of cadmium was done with a scanning electron microscope (TXL-30ESEM, PHILIPS, Holland). The acceleration voltage was 15.0 kV. Dried sample was coated with gold prior to SEM observation.

2.4.4. Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis

TG and DSC analysis of cross-linked low molecular weight chitosan pyruvic acid derivative was carried out on NETZSCH STA 449 C thermoanalyzer under nitrogen atmosphere from 25 to 600 °C. The measurement was done for 5 to 10 mg dried sample.

2.4.5. X-ray diffraction (XRD) analysis

XRD analysis of cross-linked low molecular weight chitosan pyruvic acid derivative was performed in a Rigaku diffractometer (Shimadu, Japan), in the 2θ range from 5° to 80°. The sample was powdered prior to XRD analysis.

2.4.6. Surface area and average pore size

The surface area and average pore size of cross-linked low molecular weight chitosan pyruvic acid derivative were determined using a Micromeritics ASAP 2010 gas adsorption surface analyzer. Prior to the surface area measurement, the sample was kept in an oven overnight under vacuum at 30 °C.

2.5. Standard Cd(II) solution

Cadmium stock solution (1000 mg/L) was prepared from $CdCl_2{\cdot}2.5H_2O$ (analytical grade). The stock solution was diluted to obtain the desired Cd(II) concentrations. Concentrations prior as well as subsequent to sorption were estimated by Atomic Absorption Spectrometer (AAS) (TAS-986, China).

2.6. Batch experiment

The batch experiment was conducted to establish the parameters that affect the removal of cadmium ions onto cross-linked low molecular weight chitosan pyruvic acid derivative, and to examine combined effect of those parameters using 2^3 factorial design. The factors and their levels were chosen based on preliminary studies and available literature (Goel et al., 2006) and are presented

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