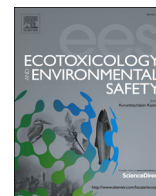




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Sorption of copper onto low molecular weight chitosan derivative from aqueous solution

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ABSTRACT

In this study, sorption of copper onto low molecular weight chitosan derivative was studied. Experimental parameters such as pH of the solution (A), temperature (B), dose of the sorbent (C), and concentration of solution (D) were considered. The statistical results indicated that the dose of sorbent (C) and Cu (II) concentration (D) influenced removal efficiency at 5% significance level. Also, some interactions such as ABCD, ACD, ABC and AC affected the removal process. The sorbent was characterized with FTIR, SEM and TG/DSC. Freundlich isotherm model was the best isotherm model. The kinetic study results correlated well with the pseudo-second-order model. The thermodynamic studies revealed that the nature of copper sorption was spontaneous and endothermic. Strong affinity of the sorbent for copper (II) was revealed by the Isothermal Titration Calorimetry (ITC) technique.

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1. Introduction

Water pollution caused by heavy metal has attracted great attention because of the noxious effect to living things. Among the heavy metal contaminations, literature demonstrates that Cu (II) causes cancer that is detrimental to aqueous fauna (Escoda et al., 2013). Cu (II) is an indispensable nutrient in small quantities but becomes noxious to flora and algae at higher levels (Davila-Rodriguez et al., 2012). Copper ions get into an aqueous environment, as a result of effluents from metal production, fertilizer manufacturing industry, among others (Gupta, 1998).

Numerous techniques have been used to remove copper contamination. Among the techniques, adsorption is a highly economical, and efficient technique for heavy metal ions elimination from an aqueous environment (Ciopec et al., 2012; Liu et al., 2013; Mahvi et al., 2005; Mahvi and Diels, 2004; Rajiv Gandhi and Meenakshi, 2012). Adsorbents such as agricultural wastes (Mahvi, 2008; Varma et al., 2004), chitosan and modified chitosan (Sivakami et al., 2013), among others have been used for the elimination of metal ions in an aquatic environment. Recently, the

focus is on biopolymers because they possess high affinity for metal ions. Among the biopolymers, chitosan (CS) possesses high potential for heavy metal sorption. Chitosan is a good sorbent due to the multifunctional groups such as amino and hydroxyl groups and has been used for the removal of heavy metal (Anirudhan and Rijith, 2009; Wan Ngah et al., 2011, 2012). Regardless of its inexhaustible use, sorption capacity of chitosan has not been adequately explored (Osifo et al., 2008). Currently, the spotlight is on modification of pristine chitosan with functional groups such as carboxybenzyl, carboxymethyl, and alkyl chitosans. The chemical modification process is aimed at improving the sorption performances of chitosan (Kousalya et al., 2010; Kyzas et al., 2013; Muzzarelli et al., 2012). Low molecular weight chitosan pyruvic acid derivative (CS₁₁PA) has numerous functional groups such as amino group, carboxyl group and hydroxyl group which are good for metal ion chelation. Our earlier works have revealed that low molecular weight chitosan derivative was able to sorb Pb (II) and Cd (II) (Boamah et al., 2015a, 2014). However, there is no literature involving the use of low molecular weight chitosan derivative as a sorbent for the removal of Cu (II) ions. Also, the use of isothermal titration calorimetry (ITC) to determine the interaction between Cu (II) and low molecular weight chitosan derivative is missing in heavy metal removal literature.

Therefore, low molecular weight chitosan derivative was prepared for the sorption of copper. The prepared sorbent was

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characterized with FTIR, SEM and TG/DSC. Full factorial design (2^4) was used to explore the important parameters such as pH of the solution, temperature, dose of the sorbent, and concentration of the solution that affect copper sorption. Purposely, full factorial design was used to restrict the number of actual experiments undertaken as well as to investigate likely interaction between the aforementioned factors and their effect on the removal efficiency (%) of copper. Also, stoichiometry (N) and other thermodynamic parameters of copper (II) binding to low molecular weight chitosan derivative were determined using Isothermal Titration Calorimetry (ITC). The results of this study will be helpful for designing a system in the treatment of aquatic media polluted by heavy metals.

2. Materials and method

2.1. Materials

Chitosan (CS) (molecular weight=200 kDa, degree of deacetylation=95%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), 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 (CS_n) ($n=11$) using microwave

CS_{11} was done in accordance with the literature described previously (Boamah et al., 2014; Zhang, 2009). The rationale was that small intermolecular distance enhances intermolecular interactions (Zhou et al., 2003).

2.3. Preparation of $CS_{11}PA$

CS_{11} (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. $CS_{11}PA$ was vacuum dried at 30 °C.

2.4. Preparation of $CS_{11}PA-GLA$

0.5 g of $CS_{11}PA$ 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 $CS_{11}PA$ with glutaraldehyde was to enhance the resistance of the product against acid, alkali and chemical (Ngah and Fatinathan, 2008; Wan Ngah et al., 2002). Methanol was used to wash the prepared $CS_{11}PA-GLA$ particles through filtration. The $CS_{11}PA-GLA$ in the form of particles was vacuum dried at 30 °C.

2.5. Characterization

2.5.1. Size exclusion chromatography (SEC)

CS_{11} molecular weight was known as reported in the previous literature (Boamah et al., 2014; Huang et al., 2013). The molecular weight of CS_{11} was determined through size exclusion chromatography (SEC) using an RI K-2301 refractive index detector (Berlin, Germany) and TSK-GEL G4000 PWXL column (30 cm × 7.5 mm) (Beijing, China). The solute was eluted with HAc/ NH_4 Ac buffer solution (pH 4.5) at a flow rate of 0.43 mL/min.

2.5.2. Fourier transform infrared spectroscopy (FTIR)

FTIR (Nicolet Nexus 470, Nicolet, USA) was also used to characterize CS_{11} , $CS_{11}PA$, and $CS_{11}PA-GLA$, before and after, sorption of copper. Dried samples were grinded with potassium bromide (KBr) powder and then pressed into pellets for FTIR measurement.

2.5.3. Scanning electron microscope (SEM)

SEM image of $CS_{11}PA-GLA$ prior and subsequent to sorption of copper was obtained 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.

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

TG and DSC analysis of $CS_{11}PA-GLA$ was carried out on NETZSCH STA 449C thermoanalyzer (NETZSCH Instrument Co. Ltd.; Germany) under nitrogen atmosphere from 25 to 600 °C. The weight losses at different stages were analyzed. The measurement was done for 5–10 mg dried sample.

2.6. Standard Cu (II) solution

Copper stock solution (1000 mg/L) was prepared from copper (II) chloride dihydrate (analytical grade). The stock solution was diluted to obtain the desired Cu (II) concentrations. Concentrations prior to, as well as, subsequent to sorption were estimated by Atomic Absorption Spectrometer (AAS) (TAS-986, China).

2.7. Batch experiment

The batch experiment was conducted to establish the parameters that affect the sorption of copper ions onto $CS_{11}PA-GLA$, and to examine the combined effect of those parameters using 2^4 full factorial design. Based on preliminary studies and available literature (Cerino-Córdova et al., 2012; Da'na and Sayari, 2011; Kannamba et al., 2010), two levels, and four factors pH (A) (4 or 5), temperature (B) (40 °C or 50 °C), dose of sorbent (C) (0.05 or 0.1 g) and Cu(II) concentration (D) (1 or 3 mg/L) were chosen correctly such that two levels of the same factor were not identical in order to explore the effect of the four factors on copper sorption. The factors and their levels are presented in Table S1. For each trial, weighed amount of $CS_{11}PA-GLA$ (0.05 or 0.1 g) was added to the flask containing 25 mL of Cu (II) concentration (1 or 3 mg/L) of desired pH (4 or 5) (potassium hydrogen phthalate/HCl or potassium hydrogen phthalate/NaOH buffer solution respectively). The solution was agitated at 200 rpm for 24 h at the required temperature (40 °C or 50 °C). The sorption experiment was done at 40 °C and 50 °C in order to investigate the temperature level required for the highest removal efficiency (%) of copper. After 24 h, filtration was performed, and the $CS_{11}PA-GLA$, and copper ion concentration were analyzed using FTIR and AAS respectively. The sorption experiment was performed in duplicate, and the average was taken.

Based on preliminary studies on effect of concentrations of Cu (II) and dosage of $CS_{11}PA-GLA$ on sorption of copper, 0.05 g of $CS_{11}PA-GLA$ was placed in a flask with 25 mL of Cu (II) concentration (1–5 mg/L) for the sorption isotherm results. 5 mg/L Cu (II) concentration with change in time (1–24 h) was monitored for the kinetic studies, and the thermodynamic studies were also done at 40 and 50 °C.

Sorption capacity (q_e) is given as:

$$q_e = \frac{C_i - C_e}{W} \cdot V \quad (1)$$

where C_i is the initial copper (II) concentration measured in mg/L, C_e is the final copper (II) concentration measured in mg/L, V is the

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