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ScienceDirect
Journal of Hazardous Materials 154 (2008) 184–191
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin

Arh-Hwang Chen *, Sheng-Chang Liu, Chia-Yuan Chen, Chia-Yun Chen

Department of Chemical and Materials Engineering, Southern Taiwan University, Tainan, Taiwan, ROC

Received 30 May 2007; received in revised form 2 October 2007; accepted 2 October 2007
Available online 10 October 2007

Abstract

The crosslinked chitosans synthesized by the homogeneous reaction of chitosan in aqueous acetic acid solution with epichlorohydrin were used to investigate the adsorptions of three metals of Cu(II), Zn(II), and Pb(II) ions in an aqueous solution. The crosslinked chitosan characterized by ^{13}CNMR, SEM, and elemental analysis, and the effects of pH and anion on the adsorption capacity were carried out. The dynamical study demonstrated that the adsorption process was followed the second-order kinetic equation. The results obtained from the equilibrium isotherms adsorption studies of three metals of Cu(II), Zn(II), and Pb(II) ions by being analyzed in three adsorption models, namely, Langmuir, Freundlich, and Dubinnin-Radushkevich isotherm equations, indicated to be well fitted to the Langmuir isotherm equation under the concentration range studied, by comparing the linear correlation coefficients. The order of the adsorption capacity (Q_m) for three metal ions was as follows: $Cu^{2+} > Pb^{2+} > Zn^{2+}$. This technique for syntheses of the crosslinked chitosans with epichlorohydrin via the homogeneous reaction in aqueous acetic acid solution showed that the adsorptions of three metal ions in aqueous solution were followed the monolayer coverage of the adsorbents through physical adsorption phenomena.

Keywords: Adsorption capacity; Heavy metals; Crosslinked chitosan; Adsorption isotherms; Comparative adsorption

1. Introduction

Chitosan, poly(β-1,4)2-amino-2-deoxy-D-glucopyranose, is prepared from chitin, a natural biopolymer extracted from crustacean shells by partially deacetylating its acetamido groups, generally more than 60%, with a strong alkaline solution. Since both chitin and chitosan exist with some unique properties like biodegradability, biocompatibility and bioactivity, they have a variety of potential applications in biomedical products, cosmetics and food processing, metal chelating agents, and the like [1].

At present, the presence of heavy metal ions in the environment has received extensive attention due to increased discharge, toxicity in the environment, and other adverse effects which heavy metal ions have on receiving waters. The potential sources of heavy metal ions from industrial wastewaters include fertilizer, metal fabrication, paints, pigments, batteries, and the like. These would endanger public health and the environment if discharged improperly. Many methods such as ion exchange, precipitation, adsorption, membrane processes, and the like have been used for removal of toxic metal ions [2–7]. In particular, adsorption is recognized as an effective and economic method for removal of pollutants from wastewaters. Activated carbon is one of the most widely used adsorbent [8,9]. However, because it is expensive, low-cost biosorbents have been considerable attention in drastically reducing the cost of an adsorption system. In particular, chitin and chitosan, two low-cost natural materials, have been used for adsorption of metal ions, dyes and proteins [10–14]. Comparing the two, chitosan is more efficient than chitin in terms of adsorption capacity due to the presence of a large number of free amino groups on chitosan chain for its adsorption [15–17]. However, unlike chitin, chitosan is soluble in dilute organic acids, such as acetic acid, formic acid, and the like. Therefore, various physical and chemical modifications have been developed to improve the chemical stability of chitosan in acid media and in its resistance to biochemical and microbiological degradation [18–28]. Although the crosslinking method may reduce the adsorption capacity of chitosan, it can enhance the resistance of chitosan against acids and chemicals.

* Corresponding author.
E-mail address: chenah@ms12.hinet.net (A.-H. Chen).

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doi:10.1016/j.jhazmat.2007.10.009

Most importantly, this study considered the adsorption characteristics of copper(II), lead(II) and zinc(II) ions on chitosan crosslinked with epichlorohydrin via the homogeneous reaction in aqueous acetic acid solution. The reaction conditions for preparation of chitosan crosslinked with epichlorohydrin and the influences of adsorption conditions such as molar ratios of crosslinker/chitosan, pH changes and anion effects were investigated. The adsorption isotherms of copper(II), zinc(II) and lead(II) ions on chitosan crosslinked with epichlorohydrin were studied to gain a good comparison, accordingly.

2. Experimental

2.1. Chemicals

Chitosan with a deacetylation percentage of approximately 75% as defined by elemental analysis and FTIR methods was purchased from Aldrich. Epichlorohydrin (ECH) of 99.6% purity was purchased from Tedia. Cupric sulfate, cupric chloride, zinc sulfate, and lead nitrate purchased from Wako were analytical-reagent grade.

2.2. Preparation and characterization

The solution of chitosan was prepared with 0.5 g of chitosan dissolved into 5.0 mL of acetic acid (5%, v/v) and added with 45 mL of distilled water. Its pH was adjusted from 3.0 to 11.0 with 1.0 M of sodium hydroxide solution. Epichlorohydrin solution was added, and the mixture was stirred for 24 h at room temperature. Then 50 mL of 1.0 M sodium hydroxide solution was added into the mixture to form the precipitate. The precipitate was filtered and washed intensively with distilled water to remove any unreacted epichlorohydrin. Subsequently, it was dried on vacuum oven for 12 h. The resulting material was grounded and sieved to collect particles with a diameter from 250 to 500 μm for this study.

The CN analyses of the particles were determined on a Heraeus CHN-O-Rapid Analyzer. Solid-state ^{13}C nuclear magnetic resonance spectra of the materials were measured on a Beucker Advance 400 NMR spectrometer. The SEM photomicrographs of the particles were taken using a Hitachi S-3000N scanning electron microscopy.

2.3. Solubility

The epichlorohydrin-crosslinked chitosan particles prepared using the molar ratios of ECH/chitosan from 0.1 to 3.0 were tested with regard to their solubility in each 10 mL of 5% acetic acid (v/v), distilled water and 1.0 M sodium hydroxide solution by adding 0.1 g of each kind of particles into each solution for a period of 24 h with stirring.

2.4. Adsorption experiments

2.4.1. pH effects

The epichlorohydrin-crosslinked chitosan materials prepared with molar ratios of ECH/chitosan from 0.1 to 3.0 were investigated to determine the pH effects of their adsorption of copper(II) ion by adding 10 mg of each kind of particles into 100 mL of 10 ppm cupric sulfate solutions. These were adjusted to pH 3.0 and 6.0 with 1.0 M hydrochloric acid solution, and then by stirring for 4 h at room temperature. Their solutions were filtered and their concentrations of Cu(II) ion were measured on a Hitachi 170-30 atomic absorption spectrophotometer at 324.8 nm. The adsorption capacity (Q_e) was calculated by the following Eq. (1):

$$Q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_o is the initial concentration of Cu(II) ion (ppm), C_e is the final concentration of Cu(II) ion (ppm), V is the volume of Cu(II) ion solution (mL) and W is the weight of the ECH-crosslinked chitosan (g) used.

2.4.2. Kinetics of adsorption

The five epichlorohydrin-crosslinked chitosan materials prepared with molar ratios of ECH/chitosan from 0.1 to 3.0 and the chitosan were studied to determine adsorption of copper(II) ion by adding 10 mg of each kind of particles into 100 mL of 10 ppm cupric sulfate solution at pH 6.0 while stirring at room temperature. Then 10 mL aliquots of these solutions at intervals of 25 min were filtered and their concentrations of Cu(II) ion were measured by atomic absorption spectrophotometer. The adsorption capacity was calculated by Eq. (1).

2.4.3. Anion effects for the adsorption of copper(II) ion

The epichlorohydrin-crosslinked chitosan materials prepared with 0.1 to 3.0 molar ratios of ECH/chitosan were evaluated to determine the anion effects of their adsorption of copper(II) ion by adding 10 mg of each kind of particles into 100 mL of 10 ppm cupric sulfate solutions or 100 mL of 10 ppm cupric chloride solutions at pH 6.0 and then by stirring for 4 h at room temperature. The adsorption capacity (Q_e) was calculated by Eq. (1).

2.5. Adsorption isotherms

The isothermal studies were conducted with 10 mg of the epichlorohydrin-crosslinked chitosan (molar ratio of ECH/chitosan = 0.5/1.0) in 100 mL of initial concentration of copper(II), lead(II) or zinc(II) ions in the range of 0–15 ppm at pH 6.0 and with stirring for 4 h at room temperature. Their solutions were filtered and the concentrations of Cu(II), Pb(II) or Zn(II) ions were measured on a Hitachi 170-30 atomic absorption spectrophotometer at 324.8, 217.0 or 213.9 nm, respectively. The amounts of copper(II), lead(II) or zinc(II) ions adsorption were calculated by Eq. (1).

3. Results and discussion

3.1. Preparation and characterization

Some reported that there was heterogeneous reaction between chitosan bead and epichlorohydrin performed in alkaline