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Utilization of chitosan–zeolite composite in the removal of Cu(II) from aqueous solution: Adsorption, desorption and fixed bed column studies

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HIGHLIGHTS

- Chitosan–zeolite composite beads were useful in the removal of metal ions.
- Maximum adsorption capacity based on Langmuir isotherm was 25.88 mg/g.
- The adsorption data were well described by pseudo-second order.
- The critical bed depth from Bed Depth Service Time (BDST) model was 3.44 cm.

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ABSTRACT

Chitosan–zeolite composite (CZ) adsorbent prepared from chitosan and zeolite was used to remove Cu(II) from aqueous solutions. Batch adsorption studies were carried out to investigate the optimum conditions for the removal of Cu(II) using CZ. The optimum conditions were later utilized in kinetic, isotherm, fixed bed column and desorption studies. The pH point of zero charge (pH_{zpc}) of CZ was 7.76 while the optimum pH for the removal of Cu(II) was 3. The removal of Cu(II) by using CZ was best described by the pseudo-second order kinetic. The isotherm was best fitted by the Redlich–Peterson and Langmuir models. The critical bed depth was 3.44 cm based on the Bed Depth Service Time (BDSR) model. The data from the fixed bed column studies was well fitted by Clark model. The percentage of Cu(II) desorption was only 47.97%, which indicated that the Cu(II) ions were strongly bonded to the CZ surface.

1. Introduction

Cu(II) ions, at low concentrations function as a bacteriostatic substance [1], fungicide [2], and wood preservative [3]. It is an essential trace nutrient to human where it can be found in tissues, liver, muscle and bones. However, in excessive amounts, they are toxic, which can lead to liver disease, several neurological defects and in severe cases, death [4]. Effluents containing Cu(II) are widely discharged from industries such as electroplating and mining, and have to be removed before entering the environment [5]. There are different methods used to remove copper in wastewater such as oxidation–reduction, flocculation, electrocoagulation and adsorption using different classes of adsorbent [6]. Biosorption is an alternative removal process, which has been widely investigated to remove heavy metal from solution by using biomass [7].

Recently, the use of natural zeolite has gained much interest in adsorption studies due to its good adsorption properties and easy modification capability [8]. Chitosan has a high potential in the removal of metal ions, since it has both amine and hydroxyl group that can serve as active sites for metal ions [9]. Therefore, chitosan and zeolite are the promising materials to be used as adsorbents. In this study, chitosan is a hydrophilic and cationic polymer product of chitin and was used to form a composite with zeolite, which is an alumino-silicate with three-dimensional framework structure containing AlO_4 and SiO_4. Modifications were made in order to improve pore size, mechanical strength, chemical stability, hydrophilicity and biocompatibility of chitosan.

The objective of this study was to use the CZ and to determine its potential in removing Cu(II) from aqueous solutions. Several parameters were carried out to determine the optimum conditions for the composite. Non-linear regression method was used when applying kinetic models, isotherms models and other related models. This is to reduce the error that might occur during the transformation from non-linear to linear from which will lead to different assumptions [10]. Data from the batch adsorptions studies were analyzed using the pseudo-first and pseudo-second order kinetic models for determining the rate of the adsorption process.

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Langmuir, Freundlich and Redlich–Peterson isotherms were used to determine the predicted maximum adsorption capacity. Column breakthrough data was analyzed using the Bed Depth Service Time (BDST) and Clark models. Desorption studies were carried out to determine the ability of CZ to be regenerated based on the strength of the metal-adsorbent bond.

2. Materials and methods

2.1. Materials

Medium molecular weight chitosan with the degree of deacetylation of 75–85% and zeolite with particle size <45 μm were supplied by Sigma–Aldrich (Malaysia). All the reagents used were of analytical-reagent grade, and distilled water was used throughout this study. Cu(II) stock solution (1000 mg/L) was prepared by dissolving 1.0 g of copper metal supplied by BDH Chemicals (England) into 10 mL of concentrated nitric acid and diluted to 1000 mL.

2.2. Preparation of the composites

The preparation of the chitosan–zeolite composite was performed according to the same procedure described previously [11]. Four grams chitosan and 4 g zeolite (ratio of 1:1) were mixed in 160 mL (5%, v/v) acetic acid. The suspension was stirred vigorously for 2 h. A 100 mL of 5% acetic acid was added to the suspension and stirred vigorously for 1 h. The suspension was added dropwise into the precipitation bath containing 500 mL (0.50 M) NaOH. The mixture was stirred at 100 rpm for 3 h. The beads formed were filtered and washed with distilled water to remove excess NaOH. Finally, the beads were air-dried before grinding to obtain the desired size (<200 μm). The beads will be used as an adsorbent.

2.3. Characterization of the chitosan–zeolite composite

The functional group identification by using Fourier Transform Infrared Spectrometer (FTIR), surface area and average pore diameter analysis, carbon, hydrogen and nitrogen analysis, thermogravimetric analysis and solubility and swelling test were carried out to determine the physical and chemical changes that took place on CZ. The characterization of the CZ had been published recently [10]. The surface morphology of CZ before and after loaded with copper was carried out using scanning electron microscope (SEM, Leo Supra 50VP, Carl Zeiss SMT, Germany).

2.3.1. pH zero point of charge (pH_{zpc})

The determination of pH_{zpc} was performed according to the solid addition method [8]. The pH_{zpc} experiments were carried out by adding 100 mg of CZ in 50 mL of 0.01 M NaCl solution for 48 h with stirring rate of 300 rpm. The initial pH of each NaCl solution was adjusted to 2.0–9.0 by using 0.01 M HCl or 0.01 M NaOH solution. After 48 h of continuous stirring, the mixture was filtered to remove the adsorbent and the filtrate was analyzed using a pH meter.

2.4. Batch adsorption studies

Batch adsorption studies were used to determine the effect of pH, agitation rate, agitation period, dosage and initial Cu(II) concentration. The amount of Cu(II) adsorbed (Q_e, mg/g) was calculated using the following equation.

$$Q_e = \left(\frac{C_o - C_e}{W}\right)V \quad (1)$$

where C_o is the initial Cu(II) concentration (mg/L), C_e is the final Cu(II) concentration (mg/L), W is the weight of CZ used (g) and V is the volume of Cu(II) solution (L). All the experiments were carried out in duplicates.

The percentage removal (R) of Cu(II) was calculated using the following equation:

$$R\ (\%) = \left(\frac{C_o - C_e}{C_o}\right)100 \quad (2)$$

The desorption percentage (DP) of Cu(II) ions is defined as:

$$\mathrm{DP}\ (\%) = \left(\frac{C_{e(des)}}{C_{e(ads)}}\right)100 \quad (3)$$

where $C_{e(des)}$ is the concentration of Cu(II) desorbed from CZ (mg/L) and $C_{e(ads)}$ is the concentration of Cu(II) adsorbed on CZ (mg/L).

2.4.1. Effect of pH

Experiments to determine the optimum pH were carried out at 25 °C by adding 50 mg of adsorbent in 50 mL (10 mg/L) Cu(II) solution at various pH values ranging from 1 to 6. The pH of the solution was adjusted with HCl and NaOH solutions. Each sample was stirred at 300 rpm for 60 min. After adsorption, the adsorbent was filtered and the final concentration of Cu(II) was analyzed by an atomic adsorption spectrometer (AAS, PerkinElmer AAnalyst 200 Model, USA) at a wavelength of 324.7 nm.

2.4.2. Effect of agitation rate

Experiments to determine the optimum agitation rate were carried out at 25 °C by adding 50 mg of adsorbent in 50 mL of 10 mg/L Cu(II) solution (pH 3.0). Each sample was stirred at different stirring rate ranging from 100 to 900 rpm for 60 min. After adsorption, the adsorbent was filtered and the final concentration of Cu(II) was analyzed by AAS.

2.4.3. Effect of adsorbent dosage

Experiments were carried out at 25 °C where different amounts of CZ ranging from 10 to 75 mg were mixed with 50 mL Cu(II) solutions. The initial Cu(II) concentration was 10 mg/L and the pH was adjusted to 3.0. The mixture was stirred at 300 rpm for 60 min to reach equilibrium. After adsorption, the adsorbent was filtered and the final concentration of Cu(II) was analyzed by AAS.

2.4.4. Effect of initial concentration and time

Experiments to determine the effect of initial Cu(II) concentration were carried out at 25 °C by adding 50 mg of CZ in 50 mL of different initial concentrations of Cu(II) solution ranging from 15 to 40 mg/L. The Cu(II) solutions were adjusted to pH 3.0. The mixture was stirred at 300 rpm at a pre-determined time interval ranging from 5 to 180 min. After adsorption, the adsorbent was filtered and the final concentration of Cu(II) was analyzed by AAS. The data from this experiment was analyzed using MATLAB 7.0.1 software.

2.5. Isotherm studies

Batch adsorption studies were carried out where different amount of adsorbents (0.025–0.4 g) were mixed with 50 mL of Cu(II) solution and stirred at 300 rpm for 60 min. The temperature, pH and the initial concentration of Cu(II) solution were 25 °C, 3.0 and 100 mg/L, respectively. The data from this experiment was analyzed using MATLAB 7.0.1 software.