



Adsorption of copper on chitin-based materials: Kinetic and thermodynamic studies



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ABSTRACT

Copper (Cu (II)) is one of the most toxic heavy metals usually found in the environment. Thus its removal from aqueous waste streams is an important issue in nowadays. The present work focuses on the comparison of the copper adsorption on chitin-based adsorbents, *i.e.* chitin (CH), chitosan (CS) and chitosan- ethylenediaminetetra-acetic acid (CS-EDTA). Chitin derivatives are carbohydrate materials well known to remove heavy metal ions from aqueous solutions. The effects of contact time, initial concentration, the temperature, pH, and mass of the adsorbent in the adsorption process were studied. The adsorption isotherms were well simulated by Langmuir and Freundlich models. The maximum adsorption capacity of CH, CS and CS-EDTA at 25 °C, pH 7.0 was found to be 58, 67 and 110 mg g⁻¹, respectively. Thermodynamic parameters of adsorption processes such as Gibb's free energy (ΔG^0), standard enthalpy (ΔH^0) and entropy (ΔS^0) were also calculated. The results showed that the studied materials could be used as effective adsorbents for removal of copper from water.

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1. Introduction

The waste water contamination by heavy metals is a worldwide environmental and social problem. Some metals like copper, chromium, mercury and lead are classified as toxic due to their non-biodegradability and bioaccumulation in living organisms [1]. Metals such as copper play important roles in certain industries. Copper is often used in the drive moving parts, brake linings, metal plating, pulp and paper industry, fertilizer mills, fungicides, insecticides, etc. [2]. Copper is considered a trace element at low doses due to the fact that human body can regulate the trace level haemostatically but it can be toxic at high concentration because of their tendency to accumulate in the vital organs [3] and their harmful impact on the environment due to the fact that they are non-biodegradable causing many diseases and disorders [4]. With bends its dangers, the presence of copper ions in water must be controlled. The maximum contamination level for Cu (II) ions in the industrial effluent required by United States Environmental Protection Agency (USEPA) is 1.3 mg L⁻¹ [5]. Several

methods, namely chemical precipitation [6], ion exchange [7], and biological treatment [8], membrane filtration [9] and adsorption [10] were currently used to remove Cu (II) from aqueous solutions. Adsorption processes have been considered effective and efficient methods to remove Cu (II) from aqueous solutions, using a wide variety of adsorbents such as rice husks [11], carbon nanotubes [12] and lignin [13]. The use of biopolymers for removal of heavy metals from water treatment plants is one of the emerging adsorption approaches because of their good ability and affinity towards these compounds in aqueous solution. Moreover, biopolymers are from renewable resources, biodegradable and have an excellent capacity to associate with a wide variety of molecules by physical and chemical interactions [14]. Among the biopolymers, chitin that is the second most abundant natural polymer in earth after cellulose (one of the main components of crustacean shells [15]), and its main derivative, chitosan, present hydroxyl group (OH) and an amino group (NH₂) in their backbone. The presence of these two different functional groups, which are good and valid chelating groups for the coordination of metal ions in aqueous solutions such as Cu (II), Cd (II) and U (VI) [16,17], reinforce their use in adsorption studies. Recently, chitin- and chitosan-based adsorbents in different physical forms (*e.g.* gel beads, membranes, sponge, fibres or hollow fibres, etc.) have been used for removal of varieties of heavy

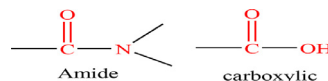
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Abbreviations

CH	Chitin
CS	Chitosan
CS-EDTA	Chitosan-ethylenediaminetetra-acetic acid
C_0	Initial copper concentration (mg L^{-1})
C_e	Concentration of copper solution at equilibrium (mg L^{-1})
q_e	Amount of copper adsorbed at equilibrium (mg g^{-1})
q_t	Amount of copper adsorbed at time (t) (mg g^{-1})
K_1	The constant adsorption pseudo-first-order model (min^{-1}).
K_2	The constant adsorption pseudo-second-order model ($\text{g mg}^{-1} \text{min}^{-1}$)
H	The initial absorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)
$q_{e, \text{cal}}$	Amount of copper calculated at equilibrium (mg g^{-1})
$q_{e, \text{exp}}$	Amount of copper of the experimental at equilibrium (mg g^{-1})
K_f	Freundlich adsorption isotherm constant (mg g^{-1})
$\frac{1}{n}$	Freundlich adsorption isotherm constant
R_l	Dimensionless separation constant
K_l	Langmuir isotherm constant related to the energy of adsorbent (L mg^{-1})
q_m	The maximum adsorption capacity (mg g^{-1})
T	Temperature ($^{\circ}\text{C}$, K)
Ca	The adsorbent phase concentration at equilibrium (mg L^{-1})
Kc	The equilibrium constant
ΔG^0	Standard free energy (kJ mol^{-1})
ΔH^0	Standard enthalpy change (KJ mol^{-1})
ΔS^0	Standard entropy change ($\text{KJ mol}^{-1} \text{K}^{-1}$)
k_p	The constant of intraparticle diffusion model ($\text{mg g}^{-1} \text{min}^{-1/2}$)
C	The thickness of the boundary layer (mg g^{-1})

metals and dyes. For instance, chitosan membranes crosslinked with glutaraldehyde and epichlorohydrin are used for adsorption of copper [18–21]. Chitosan amino and hydroxyl groups can act as chelation sites for different metals, but can also be functionalized in order to improve this property [22]. Ethylenediaminetetraacetic acid (EDTA) is known to form stable chelates with metal ions and has been used to functionalize CS to improve its chelation capacity and used as removal adsorbent of toxic metals such as Co (II) and Ni (II) [23]. In this previous work, the authors compared the affinities of metals to CS-EDTA by a kinetic study, adsorption isotherm as evaluation tool between experimental and theoretical values. This work showed that the CS-EDTA had much better affinity for Ni (II) than for Co (II) suggesting that Ni (II) could be adsorbed selectively from the contaminated water in the presence of Co (II). EDTA was also used to in other study in the development of chitosan–silica hybrid materials for the adsorption of Co (II), Ni (II), Cd (II) and Pb (II) for water treatment [24]. In this context, the aim of this study was to synthesise chitosan-ethylenediaminetetraacetic acid (CS-EDTA) derivative and compared its Cu (II) removal capacity with those of chitin and unmodified chitosan powder. The Cu (II) adsorption properties by chitin, chitosan and chitosan-EDTA were evaluated in terms of adsorption kinetics, adsorption isotherms, thermodynamic study and the adsorption mechanism. This study leads to a comparative study between a natural polymer and grafted chitosan showing the effect of chelating moiety

on the adsorption capacity due to the presence of amide and carboxylic groups on CS-EDTA.



2. Experimental

2.1. Materials

Chitosan powder (CS, degree of deacetylation of 98% and viscosity-average molecular weight of 500,000) was supplied by Mahtani Chitosan PVT. Ltd., India. CS was purified before use by a precipitation method [25]. Briefly, CS was dissolved in 1% (v/v) aqueous acetic acid solution, filtered, and precipitated by neutralization with sodium hydroxide up to a pH=8.5. The ensuing precipitate sample was washed with distilled water until a neutral pH and air-dried. Chitin (CH) powder was extracted in our laboratory from yellow lobster wastes (kindly supplied by Antarctic Seafood S.A., Chile) based on procedures previously described in references [26–29]. The degree of deacetylation was found to be 4% by ^{13}C NMR.

Ethylenediaminetetra-acetic acid (EDTA, ACS reagent, 99.4%), acetic anhydride (ACS reagent, >98%), pyridine (ACS reagent, >99%), methanol (HPLC, >99%), ethanol (ACS reagent >98%), diethyl ether (ACS reagent >99%), Copper (II) nitrate-trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, >99%), hydrochloric acid (HCl, ACS reagent, 37%), and sodium hydroxide (NaOH, reagent grade, $\geq 98\%$, pellets (anhydrous)) were all purchased from Sigma–Aldrich and used as received without further purification.

2.2. Preparation and characterization of chitosan-EDTA derivative

The preparation of the adsorbent chitosan-ethylenediaminetetraacetic (CS-EDTA) was done in two steps: (A) synthesis of EDTA anhydride, and (B) polycondensation (Fig. 1).

2.2.1. Preparation of EDTA anhydride

10.0 g of EDTA (34 mmol) was suspended in 16 mL of pyridine under a nitrogen atmosphere. Subsequently, 14.0 g of acetic anhydride (0.14 mmol) was added and the mixture was stirred at 65°C for 24 h. The final product (Fig. 1A) was then washed with an excess of acetic anhydride and diethyl ether and dried in vacuum for 24 h [30]. The chemical modification was confirmed by ATR-FTIR spectra (data not shown). Comparing with the unmodified EDTA ATR-FTIR spectrum, the EDTA anhydride spectrum clearly shows two asymmetric bands at 1804 and 1747 cm^{-1} , attributed to the two C=O groups of the anhydride function [31].

2.2.2. Preparation of CS-EDTA

Chitosan was chemically modified with EDTA anhydride according to the reaction shown in Fig. 1B. A total of 1 g chitosan (6 mmol) of glucosamine units was dissolved in 100 mL (10% vol. acetic acid), subsequently, the chitosan solution was diluted five times with methanol. A total of 6 g EDTA anhydride (0.0234 mol) were suspended in 100 mL of methanol and added to the solution of chitosan. The mixture was then stirred for 24 h at room temperature. After filtration, the precipitate (CS-EDTA) was first washed with ethanol and stirred for 12 h. After further filtration, the precipitate was dispersed in diluted 0.5 M NaOH solution (50 mL for 12 h to remove unreacted EDTA anhydride. Finally, the precipitate was washed several times with distilled water [32,33]. The solution was then neutralized with hydrochloric acid (0.1 M) and the obtained gel was dried for 24 h at 40°C . The ensuing CS-EDTA (1.9 g) derivative was characterized in terms of chemical structure (ATR-FTIR and ^{13}C solid-state NMR).

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