

Optimization of the Removal of Copper(II) Ions from Aqueous Solution on Chitosan and Cross-Linked Chitosan Beads

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The paper examines copper ion removal and recovery from mining waters using chitosan and cross-linked chitosan beads as insoluble sorbents in acidic and basic solutions. Batch adsorption experiments were carried out as a function of pH, adsorbent dosage, contact time, and initial Cu(II) ion concentration. Equilibrium data were fitted using Langmuir, Freundlich, Elovich, and Temkin models. The experimental data were best represented by using a pseudo-second order kinetic model and a Langmuir isotherm model. Recovery of Cu(II) ions from sorbents was successfully achieved by treating sorbents with an aqueous EDTA solution. A potentiometric method has been employed to detect the Cu(II) ions in synthetic water samples after the adsorption process. The results demonstrated that Cu(II) ions can be efficiently removed from synthetic aqueous solutions, similar to mining waters, using chitosan and cross-linked chitosan beads.

Keywords: Adsorption; Copper; Chitosan beads; Equilibrium; Kinetics; Isotherms

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INTRODUCTION

The presence of heavy metals ions in the environment has received extensive attention due to their increased release in rivers and their toxicity (Ngah *et al.* 2002; Chowdhury *et al.* 2012). The potential sources of copper are mining wastewaters, industrial effluents, metal cleaning and plating baths (metal purification technologies), wood pulp and paper production, and anti-fouling paints (Quek *et al.* 1998; Gupta 1998; Findon *et al.* 1993). Copper is an essential nutrient in trace amounts, but at higher levels, it is toxic to plants and to algae (Ngah and Fatinathan 2008). In humans elevated concentrations of copper can cause oxidative stress and cancer (Ho *et al.* 2002; Gupte and Mumper 2009). Excess copper can be toxic to fish at lower pH values, even at very small concentrations in natural waters (Gupta 1998).

A number of technologies, such as ion exchange, filtration, chemical precipitation, complexation, adsorption, electrodeposition and reverse osmosis, have been developed over the years. These methods show promise for treating dilute metal solutions (Kaminski and Modreyejwska 1997; Deans and Dioxin 1992). Adsorption represents a very economic and efficient technique for removing heavy metal ions from dilute solutions (Feng *et al.* 2012). Many materials such as activated charcoal (Bailey *et al.*

1999; Babel and Kurniawan 2003) or low-cost sorbents of biological origins, such as cellulose, alginates, carrageenan, lignins, proteins, chitin, and chitin derivatives have been examined as adsorbents to remove heavy metals from water and industrial effluents (Deans and Dioxin 1992; Li and Bai 2005; Guibal *et al.* 1998; Evans *et al.* 2002; Ngah *et al.* 2002). Biopolymers are widely available, environmentally-safe, and industrially attractive due to their ability to lower heavy metal ion concentrations to parts per billion level (Deans and Dioxin 1992). Chitosan is a natural polymer derived from chitin, a biodegradable, non-toxic, and environmentally friendly material (Feng *et al.* 2012). Chitosan is an efficient biosorbent in terms of adsorption capacity due to the presence of a large number of free amino and hydroxyl groups to which metal ions can bind either by chemical or by physical adsorption (Deans and Dioxin 1992; Lu, 2001). The amine and hydroxyl groups from chitosan can act as chelation sites for metal ions (Ngah *et al.* 2002).

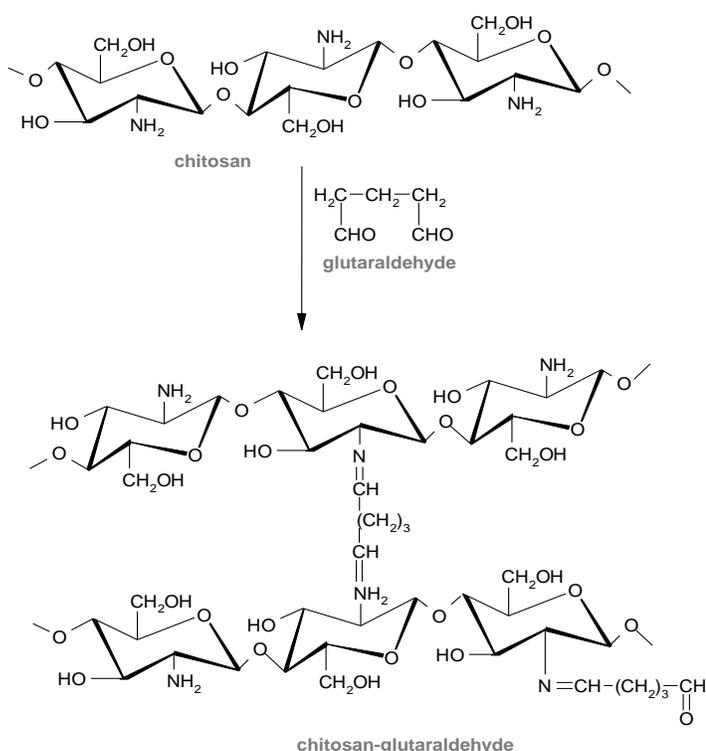


Fig. 1. Schematic representation of the cross-linking reaction of chitosan with glutaraldehyde

Chitosan is soluble in dilute organic acids, such as acetic and formic acid. For that reason, a range of physical and chemical modifications have been developed to enhance the chemical stability of chitosan in acidic environments (Ngah and Liang 1999; Ngah *et al.* 2002, 2005; Ruiz *et al.* 2000; Coelho *et al.* 2007).

One important chemical modification of chitosan is the use of a cross-linking agent (Sun and Wang 2006). This method has been used to enhance the resistance of chitosan against acid, alkali, and other chemical degradation, although it reduces the metal ion adsorption capacity (Chen *et al.* 2008). One of the most commonly used cross-linking agents is glutaraldehyde (Ngah *et al.* 2002). The cross-linking reaction of chitosan with glutaraldehyde is presented in Fig. 1.

There are many procedures for quantifying copper ion concentrations in samples, such as atomic absorption spectroscopy, cold vapor atomic absorption spectroscopy, flame atomic absorption spectroscopy - electrothermal atomization, anodic stripping voltammetry, chromatography, and gravimetric detection, which are most frequently used. Although exact and accurate, these methods are laborious due to sample preparation, and they require expensive materials and instruments to conduct. Therefore, these methods are not suitable for processing large numbers of analyses. Potentiometry, direct or by titration, is a simple procedure, which does not require a laborious sample preparation; it is fast, and therefore proper for serial determinations (Bizerea Spiridon and Bizerea 2002; Bizerea Spiridon 2010).

The present study investigates the adsorption of Cu(II) ions onto chitosan beads and chitosan–GLA (chit-GLA) beads using a potentiometric method for Cu(II) ion detection. The influence of different experimental conditions such as initial pH of solution, stirring rate, adsorbent dosage, and initial Cu(II) ions concentrations uptake were studied. Langmuir, Freundlich, Elovich, and Tempkin isotherm models were used to fit the equilibrium adsorption data. The adsorption rates were determined quantitatively and then compared with pseudo-first and pseudo-second order kinetic expressions. The findings from this study may be employed in other applications for treatment of waste effluents.

Figure 2 shows the formation of chitosan chelates with copper(II) ions (Fig. 2 a) and with GLA (Fig. 2b). The literature we are citing indicates rather a coordinate bond between the adsorbent and adsorbate, leading to a monolayer covering. Still, there are also other references showing some possible structure of the complexation of Cu(II) on different adsorbents.

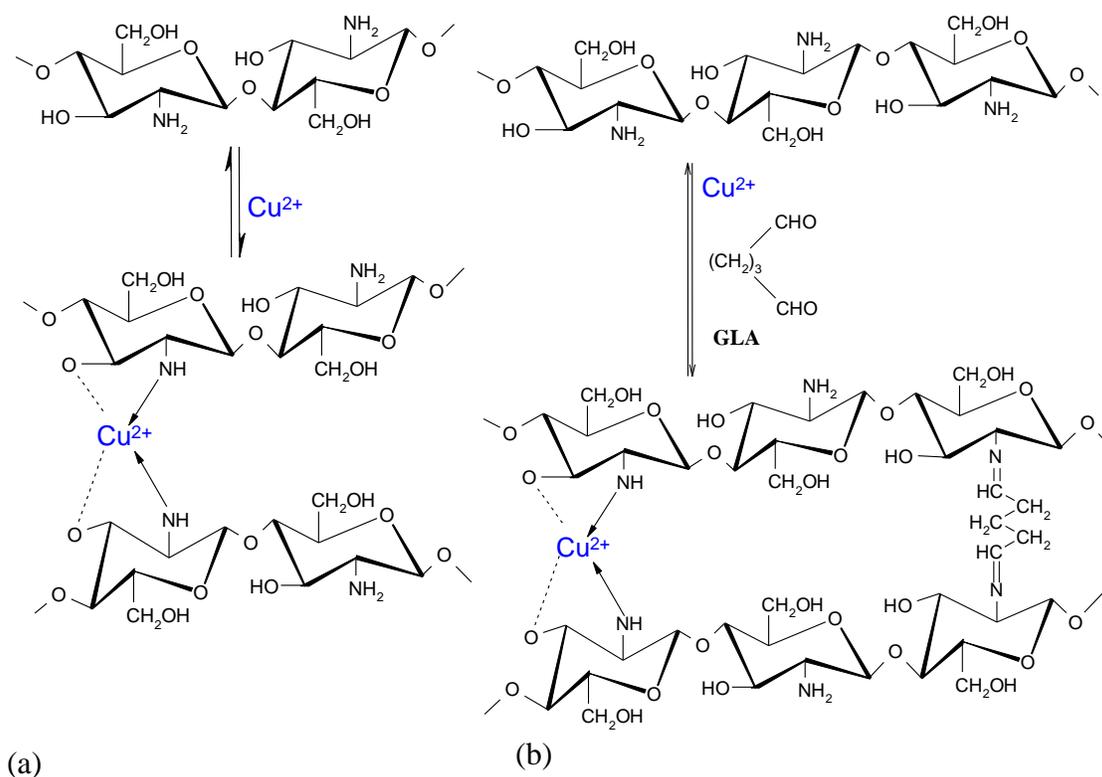


Fig. 2. Formation of copper chelates with: (a) chitosan and (b) chit-GLA

Benavente (2008) suggests a “pendant” type structure as uncharged complex identified by X-ray investigation. Moreover, at pH higher than 5.8 (the optimum pH used in the present research is 6.0) Rhazi and coworkers (2002) consider an uncharged complex, which does not imply further rejections of the free Cu(II) ions. Hernandez and coworkers mention the complexation of metal ions through –OH in the sugar unit of chitosan and other biopolymers (Hernández *et al.* 2007, 2008).

EXPERIMENTAL

Materials

Chitosan with a degree of deacetylation of approximately 75 to 85% and medium molecular mass was obtained from Sigma Aldrich Chemie GmbH (Germany). Hydrochloric acid (HCl), 65% nitric acid (HNO₃), glacial acetic acid, formic acid, sodium hydroxide (NaOH), and copper(II) nitrate hemi(pentahydrate) were purchased from Sigma Aldrich Chemie GmbH (Germany). EDTA used was from Chinoin (Budapest), whereas 50% glutaraldehyde was from Fluka (Switzerland). All reagents used in this study were of analytical grade. Deionized and distilled water was used to prepare all solutions.

A thermostated shaker (Vibramax 100 Heidolph) apparatus was used for the adsorption experiments. The shaker was set at a constant speed of 300 rpm and at a temperature 25±1°C for adsorption experiments.

Copper ion content in the samples subjected to chitosan and chit-GLA beads adsorption was determined potentiometrically using a copper-sensitive electrode type ELIT 8227 and a double junction reference electrode type ELIT 003 N (NICO2000 Ltd., UK). Measurements were made with a virtual instrument type system consisting of hardware component, NI board - USB 9215 A and software component implemented using NI LabVIEW 2009 (National Instruments, Austin, US). Attempts to optimize the method were presented in previous studies (Bizerea Spiridon *et al.* 2011a,b). Copper ions concentrations from desorption studies were determined by atomic absorption spectrophotometry using a VARIAN SpectrAA 110 spectrophotometer. All pH values were measured with a Multi 340i pH-meter.

Preparation of Chitosan Beads

A chitosan solution was prepared by dissolving approximately 1.00 g of chitosan powder into 30 mL of 2% acetic acid solution. The viscous solution was left overnight before adding drop wise into a precipitation bath containing 500 mL of 0.5 M NaOH, which neutralized the acetic acid within the chitosan gel; thus, the chitosan gel was turned into homogeneous spherical beads. The aqueous NaOH solution was moderately agitated with mild, continuous stirring. The wet chitosan gel beads were extensively rinsed with distilled water and filtered to remove residual NaOH. Prior to the adsorption experiments, the chitosan beads were kept at 4°C after adding few drops of chloroform to prevent bacterial degradation.

Preparation of Chitosan-GLA Beads

Chitosan-GLA beads were prepared by suspending wet chitosan beads (synthesized as described above) in a 0.5% glutaraldehyde solution for 24 h at room temperature. After 24 h, the cross-linked chitosan beads were filtered and washed

intensively with distilled water to remove unreacted glutaraldehyde. Then the beads were treated with 2% acetic acid solution to verify that the material was no longer soluble in weak organic acids. Finally, the chit-GLA beads were kept at 4°C after adding a few drops of chloroform to prevent bacterial degradation.

Dissolution and Swelling Test of Chitosan and Chit-GLA beads

Chitosan and chit-GLA beads were tested for their solubility in 5% acetic acid, 5% formic acid, distilled water, and 0.5 M sodium hydroxide solution. Approximately 0.1 g of chitosan or chit-GLA beads were added to each solution and stirred for 24 h.

The swelling studies of chitosan and chit-GLA beads were carried out in distilled water, at room temperature, for a period of 24 h. The swelling percentage of these beads was calculated using the following equation:

$$\text{Swelling percentage (\%)} = \frac{W_s - W}{W} \cdot 100\% \quad (1)$$

where W_s is the weight of the swollen beads (g) and W is the weight of the dry beads (g).

Adsorption Experiments

Solutions of Cu(II) ions between 10^{-2} M and 10^{-5} M were prepared by dissolving in deionized water the appropriate amount of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ measured on an analytical balance with ± 0.0001 mg error. The adsorption of Cu(II) from prepared solutions was carried out in batch processes at room temperature ($25 \pm 1^\circ\text{C}$). The batch adsorption experiments were performed by placing approximately 1.00 g of chitosan and chit-GLA beads, respectively in a 250 mL beaker with 50 mL of standard metal solutions and agitated using the thermoshaker.

Within this research, different concentrations of Cu(II) ions were used for the adsorption isotherms studies. Due to high removal degree obtained in our preliminary experiments, the most appropriate concentration of Cu(II) ions for further tests turned out to be 10^{-4} M. This value was used to investigate the effect of pH, contact time, and for kinetic studies. All measurements were done in duplicate.

Process efficiency, R (%), which is the amount of metal adsorbed and the adsorption capacity, q_e (mg/g), were determined according to the following equations, respectively:

$$R = \frac{C_0 - C}{C_0} \cdot 100 \quad (2)$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{W} \quad (3)$$

where C_0 is the initial concentration of Cu(II) ions (mg/L), C_e is the final (equilibrium) concentration of Cu(II) ions (mg/L), V is the volume of Cu(II) ions solution (mL), and W is the weight of chitosan or chitosan-GLA (g) used.

The effect of pH

The effect of solution pH on the adsorption of Cu(II) ions by chitosan and chit-GLA was studied by adding approximately 1.00 g of each kind of beads in 50 mL of 10^{-4} M copper (II) nitrate solutions, at different pH values between 2 and 6. The adsorption by chitosan or chit-GLA was done for 60 min at room temperature and with stirring. The pH adjustments were made using 0.1 M NaOH or 0.1 M HCl. Afterwards, the solutions were filtered and the Cu(II) ions concentrations in supernatant were measured with the copper-sensitive electrode.

The effect of contact time

The contact time represents the time necessary for the adsorption process to reach equilibrium. For each sample the adsorption capacity was studied as a function of time. The contact time was varied from 20 and 260 min.

The effect of contact time was studied at room temperature, while stirring at 300 rpm using a constant adsorbent dose (approximately 0.50 g). Tests were performed using 50 mL of 10^{-4} M Cu(II) solution. Afterwards, the supernatant was separated from the sorbent by filtration and Cu(II) ion concentration in the supernatant was measured.

The effect of adsorbent dosage

The variation of the adsorbent mass, within 0.05 to 1.00 g, under previously determined pH and stirring time, was also studied. The samples were stirred for 90 minutes, followed by filtration and potentiometric detection of the Cu(II) ions.

Isotherm studies

The linear forms of the isotherms are more frequently used for practical reasons, as they offer the means to determine constants and other parameters describing the adsorption kinetics from experimental data.

The mathematical correlation is usually depicted by graphs expressing the amount adsorbed on the solid-phase against its residual concentration in solution (Malek and Farooq 1996). This separation of metal ions between the aqueous and solid (gel) phases will be described by one or more adsorption isotherms and leads to empirical conclusions related to the mechanism of adsorption, such as the monolayer or multilayer models (Findon *et al.* 1993).

Langmuir adsorption isotherms have been extensively used to quantify and differentiate the adsorption of different bio-sorbents (Langmuir 1916). This empirical model assumes monolayer adsorption (one molecule thickness of the adsorbed layer), with adsorption that can only occur at a finite number of sites (Vijayaraghavan *et al.* 2006). In other words, following the occupation of a site by complexation with copper, no further adsorption can take place (Allen *et al.* 2004; Demirbas *et al.* 2008). As part of Langmuir isotherm model, uniform adsorption, constant enthalpies and sorption activation energies are presumed (Kundu and Gupta 2006).

The Langmuir isotherm model used for monolayer adsorption can be represented by the Equation (4),

$$q_e = \frac{b \cdot Q_m \cdot C_e}{1 + b \cdot C_e} \quad (4)$$

where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal ions adsorbed on adsorbent mass unit (mg/g), Q_m is the maximum adsorption capacity of metal ions (mg/g), and b is the Langmuir adsorption equilibrium constant (mL/mg). Therefore, using the linearized form of the Langmuir equation (*i.e.* Eq. (5)),

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m \cdot b} \quad (5)$$

the plot of C_e/q_e against C_e is generated, giving a straight line with a slope of $1/Q_m$ and an intercept of $1/(Q_m b)$. The essential feature of a Langmuir isotherm consists of the fact that it can be expressed in terms of the separation factor or equilibrium parameter, R_L , (Weber and Chakravorti 1974) which is given by Equation (6),

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (6)$$

where C_0 represents the initial concentration of Cu(II) (mg/L) and b is the Langmuir adsorption equilibrium constant (mL/mg).

Empirical calculations lead to the understanding that for adsorption processes a lower R_L value reflects a more favorable adsorption. A value of 1 describes a linear adsorption, whereas a value of 0 indicates irreversible adsorption reaction rather than dynamic equilibrium process. Values of R_L higher than 1 indicate unfavorable adsorption.

The Freundlich isotherm model (Freundlich 1906) is a popular multilayer adsorption model used for heterogeneous surfaces (Adamson and Gast 1997). This model describes the non-ideal and reversible adsorption, which is not restricted to the formation of a monolayer. The Freundlich model is defined by Equation (7):

$$q_e = K_F \cdot C_e^n \quad (7)$$

where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal ions adsorbed on adsorbent mass unit (mg/g), K_F is the maximum adsorption capacity of metal ions (mg/g), and n is a constant present in the non-linear Freundlich isotherm, which indicates the adsorption intensity. The linearized form of the Freundlich equation, given by Equation (8),

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (8)$$

where the factor $1/n$ is usually expressed as b_F , which represents the slope of the straight line obtained by plotting $\ln(q_e)$ versus $\ln(C_e)$. The value of b_F is important, as it is a way of describing the adsorption intensity or the surface heterogeneity. The value of b_F should be between 0 and 1, if the process of adsorption is described by chemisorption. The closer to 0 the value of b_F is, the more heterogeneous is the solid phase surface (Haghseresht and Lu 1998).

The Elovich isotherm model assumes that the adsorption sites multiply exponentially with adsorption, indicating a multilayer adsorption. The Elovich equation (Elovich and Larinov 1962) is expressed by Equation (9),

$$\frac{q_e}{Q_m} = K_E C_e^{-\frac{q_e}{Q_m}} \quad (9)$$

where K_E is the Elovich equilibrium constant (L/mg) and Q_m is the Elovich maximum adsorption capacity (mg/g). The linearized form of the Elovich equation used to plot $\ln(q_e/C_e)$ versus q_e is given by Equation (10).

$$\frac{\ln q_e}{C_e} = \ln K_E Q_m - \frac{q_e}{Q_m} \quad (10)$$

The Temkin isotherm model (Temkin 1941) is characterized by a linear decrease of the heat of adsorption of all molecules in the layer due to the interactions between sorbent and adsorbate. Another important feature of the Temkin model is the fact that adsorption, in this case, is described by a homogeneous distribution of the binding energies to all adsorption sites. The Temkin model is given by Equation (11), and its linearized form is given by Equation (12), which can be used to plot q_e vs. $\ln(C_e)$,

$$q_e = \frac{RT}{\Delta Q} \ln K_0 C_e \quad (11)$$

$$q_e = \frac{RT}{\Delta Q} \ln K_0 + \frac{RT}{\Delta Q} \ln C_e \quad (12)$$

where R is the universal gas constant ($R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$), T is the temperature, 25°C in the present study, ΔQ is the heat transfer (J mol^{-1}), and K_0 is the Temkin constant. Isotherm studies were performed varying the initial concentration of Cu(II) ions between 7.5×10^{-5} and 5×10^{-3} M. The amount of Cu(II) ions adsorbed at equilibrium per adsorbent mass unit and the adsorption capacity, respectively, were calculated using Equation (12) as a function of equilibrium concentration of Cu(II) detected potentiometrically.

Kinetic Studies

The mechanism of adsorption was investigated by pseudo-first and pseudo-second kinetic models. The pseudo-first order model given by Equation (13) describes very well, in most cases, the initial phase of the adsorption process, but is not suitable for the rest of the contact period (Ho and McKay 1999):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (13)$$

where q_e is the amount of Cu(II) ions adsorbed (mg/g) at equilibrium, q_t is the amount of Cu(II) ions adsorbed on adsorbent mass unit (mg/g) at time t and k_1 is the rate constant of the first-order adsorption (min^{-1}). In order to determine the value of k_1 , the $\log(q_e - q_t)$ versus $\log(q_e)$ plot was used.

The pseudo-second order model given by Equation (14) is considered to be the most appropriate to describe the entire process of adsorption (Chiou and Li 2003):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (14)$$

where q_e is the amount of Cu(II) ions adsorbed (mg/g) at equilibrium, q_t is the amount of Cu(II) ions adsorbed on adsorbent mass unit (mg/g) at time t and k_2 is the rate constant of the second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). In order to determine the value of k_2 , the t/q_t versus t plot was used.

The batch kinetic studies were carried out using a constant chitosan and chit-GLA beads weight (0.50 g) in 50 mL solution of 10^{-4} M Cu(II) ions. After 90 min, each solution was filtered and the concentration of Cu(II) ions in the filtrate was measured.

Desorption Studies

Desorption studies are very useful in real situations of water pollution with Cu(II) ions due to the fact that chitosan and chit-GLA beads can be recycled after removing Cu(II) ions from the aqueous stream, thus making the process more cost-efficient (Nghah *et al.* 2006). In our work, EDTA was used for the desorption studies.

The chitosan and chit-GLA beads previously exposed to Cu(II) solutions were stirred with 50 mL of 10^{-2} or 10^{-3} M EDTA solutions for 60 minutes. The potentiometric method is time- and cost-efficient in measuring free Cu(II) ions in solutions, but it is unable to detect Cu(II) in its EDTA-chelated form. The literature mentions decomplexation methods of metal ions from EDTA complexes that should further allow the potentiometric determination of the metal ions (Nghah *et al.* 2006; Tiwari *et al.* 2008; Rhoads and Davis 2004). However, in this research we chose the direct determination of Cu(II) complex by atomic absorption spectrometry (AAS).

RESULTS AND DISCUSSION

Solubility and Swelling Test of Chitosan and Chit-GLA Beads

The experimental results showed that chitosan beads were soluble in 5% acetic and 5% formic acid, but insoluble in distilled water and 0.5 M NaOH; chit-GLA beads were insoluble in all tested media (Table 1). The high solubility of chitosan beads in dilute acetic and formic acid solutions to form a hydrogel is due to the primary amine groups on the chitosan backbone.

Table 1. Solubility of Chitosan and Chit-GLA Beads in Various Aqueous Media

Beads \ Solvent	Chitosan	Chit-GLA
5% Acetic acid	Soluble	Insoluble
5% Formic acid	Soluble	Insoluble
Distilled water	Insoluble	Insoluble
0.5 M NaOH	Insoluble	Insoluble

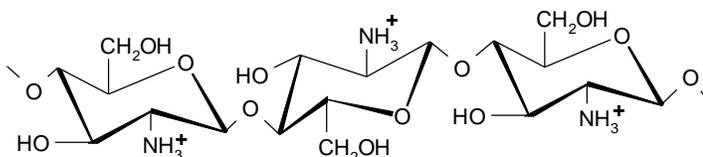
The swelling of chitosan was improved after cross-linking. The cross-linking treatment was required to reinforce the chemical stability of the beads in diluted acidic solution. The swelling percentages of chitosan and chitosan-GLA beads are specified in Table 2.

Table 2. Swelling Behavior of Chitosan and Chit-GLA Beads

Adsorbent	Percentage of swelling (%)			
	5% acetic acid	5% formic acid	Distilled water	0.1 M NaOH
Chitosan	Soluble	Soluble	37.9	34.7
Chitosan-GLA	15.8	11.3	13.1	9.8

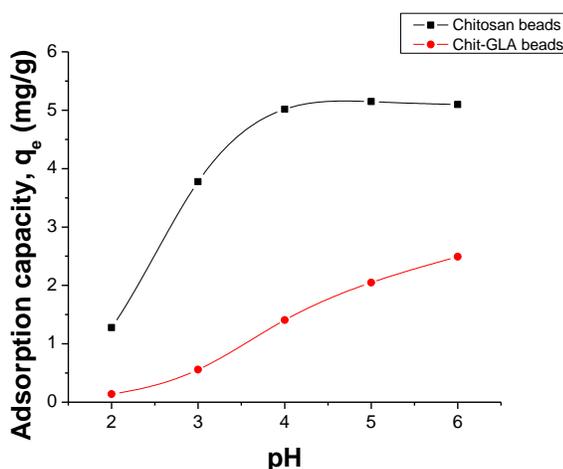
Effect of pH

Figure 3 shows the effect of pH on Cu(II) adsorption onto chitosan beads. The adsorption increased linearly along with the increase of pH of the Cu(II) solution. In acidic media (low pH), the primary amine groups were protonated with a positive charge, which electrostatically repels the cationic Cu(II) ions and inhibits their adsorption by the chitosan or chit-GLA beads.

**Fig. 3.** Chitosan in acidic environment

At pH values above 4.0, Hernandez and coworkers (2008) indicate that the complexation process is mainly through the amino group, owing to the stereochemical favorable position of the $-OH$ groups.

Similar adsorption capacities were observed for chitosan beads at pH values between 4.0 and 6.0. The chit-GLA beads exhibited their best adsorption capacity at pH 6.0. Furthermore, a pH of 6.0 was used for the rest of adsorption studies in order to prevent the formation of $Cu(OH)_2$ precipitate, which simultaneously occurs with the Cu(II) ion adsorption at pH values higher than 7.0. The formation of $Cu(OH)_2$ precipitate adversely affects chitosan or chit-GLA bead adsorption and lead to incorrect interpretation of adsorption data.

**Fig. 4.** Variation of adsorption capacity of Cu(II) ions on chitosan and chit-GLA beads as function of pH

Effect of Contact Time

The optimum contact time for Cu(II) ions adsorption onto chitosan and chit-GLA beads can be determined from the value of adsorption capacity yielded at a certain time. Figure 5 indicates the variation of adsorption capacity with contact time for an initial concentration of Cu(II) of 10^{-4} M, as this is the optimum one for which the maximum adsorption was achieved.

The adsorption of Cu(II) increased with contact time and eventually reached equilibrium, for an initial Cu(II) concentration of 10^{-4} M. Therefore, it may be stated that the optimum contact time for the adsorption of Cu(II) is 180 min for both chitosan and chit-GLA beads, under the experimental conditions tested in the work.

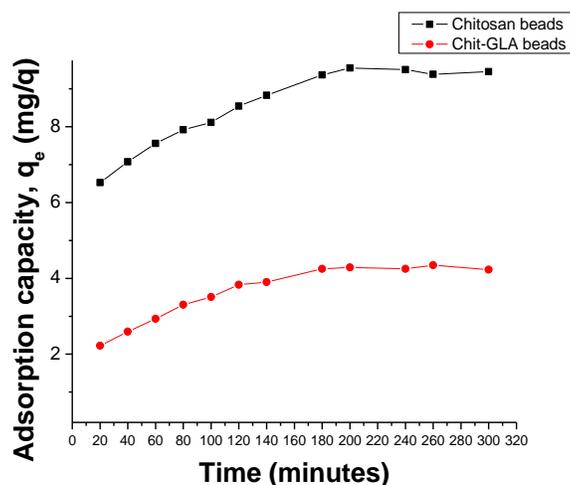


Fig. 5. Variation of adsorption capacity of Cu(II) ions on chitosan and chit-GLA beads as function of contact time

Effect of Adsorbent Dose

The investigations presented in both Figures 6 and 7 were performed under the same experimental conditions. Figure 6 shows the variation of adsorption capacity with adsorbent mass, chit-GLA beads for the initial Cu(II) ions concentration of 10^{-4} M. The amount of adsorbent used varied from 0.05 g to 1.00 g, while other parameters such as pH, concentration, contact time, and stirring rate were kept constant. A significantly reduced adsorption capacity for chit-GLA beads can be observed. The results revealed a plateau value of the adsorption capacity reached after 0.2 g of chit-GLA. Figure 7 illustrates the variation of adsorption capacity of the chitosan beads with the changes of the adsorbent dose for 10^{-4} M and 10^{-3} M concentrations of Cu(II) ions. Although the adsorption capacity was higher for Cu(II) 10^{-3} M solutions, the percentage of removal was much lower compared to Cu(II) 10^{-4} M solution. This suggests that a high number of free adsorption sites were available during the first stage of the process and then, as time passes, the free remaining sites were less and difficult to be occupied due to repulsive forces between the adsorbate particles. As a result, the binding capacity of the adsorbent tends to saturation giving a decreased overall removal percentage (Anbia and Ghaffari 2009; Kamble *et al.* 2008).

Regarding the adsorption capacity, even though the area exposed to adsorption increases along with the adsorbent dose, due to the fact that the quantity adsorbed does not increase proportionally (linearly) with the growth of the adsorbent quantity, the ratio

(adsorption capacity) between the mass of adsorbate (mg) and the mass of the adsorbent (g) decreases. When adsorbent and adsorbate from solution get in contact, the adsorption takes place rapidly in large amounts. Afterwards, as the adsorbate concentration diminishes quickly, the remaining particles in solution diffuse more slowly as a consequence of the rise of the diffusion path length and, thus, the adsorption is reduced.

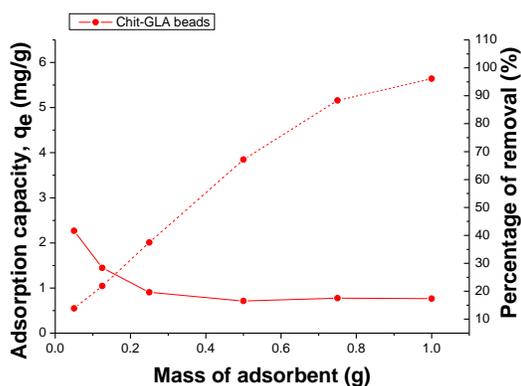


Fig. 6. Effect of adsorbent mass on adsorption capacity and percentage of removal of Cu(II) ions on chit-GLA beads for initial Cu(II) ions concentration of 10^{-4} M

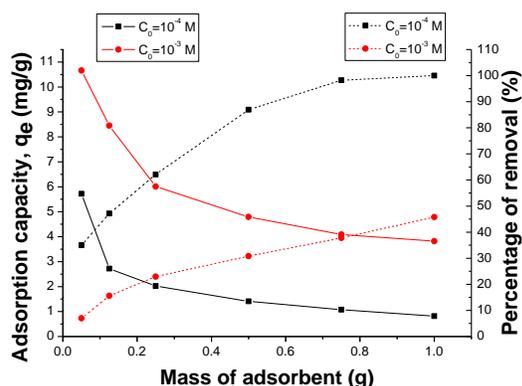


Fig. 7. Effect of adsorbent mass on adsorption capacity and percentage of removal of Cu(II) ions on chitosan beads for initial Cu(II) ions concentration of 10^{-4} M and 10^{-3} M

Adsorption Isotherms

Equilibrium isotherms are essential for describing the mechanism of adsorption for any adsorbent-adsorbate system. The equilibrium adsorption data of Cu(II) ions were subjected to four different adsorption isotherm models: Langmuir, Freundlich, Elovich, and Temkin. As an example, the experimental equilibrium isotherm, according to the Langmuir model, for the adsorption of Cu(II) ions onto chitosan and chit-GLA for an initial Cu(II) concentration of 10^{-4} M is given in Fig. 8.

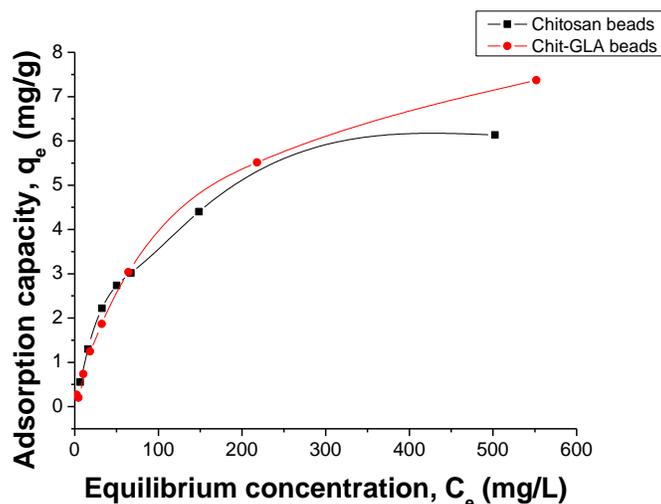


Fig. 8. Adsorption isotherm plot for the adsorption of Cu(II) ions onto chitosan and chit-GLA beads for an initial Cu(II) concentration of 10^{-4} M

The graphs in Fig. 9 present the linearized forms of the Langmuir, Freundlich, Elovich, and Temkin adsorption isotherm models for the adsorption of Cu(II) ions onto chitosan and chit-GLA for an initial Cu(II) concentration of 10^{-4} M.

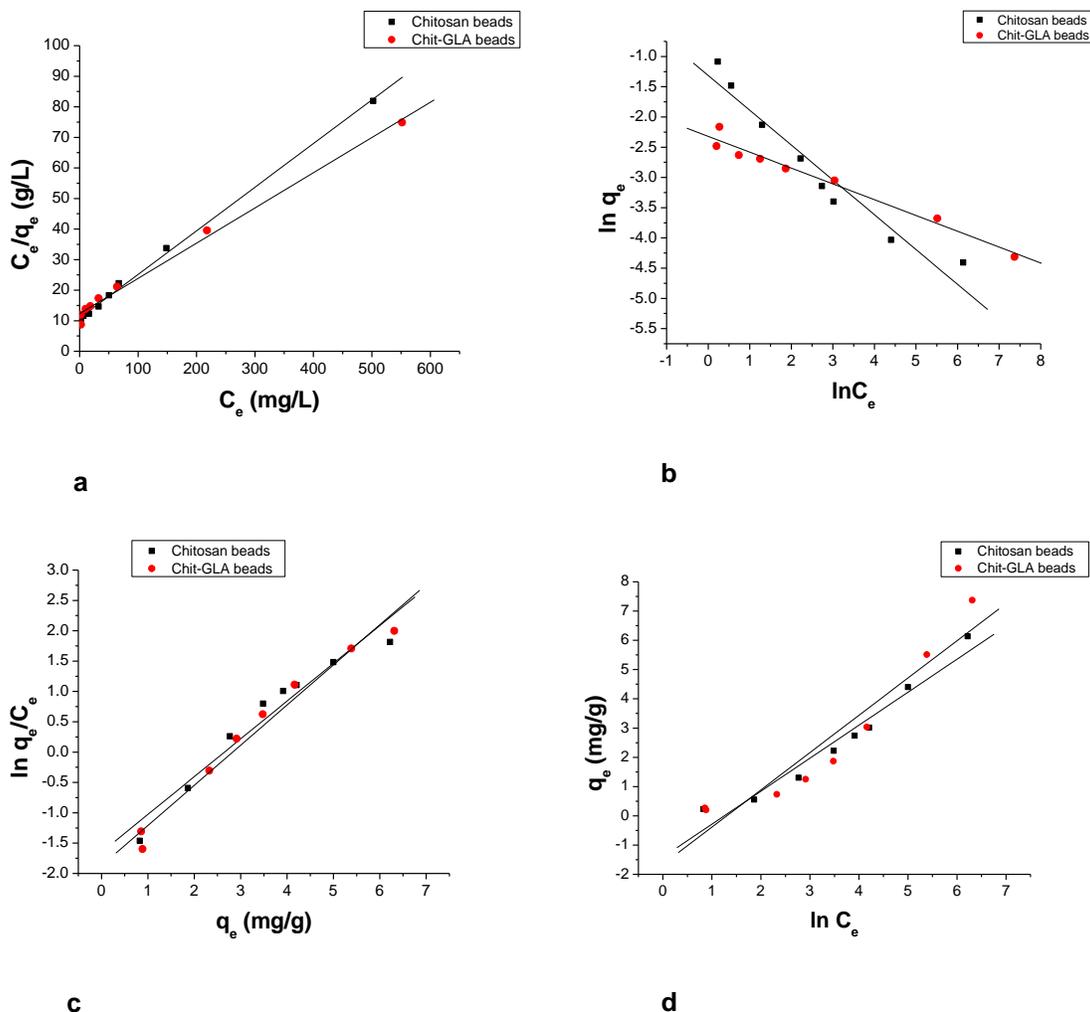


Fig. 9. Adsorption isotherms of Cu(II) ions on chitosan and chit-GLA beads, linearized according to (a) Langmuir, (b) Freundlich, (c) Elovich, and (d) Temkin models for an initial Cu(II) concentration of 10^{-4} M

Table 3 presents the calculated results. It can be observed that the Langmuir model was the best model for describing the Cu(II) ion adsorption on chitosan and cross-linked chitosan beads for the concentration range studied (correlation coefficient, $R^2 > 0.99$).

According to the Langmuir model for monolayer adsorption, the cross-linking treatment of chitosan diminished its adsorption performance by decreasing the number of free amine sites for binding Cu(II) ions since it is the amine groups that reacted with chitosan cross-linking agent, glutaraldehyde.

Table 3. Experimental Isotherm Constants and Coefficients of Determination

Adsorbent	Adsorption constants			
	<i>Langmuir model</i>			
	Q_m (mg/g)	b (mL/mg)	R_L	R^2
Chitosan	7.0025	0.0132	0.131	0.9975
Chit-GLA	8.6720	0.0094	0.162	0.9927
<i>Freundlich model</i>				
	K_F (mg ^{1-1/n} L ^{1/n} /g)	n	b_F	R^2
Chitosan	0.0224	1.6062	0.6226	0.9453
Chit-GLA	0.1540	1.5109	0.6619	0.9745
<i>Elovich model</i>				
	Q (mg/g)	K_E (L/mg)	R^2	
Chitosan	1.7365	0.1549	0.9403	
Chit-GLA	3.8222	0.0257	0.9717	
<i>Temkin model</i>				
	K_0 (L/mg)	R^2		
Chitosan	0.2858	0.9541		
Chit-GLA	0.2720	0.9078		

According to the Langmuir isotherm model, the maximum adsorption capacity (Q_m) of Cu(II) ions on chit-GLA beads reached a value a little higher than that on chitosan (8.672 mg/g on chit-GLA compared to 7.003 mg/g for adsorption on chitosan). The R_L values were 0.131 and 0.162 for the adsorption on chitosan and chit-GLA, respectively; these values were in the range of zero to one, which indicated favorable adsorption.

The adsorption parameters values for Freundlich isotherms are also presented in Table 3. The coefficients of determination were higher than 0.94, revealing a good agreement of experimental data with the Freundlich model. However, the R^2 values were lower compared to the Langmuir isotherm model. The b_F values for adsorptions on chitosan and chit-GLA were between 0 and 1, which indicated that chemisorption took place. The fact that b_F values were not very close to 0 indicated that the adsorption on the surface was more homogeneous than heterogeneous.

The Elovich modeling of the experimental data also indicated chemisorption (McLintock 1967) took place. High correlation coefficients were observed when the data were fitted to this model, especially for the case of chit-GLA beads. Nonetheless, the correlation coefficients were lower than those describing the Langmuir and Freundlich models. However, a correlation coefficient higher than 0.94, similar with that obtained for both chitosan and chit-GLA adsorptions, suggested that the adsorption of Cu(II) ions occurred by chemisorption. This was an expected result, considering that Cu(II) ions are bonded by a coordinate covalent bonds to chitosan structure, as presented in Fig. 2.

The Temkin model had the lowest values of correlation coefficient, which suggested that this model was not the best descriptor of Cu(II) ion adsorption onto chitosan and cross-linked chitosan. However, the model did indicate that Cu(II) adsorption is an exothermic process, since $\Delta Q > 0$ for both adsorbents.

Kinetic Studies

Plots of $\log(q_e - q_t)$ and t/q_t versus time t are given in Figs. 10a and 10b, respectively, for pseudo-first and pseudo-second kinetic models for the 10^{-4} M Cu(II) ion adsorption onto chitosan and chit-GLA beads. Both pseudo-first and pseudo-second

kinetic models showed a good linearity ($R^2 > 0.97$). Since pseudo-second order kinetics model had a higher correlation coefficient, it was chosen as the most appropriate kinetic model to describe the adsorption behavior. This observation was in good agreement with other literature data (Chiou and Li 2003). The values of the kinetic parameters are given in Table 4. Moreover, it can be seen that the theoretical value of the adsorption capacity ($q_{e \text{ theor}} 0.937$) is in good agreement with the experimental value ($q_{e \text{ exp}} 0.950$).

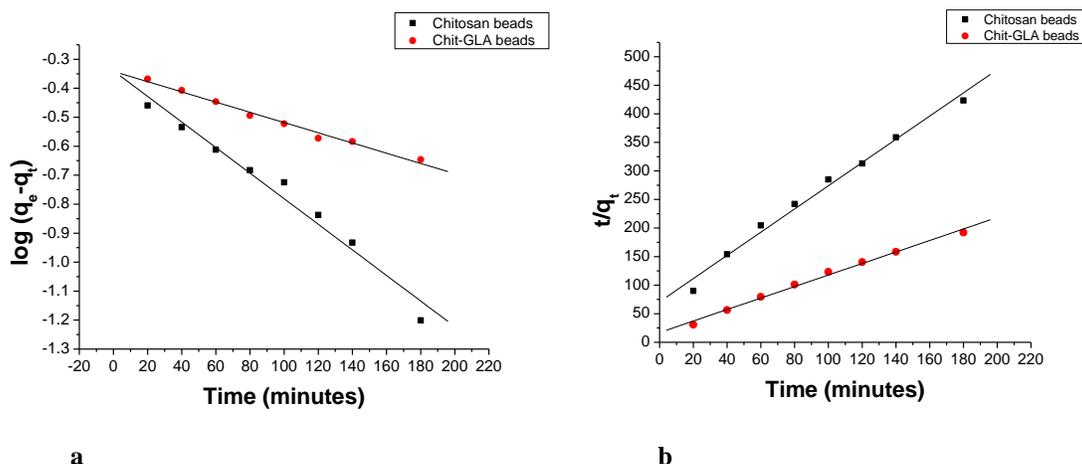


Fig. 10. Pseudo-first order plot (a) and pseudo-second order plot (b) for the adsorption of 10^{-4} M Cu(II) ions onto chitosan and chit-GLA beads

Table 4. Kinetic Parameters for 10^{-4} M Cu(II) ions onto Chitosan and Chit-GLA Beads

Adsorbant	Pseudo-first order		Pseudo-second order			
	k_1 (min^{-1})	R^2	k_2 ($\text{g mg}^{-1}\text{min}^{-1}$)	R^2	$q_{e \text{ exp}}$	$q_{e \text{ theor}}$
Chitosan	0.0175	0.9731	0.0596	0.9934	0.950	0.937
Chit - GLA	0.0041	0.9872	0.0582	0.988		

Desorption Studies

Desorption studies were performed in 10^{-2} M and 10^{-3} M EDTA solutions. Chitosan beads were soluble in $>10^{-2}$ M EDTA solutions; therefore, lower concentration of EDTA were used and provided good Cu(II) desorption from the beads. The cross-linking process increased the resistance of chit-GLA beads to dissolution in EDTA solutions. Desorption of Cu(II) from chitosan and cross-linked chitosan beads using 10^{-2} M and 10^{-3} M EDTA solutions is presented in Table 5 and it was calculated using Equation (15),

$$\text{Desorption}(\%) = \frac{C_d}{C_0} \times 100\% \quad (15)$$

where C_d is the copper concentration obtained after the desorption of copper from the EDTA solution, established by atomic absorption spectrometry, and C_0 is the initial concentration of the copper solution used to be adsorbed on chitosan and chit-GLA beads.

Table 5. Percentage Cu(II) Desorption from Complex Cu(II)-Chitosan and Cu(II)-Cross-Linked Beads

Concentration of EDTA (M)	Desorption (%)	
	Chitosan	Chit-GLA
1×10^{-2}	93.79	94.57
1×10^{-3}	74.58	79.44

CONCLUSIONS

1. A comparative study was performed regarding Cu(II) ion removal from 10^{-4} M and 10^{-3} M Cu(II) solutions by adsorption onto chitosan and glutaraldehyde cross-linked chitosan beads, respectively. Adsorption tests indicated that Cu(II) ions can be efficiently removed using chitosan and glutaraldehyde cross-linked chitosan beads. With respect to adsorption of Cu(II) from low-concentration solutions, our data were in general agreement with published reports. Our work clearly showed that although chitosan beads exhibited higher adsorption capacity than cross-linked chitosan beads, cross-linked chitosan beads can be used at low pH environments and exhibited a low degree of swelling.
2. Some initial tests indicated that copper adsorption from 10^{-4} M solutions occurred with better adsorption capacity and degree of removal than those obtained from 10^{-3} M solutions.
3. The mechanism of adsorption was best described by the Langmuir isotherm model.
4. The adsorption mechanism is given by chemisorption, which actually represents the rate controlling step. High correlation coefficients of the Elovich isotherm model, values between 0 and 1 of the b_F Freundlich constant, and pseudo-second order kinetics model, most fitting for the adsorption of Cu(II) ions onto chitosan and chit-GLA beads, support the chemisorption based mechanism.
5. Based on the experimental results obtained when applying Temkin isotherm model, one can state that copper adsorption process was an exothermic reaction.
6. Cu(II) ions recovery was successfully achieved when the beads were treated with an aqueous EDTA solution.
7. The quantification of Cu(II) ions in synthetic water samples was accurately measured using copper-sensitive electrode potentiometry. This method is less laborious and more rapid than other quantification methods, and is more suitable for processing large number of tests. Potentiometry is an accurate and time efficient alternative for quantifying Cu(II) ion compared to atomic absorption spectrometry methods.

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