

EQUILIBRIUM AND KINETICS OF COPPER ION ADSORPTION ONTO NATURAL AND CROSSLINKED CHITOSAN MEMBRANES

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Abstract

Fundamental investigation on adsorption of Cu(II) ions on natural and crosslinked chitosan membranes was performed. Batch adsorption experiments were used to determine the equilibrium and kinetics adsorption properties. The adsorption rate and the amount of adsorbed Cu(II) ions decreased when the adsorbent was crosslinked, especially in glutaraldehyde case. Experimental data were fitted to Langmuir model and the maximum adsorbed amount, at pH 5.0, were $198 \pm 8 \text{ mg.g}^{-1}$, $152 \pm 4 \text{ mg.g}^{-1}$ and $93 \pm 23 \text{ mg.g}^{-1}$, respectively to natural, epichlorohydrin-crosslinked and glutaraldehyde-crosslinked chitosan membranes (in dry basis). The kinetic data were adjusted to the pseudo first-order, pseudo second-order and intraparticle diffusion models. The pseudo second-order model presented a better correlation and intraparticle diffusion model shows different regions indicating that adsorption rate is possibly controlled by different mechanisms.

Introduction

Polysaccharide biopolymers isolated from marine organisms constitute a new class of adsorbents that present low cost, is environmentally benign and exhibit reactivity towards metal ions. Chitosan, a linear polysaccharide based on glucosamine unit, has been studied as a very promising material. It is obtained from deacetylation of chitin, which is the major component of crustaceans shells. It is one of the most available polysaccharide in nature. Chitosan has been described as a suitable biopolymer for removal of heavy metal ions from wastewater [1-15] since its chemical groups can act as chelation sites.

The presence of heavy metals in the environment is a subject of great concern because of their increasing waste volume, toxic nature and other adverse effects for water streams. The potential sources of copper in industrial effluents include metal cleaning and plating baths, paper and paper board mills, wood pulp production, etc [16]. Cu(II) ions are essential nutrients, required by the body in small quantities, but when people are exposed to copper levels of above 1.3 mg/l for short periods of time, stomach and intestinal problems can occur. Long-term exposure to Cu(II) ions leads to kidney and liver damage [17].

Several methods have been used to modify natural chitosan either physically or chemically. Crosslinking with glutaraldehyde (GLA) or epichlorohydrin (ECH) are examples of chemical modifications on chitosan. Since glutaraldehyde binds to amino groups and epichlorohydrin binds preferentially to hydroxyl groups, it is possible to use both crosslinking processes to better understanding the adsorption mechanism [4], identifying the chemical functionality, which is responsible for metal-chitosan interaction. Figures 1 (A) and (B) show the possible structures formed by crosslinking using glutaraldehyde and epichlorohydrin, respectively.

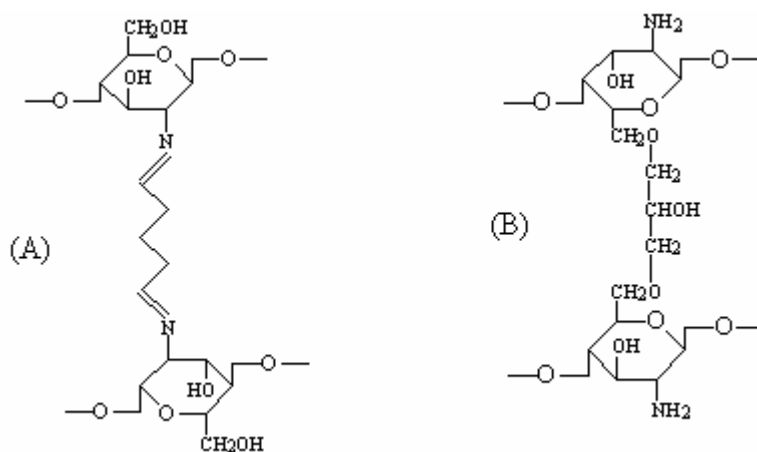


Figure 1 : Possible structures formed by crosslinking using glutaraldehyde (A) and epichlorohydrin (B)

The aim of this study was to compare equilibrium and kinetic behavior of Cu(II) ions on natural and crosslinked chitosan membranes. The influence of experimental conditions of Cu(II) ion concentration and the type of crosslinking was evaluated. The experimental equilibrium parameters, such as maximum adsorption amount and the Langmuir dissociation constant, were obtained by fitting experimental data to the Langmuir equation. The constants of adsorption rate were obtained by using three different models, to identify the limiting steps in the adsorption models.

Material and Methods

Materials. Chitosan with molecular weight 9.90×10^5 g/mol was purchased from Sigma (USA). All other chemicals (copper sulfate, glutaraldehyde, epichlorohydrin) were of analytical grade. Aqueous solutions were prepared using deionized water (Milli-Q ultrapure water).

Preparation and chemical modification of chitosan membranes. In order to obtain porous membranes, a chitosan solution of 2.5 % (w/w) was spread on a Petri dish. The dish was kept at 60°C until a reduction of 50 % of its initial weight. The membranes were then immersed in NaOH solution (1 mol/L) during 24 h for neutralization, followed by rinsing with Milli-Q water. The membranes were then stored in Milli-Q water at 4°C .

Natural (pristine) chitosan membranes were heterogeneously crosslinked in 0.75 % (w/w) aqueous glutaraldehyde solution (3.0 g of wet chitosan membrane in 50 mL of glutaraldehyde solution), without agitation, at room temperature for 2 h, followed by rinsing with deionized water to remove the unreacted glutaraldehyde residue. The molar ratio glutaraldehyde/ NH_2 was 5.0. For crosslinking with epichlorohydrin the procedure was: 3.0 g of wet natural chitosan membranes were immersed in 50 mL of epichlorohydrin solution 0.01 mol/L (prepared in NaOH solution 0.067 mol/L) at 40°C under continuous agitation for 2 h [18]. After this period, the membranes were rinsed with deionized water to remove unreacted epichlorohydrin. The molar ratio of epichlorohydrin/ NH_2 was 0.02.

Adsorption Experiments. Copper solution was prepared by dissolving 1.47 g of copper sulfate hydrated ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 1.0 L of Milli-Q water, obtaining a stock solution of 375 mg/L of Cu(II) ions. This solution was adjusted to pH 5.0 with NaOH solution (0.1 mol/L) and was then diluted to obtain the standard solutions (37.5 mg/L-375mg/L).

Batch kinetic experiments were carried out by soaking 1.2 g of natural or crosslinked chitosan membranes in 100 mL of Cu(II) solution (150 and 375 mg/L) at pH 5.0, 25°C and under stirring of 150 rpm. The samples were withdrawn at fixed time intervals and analyzed for copper content with atomic absorption spectrophotometer (Perkin Elmer Analyst 100) in air-acetylene flame. The adsorption capacity of chitosan was calculated based on the difference of Cu(II) concentration of bulk solution, after fixed time and the initial concentration.

Batch equilibrium experiments were conducted by soaking 0.30 g of natural or crosslinked chitosan membranes in 25 mL of Cu(II) solution (ranging from 37.5-375 mg/L) at pH 5.0, for 60 hours at 25°C under stirring. The time of 60 h was chosen from the kinetic behavior of Cu(II) ions on chitosan membranes. The concentrations of Cu(II) ions in the supernatant were analyzed with

atomic absorption spectrophotometer. The adsorption capacity of chitosan was calculated based on the difference of Cu(II) concentration in bulk solution before and after adsorption.

Results and Discussion

Properties of Chitosan Membranes. Some properties of natural and crosslinked chitosan membranes are shown in Table 1. The porosity of the adsorbent (ϵ_{ads}) was obtained as described by Zeng and Ruckenstein, 1996 [19]. This was determined by measuring the amount of water within the pores, by weighing the wet adsorbent before and after extracting the water that filled the pores with a vacuum pump for 20 min. A reduction in porosity after the crosslinking was observed; this occurrence may be associated with a decrease in the crystallinity of the adsorbent as a result of alkyl group introduction by crosslinking reactions [20]. The conversion factors of wet-base to dry-base for chitosan membranes were measured by weighing the wet adsorbent, which was freeze-dried and weighed again. This conversion factor is important in order to allow a comparison between the results from this investigation and the experimental data from the literature, where the majority of data are presented as dry-basis results.

Table 1: Properties of natural and crosslinked chitosan membranes

	Width (mm)	Diameter (cm)	Porosity	Conversion Factor in dry-base
Natural Chitosan	1.83±0.07	15.2±0.2	74.7 ± 6.7	93.9
ECH-Chitosan	1.94±0.05	14.6±0.1	50.7 ± 12.9	93.1
GLA-Chitosan	1.93±0.12	14.8±0.4	43.9 ± 8.7	91.5

Figure 2 shows the general aspect of chitosan membranes before and after Cu(II) adsorption. The natural and epichlorohydrin-crosslinked chitosan membranes after Cu(II) adsorption showed a strong blue color, resulting from interaction between the coordination sphere of copper and amino groups of chitosan [21]. The glutaraldehyde-crosslinked chitosan membrane presented yellow color, which indicates the formation of double bounds [22] and imino bounds. The glutaraldehyde-crosslinked chitosan membrane after copper adsorption presented a green color [23].

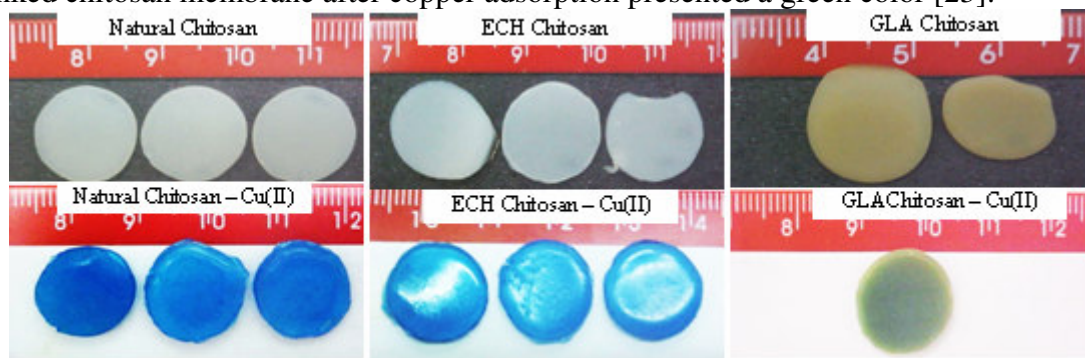


Figure 2 : Macroscopic aspect of chitosan membranes before and after Cu(II) adsorption

Adsorption Kinetics of Cu(II) Ions. The adsorption kinetics involves several steps including diffusion and reaction processes [24-26]. Four steps can be considered for copper ion removal: (a) *Bulk diffusion* — copper ion transfer from the bulk solution to the boundary film surrounding the sorbent surface; (b) *Film diffusion* — copper ion transport from the boundary film to the surface of the sorbent; (c) *Intraparticle diffusion* — transfer of the copper(II) ion from the surface to the intraparticle active sites; (d) *Chemical Interaction* — uptake of the metal ion on the active sites, via chelation, ion-exchange or complexation [27]. In order to investigate the rate and the constants of adsorption of copper ions on chitosan three different models were tested.

For calculating the rate constant of pseudo first-order adsorption [28], the Equation 1 can be used.

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} t \quad (1)$$

K_1 (L/h) is the pseudo first-order adsorption rate constant, Q_e is the amount of copper ions adsorbed at equilibrium (mg/g wet chitosan) and Q_t is the amount of copper ions at time t (mg/g wet chitosan). The ordinate intercept of $\log(Q_e - Q_t)$ against t should be equal to $\log(Q_e)$. This is an important criterion for the validation of the modeling. The used Q_e was that obtained from Langmuir model, based on experimental equilibrium data.

Ho and McKay [29-31] proposed a pseudo second-order adsorption, based on the adsorption equilibrium capacity, as described in Equation 2.

$$\frac{dQ_t}{dt} = K_2 \cdot (Q_e - Q_t)^2 \quad (2)$$

Equation (2) can be, after integration, rearranged to obtain the linear form given in Equation 3.

$$\frac{t}{Q_t} = \frac{1}{K_2 \cdot Q_e^2} + \frac{1}{Q_e} \cdot t \quad (3)$$

where K_2 is the pseudo second-order rate constant and Q_e is the amount of copper ions adsorbed at equilibrium (mg/g wet chitosan). These constants can be determined by plotting (t/Q_t) against t .

The rate parameter of intraparticle diffusion can be defined as [32]:

$$Q_t = K_i \cdot t^{0.5} \quad (4)$$

where K_i is intraparticle diffusion rate constant ($\text{mg/g.h}^{0.5}$) and is calculated from the slopes of the straight line portions of the respective plots.

The adsorption kinetic curves were adjusted to the pseudo first-order adsorption, pseudo second-order adsorption and intraparticle diffusion, as described in the Equations 1, 3 and 5, respectively. For the pseudo first-order $\log(Q_e - Q_t)$ was plotted versus t , using Q_e obtained from the Langmuir equation. This figure was not showed, only the parameters obtained (Table 2). In the case of pseudo second-order equation, t/Q_t was plotted versus t (Figure 3) while for intraparticle diffusion of the adsorbed capacity at time t Q_t was plotted versus $t^{0.5}$ (Figure 4). The constants of adsorption rate K_1 , K_2 and K_i can be determined using these graphs. Table 2 summarizes the adsorption rate constants and their corresponding correlation coefficients R^2 , obtained by the least square method.

Table 2: Adsorption rate constants and their corresponding R^2 correlation coefficients for the three different kinetics adsorption models

	C_i^0 mg/L	Pseudo first-order Model			Pseudo second-order Model			Intraparticle Diffusion Model			
		Q_e mg/g	$K_1 \times 10^3$ L/min	R^2	Q_e mg/g	$K_2 \times 10^4$ g/mg.min	R^2	$K_{i,1} *$	R_1^2	$K_{i,2} *$	R_2^2
Natural Chitosan	150	8.94	0.22	0.78	8.53	5.2	0.998	1.83	0.95	0.18	0.92
	375	5.75	0.30	0.78	8.34	9.9	0.998	2.64	0.83	0.48	0.93
ECH-Chitosan	150	2.48	0.47	0.67	5.76	2.1	0.993	2.06	0.96	-	-
	375	3.05	1.50	0.64	10.12	9.6	0.997	3.10	0.91	-	-
GLA-Chitosan	150	5.22	14.0	0.88	9.90	8.2	0.997	0.93	0.83	0.24	0.73
	375	6.74	30.0	0.94	8.80	8.2	0.999	2.28	0.90	0.18	0.52

* ($\text{mg/g.min}^{0.5}$)

From Table 2 the Q_e values obtained from pseudo first-order model are much lower than experimental equilibrium data obtained from Langmuir model (Table 3). Their low correlation coefficients and the pattern of residuals suggest that the reaction is not of the first order. The pseudo second-order model shows the highest correlation coefficients and calculated Q_e are similar to the ones obtained from experimental equilibrium data.

The modelling of experimental data using the intraparticle diffusion equation [32] shows the coexistence of two linearized regions characterized by two constants ($K_{i,1}$ and $K_{i,2}$). The initial slope is higher than that of the second section, indicating the contribution of two successive and different mechanisms. The second set of data on epichlorohydrin crosslinked chitosan could not be adjusted to the linear model.

These different sections in these graphs can be associated to different chemical or physical restrictions, as film effect, intraparticle diffusion or chemical interaction. To investigate if the diffusion-controlled-mechanism is predominant, experiments with different thickness of the membranes will be performed in order to evaluate the contribution of intraparticle diffusion.

Although high correlation coefficients were obtained for the pseudo second-order model, it is not possible to affirm if the overall rate of the Cu(II) ions adsorption on chitosan membranes is controlled by chemical process or physical diffusion, being necessary the analyse the intraparticle diffusion model in a more detailed way.

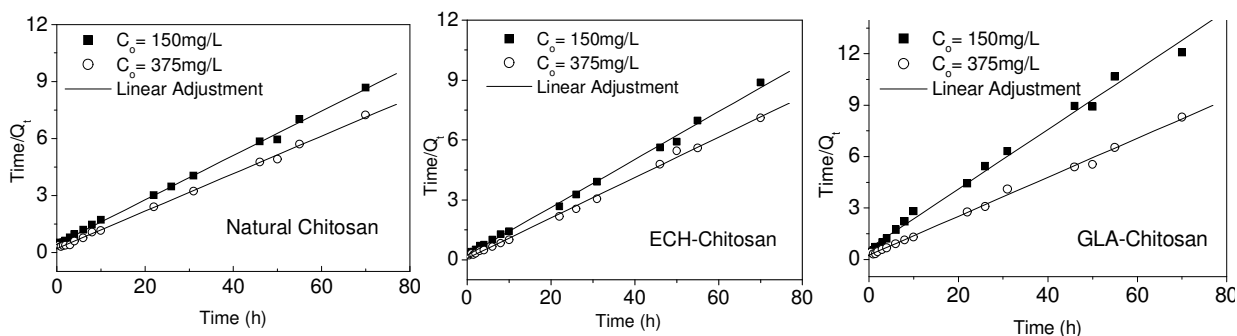


Figure 3 : Adsorption kinetic curves adjusted to the pseudo second-order model for natural, epichlorohydrin-crosslinked and glutaraldehyde-crosslinked chitosan membranes

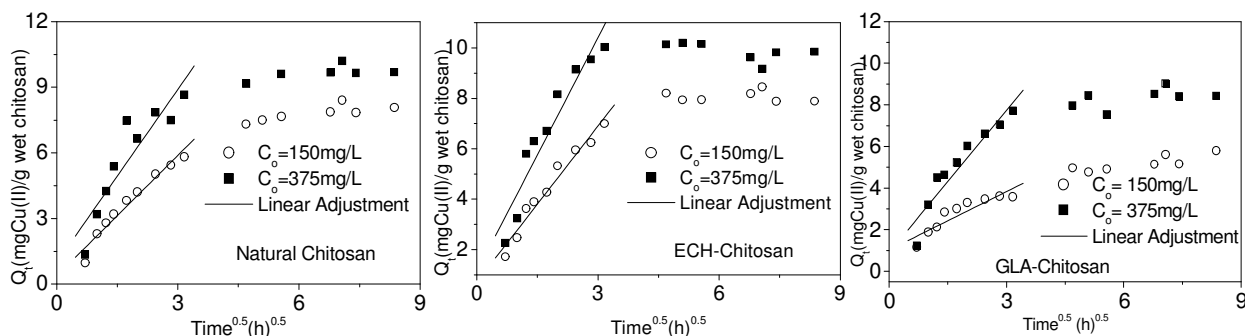


Figure 4 : Adsorption kinetic curves adjusted to the intraparticle diffusion model for natural, epichlorohydrin-crosslinked and glutaraldehyde-crosslinked chitosan membranes

Equilibrium Adsorption of Cu(II) Ions. Langmuir model [33] was used to describe the data obtained for the equilibrium of Cu(II) adsorbed onto natural and crosslinked chitosan (Equation 5).

$$Q = \frac{Q_e \cdot k \cdot C_e}{1 + k \cdot C_e} \quad (5)$$

where C_e is the final Cu(II) concentration (mg/L), Q_e (mg/g wet chitosan) is the maximum amount adsorbed on a monolayer at equilibrium and k (L/mg) is the Langmuir constant, which is related to the adsorption energy.

Table 3 shows Langmuir equilibrium constants and the correlation coefficients R^2 (to check the statistical quality of data fitting), which were obtained by the least square method. The equilibrium data are also presented in dry-base, since the membrane water content differed in each material. It is then possible to compare the results with the experimental data from literature, since the most data are presented in dry-basis. Figures 5 (A), (B) and (C), exhibit the adsorption isotherms for Cu(II) ions on natural, epichlorohydrin-crosslinked and glutaraldehyde-crosslinked chitosan membranes, at pH 5.0, as described by the Langmuir model. The fitting can be considered as good, taking into account the variability that each piece of chitosan membrane may have, from pore size to deacetylation degree.

Table 3: Parameters of the Langmuir model fitted to the experimental adsorption data

		Langmuir Model			
	pH	Q_e (mg.g ⁻¹ wet chitosan)	Q_e (mg.g ⁻¹ dry chitosan)	k (L.mg ⁻¹)	R ²
Natural Chitosan	5.0	12.1±0.5	198±8	0.073±0.018	0.932
ECH-Chitosan		10.5±0.3	152±4	0.113±0.024	0.937
GLA-Chitosan		7.9±2.0	93±23	0.011±0.008	0.964

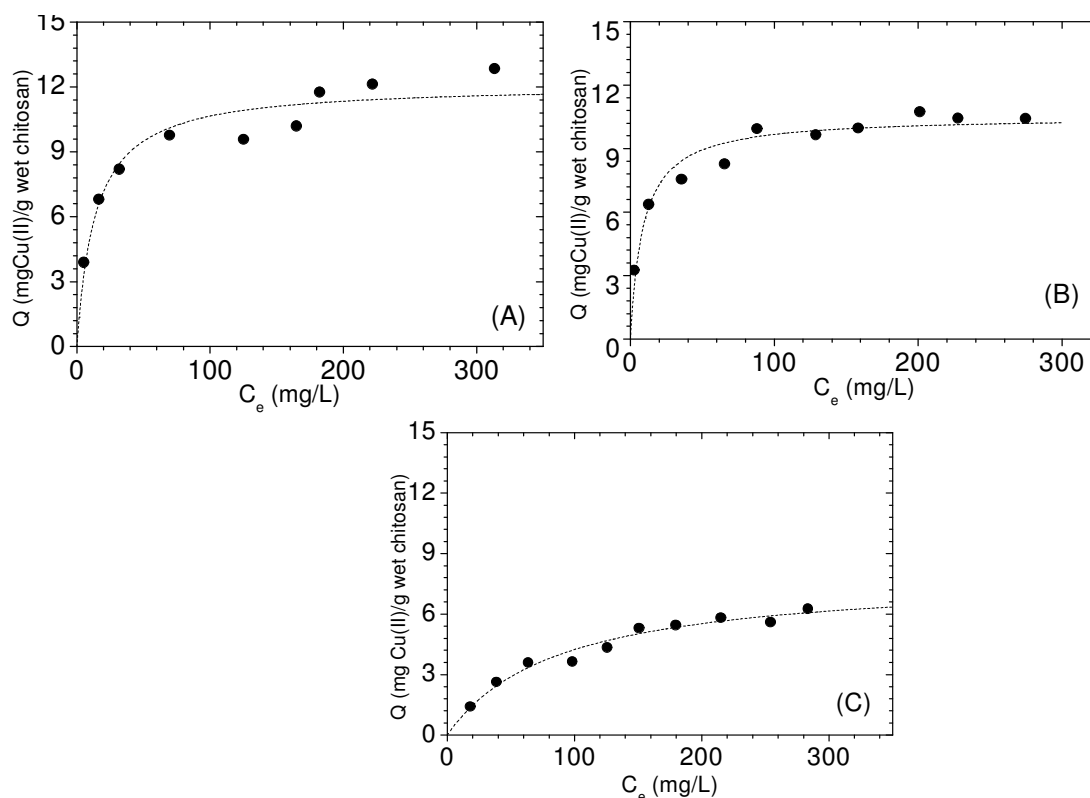


Figure 5 : Isotherms of Hg(II) ion adsorption on natural (A), glutaraldehyde-crosslinked (B) and epichlorohydrin-crosslinked (C) chitosan membranes, at pH 5.0. The line represents the Langmuir model

The crosslinking treatment decreases adsorption performances probably by decreasing the number of free amino groups. This result is different from that showed by Vieira and Beppu [1-3] that showed the increase of Hg(II) adsorption, after glutaraldehyde-crosslinking reaction. This means that the structure resulting from amino and glutaraldehyde reaction (imine bond) remains capable to adsorb Hg(II) ions.

In the case of epichlorohydrin-crosslinked chitosan the hydroxyl groups on chitosan are blocked by the crosslinking treatment, which decrease slightly the adsorption capacity, indicating that the interaction of Cu(II) ions and chitosan occur either on amino and hydroxyl groups.

These adsorption results could be compared with other studies presented in the literature. Nghah *et al.*, 2002 [8] evaluated the Cu adsorption capacity as approximately 80.7, 62.5, 59.7 mg.g⁻¹ for dry natural, epichlorohydrin-crosslinked and glutaraldehyde-crosslinked chitosan beads, respectively. In this study, a higher adsorption capacity for the membranes was observed probably due to the fact that chitosan concentration is higher in the membranes than in beads, since its preparation methodology required the chitosan solution to dry until a reduction of 50% gravimetric weight.

Conclusions

The present study confirms that natural and crosslinked chitosan membranes can be used for removal of Cu(II) ions from aqueous solutions. The natural membranes showed higher adsorption capacity than the values observed for crosslinked chitosan membranes, but crosslinked chitosan membranes can be used in acidic solutions. The highest adsorption capacity values were observed when the amino groups were not blocked, but available to interact with ions copper in solution. The kinetic data revealed that the overall rate for Cu(II) adsorption is possibly controlled by different mechanisms, as chemical process and physical limitation. This aspect will be analyzed doing kinetic experiments with different thickness of the chitosan membranes.

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References

- [1] R.S. Vieira, M.M. Beppu, *Adsorption*, 11 (2005) 731-736.
- [2] R.S. Vieira, M.M. Beppu, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 279(2006) 196-207.
- [3] R.S. Vieira, M.M. Beppu, *Water Res.*, 40(8) (2006) 1726-1734.
- [4] E. Guibal, *Sep. Purif. Technol.*, 38 (2004) 43-74.
- [5] M.M. Beppu, E.J. Arruda, R.S. Vieira, N.N. Santos, *J. Memb. Sci.*, 240 (2004) 227-235.
- [6] J.D. Merrifield, W.G. Davids, J.D. MacRae, A. Amirbahman, *Water Res.* 38(13) (2004) 3132-3138.
- [7] K.H. Chu, *J. Hazardous Mater.*, B90 (2002) 77-95.
- [8] W.S.W. Ngah, C.S. Endud, R. Mayanar, *React. Funct. Polym.*, 50 (2002) 181-190.
- [9] S. Babel, T.A. Kurniawan, *J. Hazardous Mat.*, B97 (2003) 219-243.
- [10] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, *Water Res.*, 33 (1999) 2469-2479.
- [11] R. Bassi, S.O. Prasher, B.K. Simpson, *Sep. Sci. Technol.*, 35(4) (2000) 547-560.
- [12] Penichecovas, L.W. Alvarez, W. Argüelles-Monal, *J. Appl. Polym. Sci.*, 46 (1992) 1147-1150.
- [13] E. Guibal, M. Jansson-Charrier, I. Saucedo, P. Le Cloirec, *Langmuir*, 2 (1995) 591-598.
- [14] Y. Kawamura, M. Mitsuhashi, H. Tanibe, H. Yoshida, *Ind. Eng. Chem. Res.*, 32 (1993) 386-391.
- [15] E. Onsoyen, O. Skaugrud, *J. Chem. Technol. Biotechnol.*, 49 (1990) 395-404.
- [16] V.K. Gupta, *Ind. Eng. Chem. Res.* 37 (1998) 192-202.
- [17] G.C. Steenkamp, K. Keizer, H.W.J.P. Neomagus, H.M. Krieg, *J. Memb. Sci.* 197 (2002) 147-156
- [18] Y.C. Wei, S.M. Hudson, J.M. Mayer, D.L. Kaplan, *J. Polym. Sci. – Part A: Polym. Chem.*, 30(1992) 2187-2193.
- [19] X. Zeng, E. Ruckenstein, *Ind. Eng. Chem. Res.*, 35 (1996) 4169-4175.
- [20] Y. Koyama, A. Taniguchi, C.P. Huang, D.W. Blakeship, *J. Appl. Polym. Sci.*, 31 (1986) 1951-1954.

- [21] L. Dambiens, C. Guimon, S. Yiacoumi, E. Guibal, Colloids and Surfaces A: Physicochem. Eng. Aspects, 177 (2001) 203-214.
- [22] H. Rhazi, J. Desbrieres, A. Tolaimate, M. Rinaudo, P. Vottero, A. Alaguai, Polymer, 43 (2002) 1267-1276.
- [23] G.A.F. Roberts, "Chitin Chemistry", The Macmillian Press Ltd, London, 1992
- [24] W. Fritz, W. Merk, E.U. Schlunder, Chem. Eng. Sci., 36 (1981) 731–741.
- [25] D.W. Hand, J.C. Crittenden, W.E. Thacker, J. Environ. Eng. Div., 109 (1983) 82–101.
- [26] G. McKay, Chem. Eng. Sci., 39 (1984) 129–138.
- [27] S.T. Lee, F.L. Mi, Y.L. Shen, S.S. Shyu, Polymer, 42 (2001) 1879-1892.
- [28] S. Lagergren, Kungliga Svenska Vetenskapsakademiens. Handlingar, 24(4) (1898) 1–39.
- [29] Y.S. Ho, G. McKay, Process Biochemistry, 34 (1999) 451-465
- [30] Y.S. Ho, G. McKay, Chem. Eng. Sci., 55 (2000) 817-825.
- [31] Y.S. Ho, G. McKay, Chem. Eng. J., 70 (1998) 115-124.
- [32] W.J. Weber Jr., J.C. Morris, Advances in Water Pollution Research, Pergamon Press, New York (1962) 231–266.
- [33] I. Langmuir, J. Am. Chem. Soc., 40 (1918) 1361-1403.