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Mercury Ion Recovery Using Natural and Crosslinked Chitosan Membranes

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Abstract. The adsorption and desorption of Hg(II) ions onto natural and crosslinked chitosan membranes were investigated. Batch adsorption experiments were carried out as function of pH, concentration of Hg(II) ions, type of crosslinking (glutaraldehyde (GLA) or epichlorohydrin (ECH)) and desorbent solution (NaCl (1M) or EDTA (10^{-4} M)). Isotherm studies indicated that Hg(II) ions can be effectively removed by chitosan membranes, mainly by the glutaraldehyde-crosslinked chitosan, at pH = 6.0, and can be easily removed by elution with NaCl (1M) solution.

Keywords: adsorption, desorption, chitosan, crosslinking, mercury

1. Introduction

Contamination of water by heavy metal ions is becoming a serious ecological and health hazard due to their toxic effects even at very low concentrations (Rapsomanikis and Craig, 1991). Mercury, which is very toxic, can be introduced into natural environment from a variety of sources, where it can be converted into more toxic forms.

Several methods exist for removal of toxic metals from aqueous solution such as ion-exchange, reverse osmosis, adsorption, complexation and precipitation (Crist et al., 1996; Huang and Blankenship, 1984; Juang and Shao, 2002). Adsorption is an effective and economical method for removal of pollutants from wastewater (Ng et al., 2002). The capacity of adsorption of several low-cost-adsorbents has been investigated, mainly biopolymers, which are obtained from renewable sources, present relatively low-cost and selectively adsorbs several metallic ions (Hsien e Rorrer, 1999).

Among these biopolymers, chitosan has been investigated as a very promising material. Chitosan is a linear polysaccharide based on a glucosamine unit (Fig. 1). It is obtained from deacetylation of chitin, which is the major component of crustaceans shells and is the second most abundant biopolymer in nature. Chitosan was described as a suitable biopolymer for removal of metal ions from wastewater (Bassi et al., 2000; Chu, 2000; Ngah et al., 2000), since the amino and hydroxyl groups present on chitosan chain can act as chelation sites.

Several methods have been used to modify natural chitosan either physically or chemically. Crosslinking with glutaraldehyde (GLA) or epichlorohydrin (ECH) can be cited as examples of chemical modifications promoted on chitosan. These reactions are done in order to prevent its dissolution in acidic solutions or to improve metal sorption properties (to increase sorption capacity or to enhance sorption selectivity). As glutaraldehyde tends to crosslink chitosan bonding though the amino groups and epichlorohydrin does it preferably through the hydroxyl groups, it is possible to understand the adsorption mechanism (Guibal, 2003), identifying which chemical functionality is responsible for metal-chitosan interaction.

The aim of this study was to compare the adsorption and desorption behavior of Hg(II) ions on natural and crosslinked chitosan membranes. The influence of experimental conditions such as pH, Hg(II) ion

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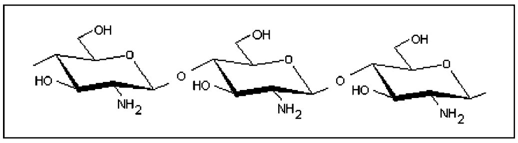

Figure 1. Molecular structure of chitosan.

concentration, type of crosslinking and type of desorbent was evaluated.

2. Materials and Methods

2.1. Materials

Chitosan was purchased from Sigma (USA) with molecular weight and deacetylation degrees of 9.90×10^5 and 82%, respectively. All other chemicals (mercuric chloride, glutaraldehyde, epichlorohydrin) were of analytical grade. The aqueous solutions were prepared in deionized water (Milli-Q ultrapure water).

2.2. Preparation and chemical modification of membranes chitosan

In order to obtain membranes, a chitosan solution 2.5% (w/w) was spread on a Petri dish. The dish was kept at 60°C, until a reduction of 50% in its initial weight was reached. The membranes were then immersed in NaOH solution (1 M), for 24 h to neutralize amino groups, followed by rinsing and storage in water at 4°C.

The 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, then it was rinsed with deionized water to remove the unreacted glutaraldehyde residues. In the epichlorohydrin crosslinking process 3.0 g of wet natural chitosan membranes were immersed in 0.01 M epichlorohydrin solution, which was prepared in 0.067 M NaOH solution, at 40°C under continuous agitation for 2 h (Wei et al., 1992), it was rinsed with deionized water to remove the unreacted epichlorohydrin.

2.3. Adsorption and Desorption Experiments

Mercury solution was prepared by dissolving 0.5 g of mercuric chloride ($HgCl_2$) in 1.0L of phosphate buffer solution (0.2 M), pH 5.0, 6.0 and 7.0, obtaining a stock solution of 375 ppm of Hg(II) ions. This solution was then diluted to obtain the standard solutions (375–37.5 ppm).

Batch adsorption experiments were conducted by soaking 0.30 g of natural or crosslinked chitosan membranes in 25 mL of Hg(II) solution (ranging from 375–37.5 ppm) at pH 5.0, 6.0 and 7.0, for 24 hours, under stirring, at room temperature and in a gas tight container, in order to avoid changes in concentration of the solution. The concentrations of Hg(II) ions in the supernatant were analyzed by UV-Visible spectrophotometer method (Snell et al., 1959). The adsorption capacity of chitosan was calculated based on difference of Hg(II) concentration in the bulk of solution before and after adsorption, as depicted in Equation 1.

$$Q = \frac{V^*(C_i - C_f)}{W} \tag{1}$$

where Q is the amount of Hg(II) ions adsorbed by the wet chitosan membranes ($mg.g^{-1}$), V is the volume of Hg(II) solution (L), C_i is the initial Hg(II) concentration (ppm), C_f is the final Hg(II) concentration (ppm) and W is the weight of adsorbent (in our case, weighed in wet base, in grams).

In the desorption experiments, chitosan membranes were immersed in 15 mL of either NaCl 1 M or EDTA 10^{-4} M solution for 24 h under a stirring. The bulk metal concentration in solution was measured as previously described. These experiments were performed in order to evaluate the possibility to recover metal through desorption and to understand the nature of interaction between metal and chitosan.

3. Results and Discussions

3.1. Properties of Chitosan Membranes

Some properties of natural chitosan membranes were determined and are shown in Table 1.

The morphology of fracture surface was observed by scanning electron microscopy, SEM, (Fig. 2) and the micro porous structure of these membranes could be confirmed.

Table 1. Properties of natural chitosan membranes.

	Aspect	Width (cm)	Diameter (cm)	Porosity
Natural chitosan	Opaque	0.11	1.80	51.0 ± 1.36

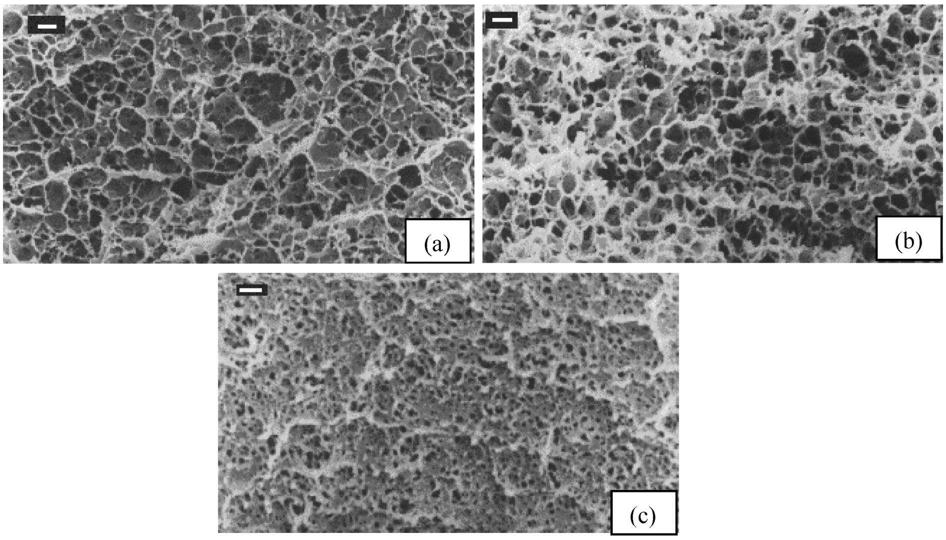

Figure 2. SEM of fracture surface in natural (a), epichlorohydrin-crosslinked (b) and glutaraldehyde-crosslinked (c) chitosan membranes. Bars correspond to 1 μm.

3.2. Adsorption and Desorption Study

Langmuir and Henry adsorption isotherms were used to analyze thermodynamical equilibrium of Hg(II) onto natural and crosslinked chitosan. Henry model approximates Langmuir isotherm behavior for low bulk concentrations. Equations 2 and 3 show Henry and Langmuir models, respectively.

$$Q = K_H^* C_f \tag{2}$$

$$Q = \frac{Q_{\max} * k^* C_f}{1 + k^* C_f} \tag{3}$$

where K_H is Henry model equilibrium constant (partition coefficient) ($\text{L} \cdot \text{g}^{-1}$), $Q_{\max}$ ($\text{mg} \cdot \text{g}^{-1}$) is the maximum amount adsorbed on a monolayer and k ($\text{L} \cdot \text{mg}^{-1}$) is the Langmuir dissociation constant, which is related to adsorption energy. The product $Q_{\max} * k = K_l$, is Langmuir equilibrium constant ($\text{L} \cdot \text{g}^{-1}$).

Table 2 shows Henry equilibrium constants and their correspondent R^2 adjustment coefficients, which were obtained through a linear regression of the lowest equilibrium concentration points in each of the bioadsorbents, in pH 5.0, 6.0 and 7.0. The range for linear adjustment was chosen up to the value that still provided an acceptable (higher than 0.8) R^2 coefficient. Through this method, only low concentration data were used to determine Henry equilibrium constants, as its equation is only valid in this range. $Q_{\max}$, k, K_L and the R^2 coefficient were obtained by the application of least squares method for Langmuir model, which values are shown in Table 2, at each pH. Fig. 3(a)–(c), depict the adsorption isotherms for Hg(II) ions on natural, epichlorohydrin (ECH) and glutaraldehyde (GLA)-crosslinked chitosan membranes, at pH 5.0, adjusted by Langmuir model. The behaviors of curves were similar for pH 6.0 and 7.0.

From Table 2, it is possible to observe that the Langmuir equilibrium constant was normally higher than Henry's. Hence, it is probable that the real adsorption phenomenon has more factors involved than those predicted by Henry's model. The regression coefficients obtained for Langmuir model were normally higher than those obtained for Henry's, indicating a better fit to the experimental system.

The maximum adsorption amount increased from pH 5.0 to 6.0 and decreased to pH 7.0 in all cases. This could be explained by the fact that in low pH, chitosan amino groups are easily protonated, which induced an electrostatic repulsion with Hg(II) ions. Therefore, competition existed between positively charged amino groups and Hg(II) ions for adsorption sites and adsorption capacity was decreased (Ngah et al., 2002). At higher pH values, the maximum adsorption amount can decrease at higher pH values. Juang and Shao (2002) attribute this fact to the uncoordinated –OH groups on chitosan chains, which become –O– at high pH, leading to an

Table 2. Langmuir and Henry parameter adjusted for experimental points.

		Langmuir Model				Henry Model	
	pH	$Q_{\max}$ ($mg \cdot g^{-1}$)	k ($L \cdot mg^{-1}$)	K_L ($L \cdot g^{-1}$)	R^2	K_H ($L \cdot g^{-1}$)	R^2
Natural chitosan	5.0	16.13	5.42×10^{-2}	0.874	0.911	0.403	0.543
	6.0	25.35	3.54×10^{-2}	0.897	0.919	0.827	0.815
	7.0	24.70	7.25×10^{-2}	1.791	0.921	0.755	0.876
ECH-chitosan	5.0	16.26	6.21×10^{-2}	1.010	0.902	0.556	0.859
	6.0	30.33	4.61×10^{-2}	1.398	0.858	1.431	0.785
	7.0	22.88	1.51×10^{-1}	3.455	0.860	2.417	0.869
GLA-chitosan	5.0	22.30	6.59×10^{-2}	1.470	0.922	0.933	0.918
	6.0	75.47	1.30×10^{-2}	0.980	0.910	1.035	0.901
	7.0	37.55	4.59×10^{-2}	1.723	0.806	1.187	0.958

increase in the degree of solubility of metal-chitosan complexes.

From comparing natural and glutaraldehyde-crosslinked chitosan, an increase in maximum adsorption amount is noticed for the latter even assuming the amino group blockage. According to Hsien and Rorrer (1995), the crosslinking can enlarge the space between the chitosan chains improving the accessibility of amino groups for metal ions. Therefore, an increase in the maximum adsorption amount can be interpreted in terms of the decrease of crystallinity caused by crosslinking (Koyama and Taniguchi, 1986). Kurita et al. (1979) also cites that crystallinity is a key parameter in the accessibility of internal sites for metallic ions and many studies have been trying to demonstrate that a decrease in crystallinity can improve adsorptive characteristics (Hsien and Rorrer, 1995). Another explanation was provided by Monteiro and Airoldi (1999) that studied the adsorption of Cu(II) ions on natural and crosslinked chitosan proposed that the structure resulting from the primary amino and glutaraldehyde reaction (imine bond) is also capable of adsorbing metallic cations. This idea was demonstrated through the presence of a peak in IR spectra at 1384 cm^{-1}, indicating that even after crosslinking the cation was still adsorbed by the polymeric matrix.

From the comparison between the results of natural and epichlorohydrin-crosslinked chitosan, it is possible to observe similar results, indicating that the interaction of metal and chitosan probably does not occur through the hydroxyl groups, as the results did not change when this group was blocked by crossliking.

The Table 3 depicts the desorption percentage using EDTA (10^{-4} M) and NaCl (1.0 M) solution as eluents at pH 6.0. Higher values are observed for NaCl when compared to EDTA indicating that possibly the adsorption follows an electrostatic interaction, being influenced by the ionic strength of solutions.

The low percentage of desorption obtained by using EDTA solution, in opposition to the known fact that Hg(II) ions are easily complexed by EDTA, suggests that the adsorption mechanism does not occur by chelation of the metallic species on chitosan. On the other hand, the high percentages of desorption obtained when NaCl solution was used for desorption indicates that the adsorption is preferentially electrostatic nature: the desorption promoted by NaCl solution can be explained through the compression of the double electric layer of Hg(II) ions promoted by charged species in solution.

It was possible to observe low percentage of desorption on glutaraldehyde-crosslinked chitosan membranes. This fact can be explained by the reduction of available amino groups, increasing the hidrophobicity of chitosan and causing a stronger repulsive effect of negative species.

Table 3. Percentage of desorption of Hg(II) on chitosan.

	EDTA (10^{-4} M)	NaCl (1 M)
Natural chitosan	52.318 ± 25.757	73.143 ± 15.855
ECH-chitosan	50.531 ± 28.448	86.649 ± 5.925
GLA-chitosan	19.905 ± 6.085	43.210 ± 30.031

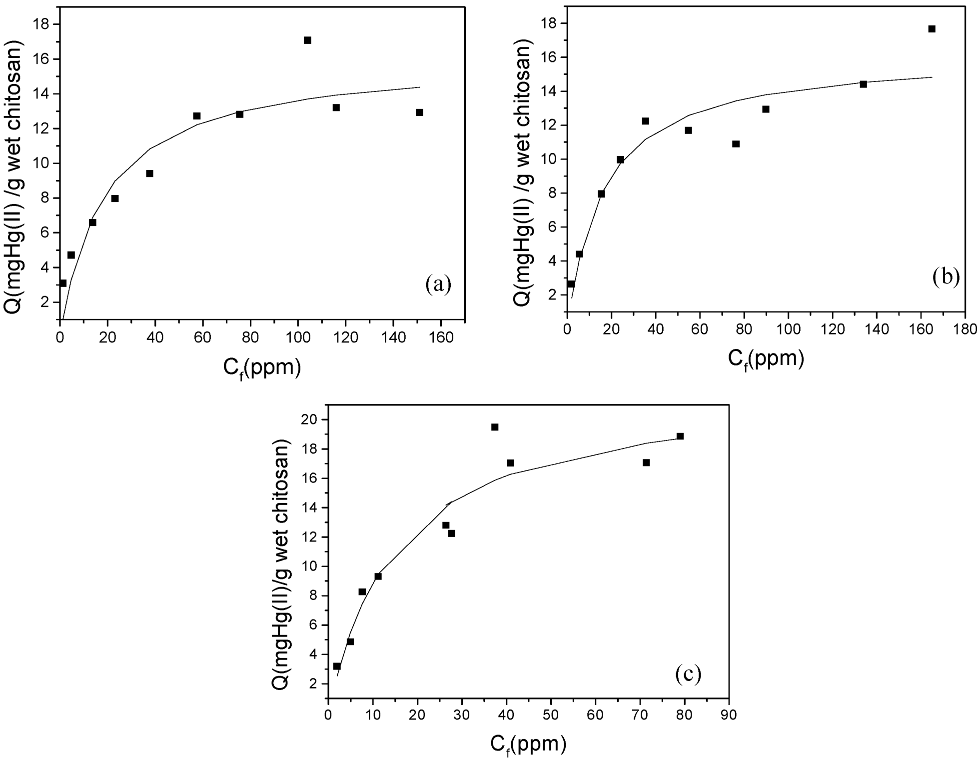

Figure 3. Isotherms of Hg(II) ion adsorption on natural (a), epichlorohydrin -crosslinked (b) and glutaraldehyde-crosslinked (c) chitosan membranes. The line represents the Langmuir model adjusted for experimental points.

4. Conclusions

In this study, we observed the viability of natural and crosslinked chitosan membranes for removal of Hg(II) ions aqueous solutions. The amount of adsorption and desorption was influenced by some parameters as the initial Hg(II) concentration, pH of solution, type of crosslinking and desorbent solution. The maximum adsorption amount was observed on glutaraldehyde-crosslinked chitosan, at pH 6.0. However, it presents low percentage of recovery. Besides having a greater adsorption capacity, it is chemically stable at low values of pH, allowing its use in acidic solution and continuous stages of adsorption and desorption.

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