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Adsorption and desorption of binary mixtures of copper and mercury ions on natural and crosslinked chitosan membranes

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Abstract Copper and mercury ion adsorption on chitosan membranes was investigated in batch systems (with both single and binary solutions). The Langmuir model and its extensions (extended Langmuir, Jain-Snoeyink, and Langmuir-Freundlich models) were tested for the modeling of experimental data. Chitosan membranes presented more affinity for Hg ions than for Cu ions. The decrease of the amount of metal adsorbed on natural chitosan in binary systems (compared to single-metal solutions) showed the competition effects between the two metal ions. For glutaraldehyde-crosslinked chitosan and epichlorohydrin-crosslinked chitosan, the mixture effect was present, producing unexpected result such as higher adsorption capacities, when compared to the monocomponent solution of each metal. The desorption of the metals was also investigated, and copper and mercury ions could be selectively recovered using a combined process by using NaCl and H_2SO_4 as eluant.

Keywords Copper · Mercury · Chitosan · Multicomponent adsorption

Abbreviations

b_i	heterogeneity parameter for each component, dimensionless
C	concentration of the singe component at equilibrium, mmol·L^{-1}
C_i	concentration of each component at equilibrium, mmol·L^{-1}
E_i	root mean square error
K	monocomponent Langmuir adsorption constant of the single component, L·mmol^{-1}
K_i	individual Langmuir adsorption constant of each component, L·mmol^{-1}
Q	adsorbed amount of the single component per gram of dried chitosan membrane at equilibrium, mmol·g^{-1} dry chitosan
Q_i	adsorbed amount of each component per gram of dried chitosan membrane at equilibrium, mmol·g^{-1} dry chitosan
$Q_{\max}$	maximum adsorbed amount of the single component per gram of dried chitosan membrane at equilibrium, mmol·g^{-1} dry chitosan
$Q_{\max,i}$	maximum adsorbed amount of each component per gram of dried chitosan membrane at equilibrium, mmol·g^{-1} dry chitosan
Q_i^{mod}	calculated maximum amount adsorbed of each component adsorbed
n	number of experimental data
R^2	adjustment coefficients from minimum square method for Langmuir model

1 Introduction

The contamination of waste streams due to the uncontrolled discharge of industrial wastewaters has induced considerable changes in the regulations regarding effluent treatments. National regulatory agencies are considering with increased attention, the potential impact of heavy metals on

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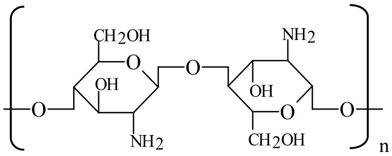

Fig. 1 Molecular structure of chitosan

health and environmental quality. Heavy metal ions, due to their high level of toxicity, their ability to be incorporated in the food chain and their poor biodegradability, are part of the most hazardous group of compounds, requiring treatment before being discharged in the environment to meet the strict environmental quality standards.

Several treatments can be used for metal recovery including precipitation, solvent extraction or sorption (on resins, activated carbon, mineral sorbents). These processes frequently meet limitations such as poor efficiency (not enough to reach low concentrations levels for precipitation, for example) or poor competitiveness (solvent extraction for dilute effluents). Low-cost adsorbents (biomass, agriculture residues, etc.) represent a promising alternative to conventional sorbents. Biopolymers have been calling an increasing attention of researchers in the last decades, due to their availability (as a renewable resource) and their remarkable ability to bind metal ions (Ngah et al. 2002).

Chitosan, an aminopolysaccharide, is prepared by the deacetylation of chitin, which is the major component of crustacean shells and one of the most abundant biopolymers in nature. This biopolymer was widely investigated for adsorption of heavy metal ions (Chu 2002; Guibal 2004; Juang and Shao 2002; Kawamura et al. 1997; Onsoyen and Skaugrud 1990; Vieira and Beppu 2005, 2006a, 2006b). Its chelating properties are attributed to the amino and hydroxyl groups in chitosan chain (Fig. 1), that can act as chelation sites for different metal cations at near neutral pH. The protonation of amino groups in acidic solutions gives to the biopolymer cationic properties; this cationic behavior allows metal-containing anions to be preferably bound through electrostatic attraction mechanisms.

The solubility of chitosan in acidic media (except in sulfuric acid) requires a crosslinking treatment to prevent polymer degradation. Crosslinking reactions with chitosan are performed using specific bifunctional chemicals (glutaraldehyde and epichlorohydrin) that react with specific groups of the biopolymers. Glutaraldehyde preferably reacts with amino groups (through Schiff's base reaction) while epichlorohydrin reacts with hydroxyl groups (although there is the possibility of epichlorohydrin also reacting with amino groups).

Most of the studies dedicated to metal ion sorption on chitosan materials are performed using synthetic mono-component solutions. Since real effluents are generally constituted of metal mixtures, it is important to study the selectivity of the process proceeding to the binding of metal ions from multi-component solutions. The purpose of this study was to investigate the adsorption of two heavy metal ions (Cu and Hg) mixed together, onto natural and crosslinked chitosan membranes. The influence of experimental conditions, e.g. metal ion concentration (Cu and Hg), individually or in mixture, and crosslinking agent (glutaraldehyde and epichlorohydrin) were evaluated on sorption isotherms. The Langmuir model was used for the modeling of experimental data (from single-component solutions). Different models, including the extended Langmuir equation and the so-called Jain-Snoeyink and Langmuir-Freundlich models were used to characterize the simultaneous adsorption of Cu and Hg ions from bi-component solutions in order to evaluate the competition of different metal ions on chitosan chelation sites. Desorption experiments were performed in two steps, using NaCl solution and then H_2SO_4 solution, with the objective of recovering selectively these species.

1.1 Equilibrium models

The adsorption isotherms serve to establish the solute distribution (alone or in mixture) between the liquid and the solid phases at equilibrium. The equilibrium constants allow the comparison of the affinity for different systems using objective criteria.

The most widely applied isotherm for equilibrium data modeling is the Langmuir equation (Langmuir 1918) given by (1):

$$Q = \frac{Q_{\max} \cdot K \cdot C}{1 + K \cdot C} \tag{1}$$

where C is the equilibrium metal concentration (mmol/L), $Q_{\max}$ (mmol/g dry chitosan) is the maximum amount adsorbed on a monolayer at equilibrium and K (L/mmol) is the Langmuir adsorption constant, which is related to the adsorption energy.

Several isotherms have been proposed in order to describe equilibrium and competitive distribution of multi-component adsorptions systems. For example, Markhan and Benton (1931) developed a model for binary adsorption systems, based on the Langmuir equation; that is generally called extended Langmuir isotherm.

$$Q_i = \frac{Q_{\max,i} * K_i * C_i}{1 + \sum_{j=1}^{N} K_j * C_j}(2) \tag{2}$$

where Q_i is the amount adsorbed of each component adsorbed per unit weight of adsorbent at equilibrium concentrations C_i. $Q_{\max,i}$ is the maximum adsorbed amount for each component (mmol/g dry chitosan), respectively. K_i is the individual Langmuir adsorption constants of each component (L/mmol).

Jain and Snoeyink proposed another model, based on the extended Langmuir model, for the simulation of sorption from binary systems. This proposed model includes a new term based on the hypothesis that, in a multicomponent system, adsorption occurs both with and without competition. It is assumed that the number of adsorption sites for which there was no competition is given by the difference $Q_{\max,1} - Q_{\max,2}$, where $Q_{\max,1} > Q_{\max,2}$. This model adds a competition term in the (2), as described in (3).

$$Q_1 = \frac{(Q_{\max,1} - Q_{\max,2}) * K_1 * C_1}{1 + K_1 * C_1} + \frac{Q_{\max,2} * K_1 * C_1}{1 + K_1 * C_1 + K_2 * C_2} \tag{3}$$

The first term on the right side of (3) is the Langmuir expression for the adsorbed amount of species 1 that adsorb without competition proportional to $Q_{\max,1} - Q_{\max,2}$. The second term represents the amount of species 1 adsorbed on the surface area, proportional to $Q_{\max,2}$, under competition with species 2, and is based on the Langmuir model for competitive adsorption. The adsorbed amount of species 2 adsorbed on surface area proportional to $Q_{\max,2}$ under competition with species 1 can be calculated with (2).

Another possible approach is the extended Langmuir–Freundlich model for binary system as described in (4) and (5).

$$Q_1 = \frac{Q_{\max,1} * (K_1 * C_1)^{b_1}}{1 + (K_1 * C_1)^{b_1} + (K_2 * C_2)^{b_2}} \tag{4}$$

$$Q_2 = \frac{Q_{\max,2} * (K_2 * C_2)^{b_2}}{1 + (K_1 * C_1)^{b_1} + (K_2 * C_2)^{b_2}} \tag{5}$$

where K_1 and K_2 (L/mmol) are the average association constants and b_1 and b_2 (dimensionless) are the heterogeneity parameters (Ruthven 1984). The Langmuir-Freundlich model treats the adsorbent surface as having an energetically heterogeneous sites, in which K is the average affinity constant. This model is considered to be purely predictive, where the capacity, heterogeneity and affinity parameters used are obtained from single-component behavior.

The mono-component adsorption parameters were not used to simulate the adsorption behavior of binary systems. Experimental binary data were used to determine the isotherm parameters. This was done numerically, for each equilibrium model, using the simplex optimization method for non-linear equation, minimizing the objective function (E_i).

$$E_i = \sum_{i=1}^{n} \left(\frac{Q_{1,i}^{\exp} - Q_{1,i}^{\mathrm{mod}}}{Q_{1,i}^{\exp}} \right)^2 + \sum_{i=1}^{n} \left(\frac{Q_{2,i}^{\exp} - Q_{2,i}^{\mathrm{mod}}}{Q_{2,i}^{\exp}} \right)^2 \tag{6}$$

$Q_j^{\exp}$ is the experimental maximum adsorbed amount of each component, Q_j^{mod} is the calculated maximum adsorbed amount of each component and n is the number of experimental data.

2 Materials and methods

2.1 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 immersed in a solution of NaOH (1 mol/L) for 24 hours to neutralize the amino groups. The membranes were exhaustively washed with distilled water until all alkali was removed. The membranes were then stored in water (Beppu and Santana 2003).

Raw chitosan membranes were heterogeneously crosslinked by contacting with a 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 unreacted glutaraldehyde residues. The crosslinking with epichlorohydrin was performed by contact wet raw chitosan membranes (3.0 g), which were immersed in 50 mL of a 0.01 M epichlorohydrin solution (prepared in 0.067 M NaOH solution) maintained at 40 °C, under continuous agitation for 2 h (Wei et al. 1992). Afterwards, the membranes were rinsed with deionized water to remove unreacted epichlorohydrin.

2.2 Adsorption and desorption experiments

Copper or mercury stock solutions were prepared by dissolving hydrated copper sulfate ($CuSO_4 \cdot 5H_2O$) or mercuric chloride ($HgCl_2$). These solutions were adjusted to the desired pH using NaOH or H_2SO_4 solutions (0.1 mol/L) and were then diluted to obtain the standard solutions.

Batch adsorption experiments were carried out by soaking 0.30 g (wet base) of raw or crosslinked chitosan membranes with 25 mL of copper or mercury solution at pH 5.0, during 60 h, at 20 °C and 150 rpm stirring rate. Metal concentration in the supernatant was analyzed by inductively coupled plasma atomic emission spectrometry (using a JY 2000 spectrometer, Jobin-Yvon, Longjumeau, France). For single metal systems, the initial metal concentration was varied from 50 to 750 mg/L for mercury and 20 to 200 mg/L for copper. For binary metal systems, one metal concentration was kept constant (25 or 50 mg/L for Hg or Cu) and the concentration of the other metal was varied (50 to 750 mg/L for Hg ions and 30 to 300 mg/L for Cu ions).

Metal desorption was performed by contact of loaded membranes with NaCl (1 mol/L) and H_2SO_4(0.1 mol/L) solution as eluant. Desorption experiments were conducted by

Table 1 Parameters of the Langmuir model fitted to the Cu and Hg experimental adsorption data

	Langmuir model					
	Copper			Mercury		
	Q_{maxCu} (mmol·g^{-1})	K_{Cu} (L·mmol^{-1})	R^2	Q_{maxHg} (mmol·g^{-1})	K_{Hg} (L·mmol^{-1})	R^2
Natural chitosan	2.0 ± 0.1	14.1 ± 2.5	0.96	2.9 ± 0.1	13.7 ± 1.5	0.97
GLA-chitosan	2.8 ± 0.1	1.0 ± 0.1	0.99	3.3 ± 0.1	4.7 ± 0.6	0.98
ECH-chitosan	2.3 ± 0.1	9.1 ± 1.4	0.97	3.5 ± 0.2	7.4 ± 1.3	0.96

using NaCl (1 mol/L) and H_2SO_4 (0.1 mol/L) solution as eluant. These experiments were performed by immersing the chitosan membranes in 15 mL of eluant solution for 24 h with stirring at 150 rpm speed. The bulk metal concentration in solution was measured as previously described. For binary systems, this process was conducted in two stages, initially by using NaCl solution (24 h) and finally H_2SO_4 solution (24 h), in order to evaluate the possibility of concentrating and selectively separate the metal species.

3 Results and discussion

3.1 Monocomponent adsorption results

Initially, in order to understand how the metallic species are in aqueous solution, a distribution of mercury and copper species as function of pH, for a defined metal ion concentration, was simulated using HYDRA (Hydrochemical Equilibrium-Constant Database) software (Puigdomenech 2004). Mercury speciation presents mostly the forms $HgCl_2$, $Hg(OH)_2$ and HgClOH at pH 5.0, and not the Hg free cationic form. In these same conditions, the majority of copper ions are present in cationic form, such as Cu^{2+}. These findings are very useful to understand if the adsorption mechanism would take place mainly by chelation or electrostatic interaction. At pH 5.0, a significant amount of chitosan amino groups are protonated as NH^{3+}. In this case, the mercury adsorption would mainly be controlled by electrostatic interaction and cooper adsorption would occur by chelation.

The Langmuir model was used to describe the monocomponent equilibrium data of mercury and copper adsorption on raw and crosslinked chitosan membranes. Table 1 summarizes the Langmuir constants and the correlation coefficients R^2 (to check the statistical quality of data fitting), which were obtained by the least square method.

The adsorption capacity for mercury ions was higher than for copper ions on chitosan membranes. This fact can be correlated with the ionic radii: Cu(II) (0.73 Å) $<$ Hg(II) (1.02 Å). These results are consistent with those given by Choy and McKay (2005), using bone char for Cu and Cd sorption. They showed that adsorption capacity for Cu ions is higher than for Cd ions. This trend follows the reversed order of hydrated ionic radii (Cu^{2+} (4.19 Å) $>$ Cd^{2+} (4.26 Å)), electronegativity (Cu^{2+} (1.90) $>$ Cd^{2+} (1.69)) and is proportional to ionic radii ((Cu^{2+} (0.73 Å) $<$ Cd^{2+} (0.95 Å)). Lee and Moon (2001) studied the metallic ions adsorption on natural zeolites; they observed that the selectivity follows the order $Cs^+ \gg Pb^{2+} > Cd^{2+} \geq Cu^{2+}$, which was associated with the reserve order of hydrated ionic radii [Cs^+ (3.30 Å) $>$ Pb^{2+} (4.01 Å) $>$ Cu^{2+} (4.19 Å) $>$ Cd^{2+} (4.26 Å)].

The highest sorption capacities were found for crosslinked chitosan. According to Hsien and Rorrer (1995) the crosslinking causes an increase in the space between the chitosan chains, which is responsible for the improvement in the accessibility of the metal ions to amino groups. In this way, an enhancement in the adsorption capacity can be interpreted as the result of the increase in the accessibility of metal ions to sorption sites. Koyama et al. (1986) attribute this enhancement of sorption capacities for crosslinked materials to the partial destruction of the crystalline structure. According to Kurita et al. (1979) the crystallinity has a fundamental role in the accessibility of adsorbent groups to metallic ions. Many studies have concluded that when crystallinity is reduced, the adsorptive capacity is improved. Kurita et al. (1986) observed an improved adsorption capacity for copper ions on chitosan beads. Monteiro and Airoldi (1999) also studied the adsorption of copper ions on natural and crosslinked chitosan and found that the structure resulting from the primary amino and glutaraldehyde reaction (imine bond) is also capable of adsorbing metallic cations.

3.2 Adsorption from bi-component solution

In order to describe the equilibrium data and to obtain the competitive effect of mercury and copper ions on natural and crosslinked chitosan membranes, the extended Langmuir, Jain-Snoeyink, and Langmuir-Freundlich models were fitted to experimental data. In these systems, the metal concentration of one component was kept constant (25 or 50 mg/L for

Table 2 Parameters of the equilibrium modeling data on natural chitosan with variable initial mercury concentration and fixed copper concentration

Natural chitosan	Hg	Cu (mg/L)	Extended-Langmuir model						
	Changed		$Q_{\max,1}$ (mmol/g)	$Q_{\max,2}$ (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	E		
		25	0.49	3.73	55.1	35.6	4.80		
		50	0.81	3.20	168.5	183.9	3.18		
			Jain & Snoeyink model						
			$Q_{\max,1}$ (mmol/g)	$Q_{\max,2}$ (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	E		
		25	0.43	2.52	54.2	15.7	4.02		
		50	0.77	2.29	41.9	21.74	2.35		
			Langmuir-Freundlich model						
			$Q_{\max,1}$ (mmol/g)	$Q_{\max,2}$ (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	b_1	b_2	E
		25	0.38	4.80	51.1	24.9	0.539	0.704	4.02
		50	0.80	3.56	195.4	69.2	1.546	0.988	2.29

Table 3 Parameters of the equilibrium modeling data on glutaraldehyde-crosslinked chitosan with variable initial mercury concentration and fixed copper concentration

GLA-chitosan	Hg	Cu (mg/L)	Extended-Langmuir model						
	Changed		$Q_{\max,1}$ (mmol/g)	$Q_{\max,2}$ (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	E		
		25	0.13	8.32	132.5	99.5	5.91		
		50	8.01	2.95	0.085	10.12	4.16		
			Jain & Snoeyink model						
			$Q_{\max,1}$ (mmol/g)	$Q_{\max,2}$ (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	E		
		25	0.11	9.56	262.3	3.68	3.77		
		50	2.10	2.06	0.57	23.08	3.05		
			Langmuir-Freundlich model						
			$Q_{\max,1}$ (mmol/g)	$Q_{\max,2}$ (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	b_1	b_2	E
		25	0.54	2.99	0.70	142.7	1.8×10^{-4}	1.42	2.31
		50	14.80	2.48	0.03	12.60	5.2×10^{-4}	0.98	2.06

Hg or Cu) and the concentration of the other one was varied. Tables 2, 3 and 4 show the model parameters adjusted using the three models, where the initial mercury concentration changed and initial copper concentration was kept constant (25 mg/L and 50 mg/L) on raw, glutaraldehyde-crosslinked and epichlorohydrin-crosslinked chitosan membranes. The results obtained for the experiments with variable copper concentration and fixed mercury concentration were similar (not shown).

For natural chitosan, $Q_{\max,2} > Q_{\max,1}$ was observed, so that the mercury ions (species 2) were more adsorbed than the copper ions, indicating a stronger interaction between

Table 4 Parameters of the equilibrium modeling data on epichlorohydrin-crosslinked chitosan with variable initial mercury concentration and fixed copper concentration

ECH-chitosan	Hg	Cu (mg/L)	Extended-Langmuir model						
	Changed		$Q_{\max,1}$ (mmol/g)	$Q_{\max,2}$ (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	E		
		25	5.87	3.08	2.48	5.57	0.63		
		50	1.96	3.30	10.4	6.68	0.40		
			Jain & Snoeyink model						
			$Q_{\max,1}$ (mmol/g)	$Q_{\max,2}$ (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	E		
		25	3.05	2.70	5.18	9.51	0.29		
		50	0.97	2.75	52.9	8.48	0.07		
			Langmuir-Freundlich model						
			$Q_{\max,1}$ (mmol/g)	$Q_{\max,2}$ (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	b_1	b_2	E
		25	6.56	2.92	2.87	4.91	1.09	0.86	0.30
		50	1.77	3.52	10.9	4.81	1.02	0.80	0.07

the first species and the biopolymer. These results are in accordance with the study of mono-component solutions, which indicated that mercury ions presented an increased affinity for chitosan membranes when compared to copper ions. The adsorbed amount of copper ions in binary systems was significantly reduced when compared to the single system, indicating a reduction of the active sites for adsorption, attributed to the competition of mercury ions.

For glutaraldehyde-crosslinked and epichlorohydrin-crosslinked chitosan, an expected behavior was not observed in the studied range of adsorbate concentration. In some cases, the adsorbed amount in binary systems was higher than for monocomponent systems, indicating an effect of mixture that produced better conditions for adsorption of the species containing the metals when compared to the solutions of each metal alone. This may be explained by the positive synergy of different mechanisms of interaction (electrostatic and chelation) that may take place with the several chemical groups and their forms (charged or not) available in chitosan at the studied pH.

Figures 2, 3 and 4 compare the experimental values and the calculated values for the different models for natural, epichlorohydrin-crosslinked and glutaraldehyde-crosslinked chitosan membranes, when the initial mercury concentration changed and initial copper concentration was kept constant at 50 mg/L.

Figures 1–3 show that the extended Langmuir model did not fit well the experimental data. In these cases, high values for E_i were observed, especially for copper ions, probably due to the low influence of these ions on the adsorption capacity.

Comparing the fitting results to Jain and Snoeyink model, it was possible to observe that $Q_{\max,1} - Q_{\max,2}$ is smaller than $Q_{\max,2}$. From this model, the parameters $Q_{\max,1} - Q_{\max,2}$ corresponds the adsorbed amount of specie 1 that are adsorbed without competition, and $Q_{\max,2}$ represents the adsorbed amount of specie 1 under competition with specie 2. In this way, as $Q_{\max,1} - Q_{\max,2}$ is smaller than $Q_{\max,2}$, the competitive effect has significant importance in these systems.

The Langmuir-Freundlich model fitted well experimental data, indicating that the heterogeneity of chitosan membranes may have an effect. In addition, this model presents more adjustable parameters that the other ones. Pagnanelli et al. (2001) commented that models for multicomponent systems involving more adjustable parameters succeed in fitting better experimental data.

3.3 Desorption study

Desorption was carried out in order to recover and separate the metal (copper and mercury) ions that were simultaneously loaded on chitosan membranes. Adsorption experiments were conducted using a mixture of 100 mg/L of Cu and Hg for 60 h, which were desorbed in two steps with NaCl and H_2SO_4 solutions. Figures 5a, 5b and 5c show the

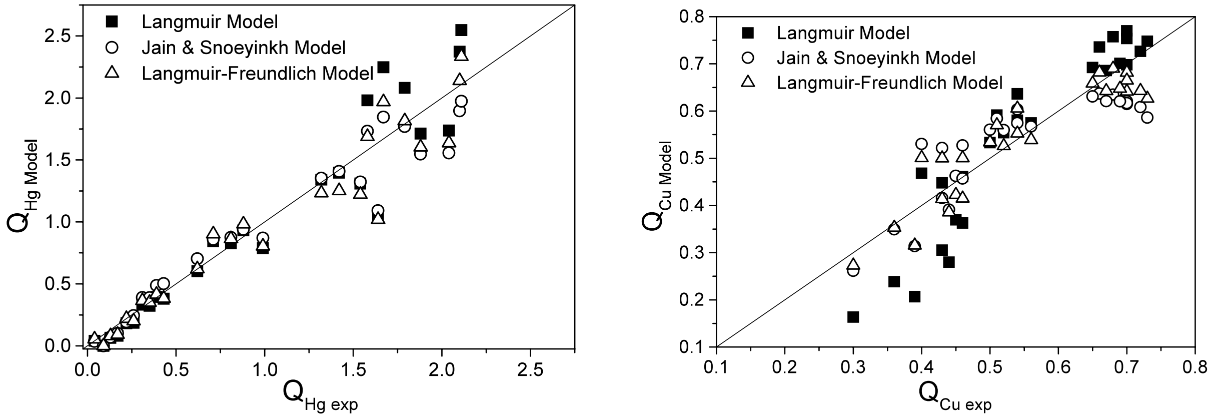

Fig. 2 Relationship between measured and predicted equilibrium adsorption capacity for natural chitosan with variable initial mercury concentration and fixed copper concentration (50 mg/L)

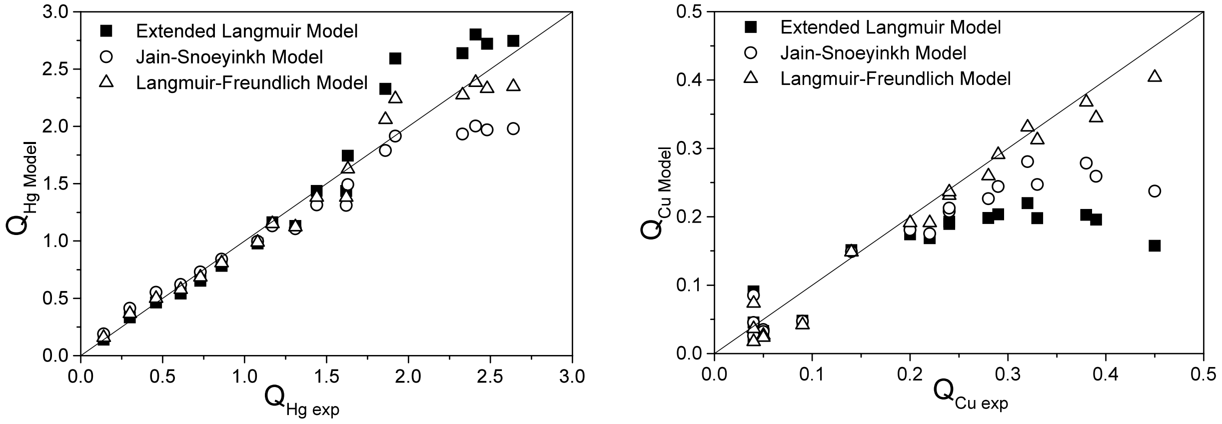

Fig. 3 Relationship between measured and predicted equilibrium sorption capacity for glutaraldehyde-crosslinked chitosan with variable initial mercury concentration and fixed copper concentration (50 mg/L)

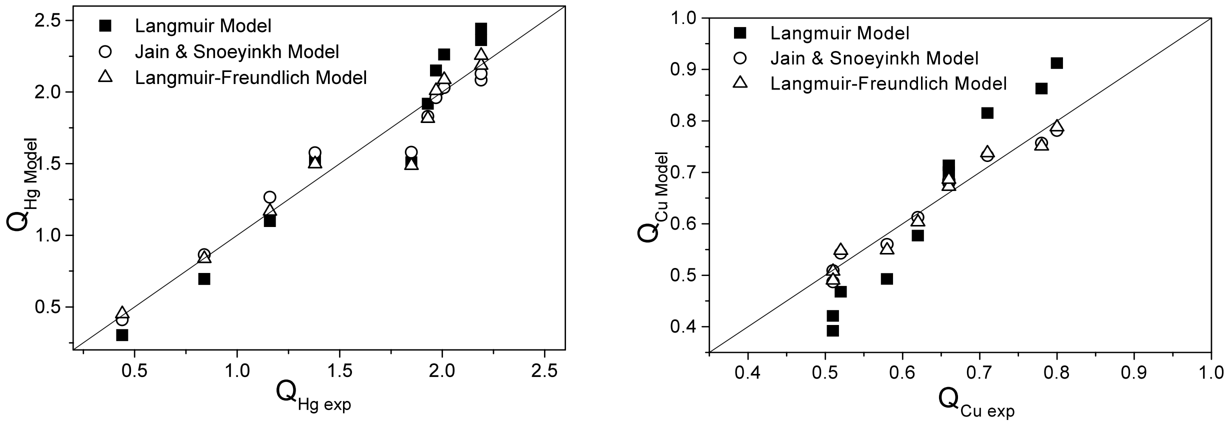

Fig. 4 Relationship between measured and predicted equilibrium sorption capacity for epichlorohydrin-crosslinked chitosan with variable initial mercury concentration and fixed copper concentration (50 mg/L)

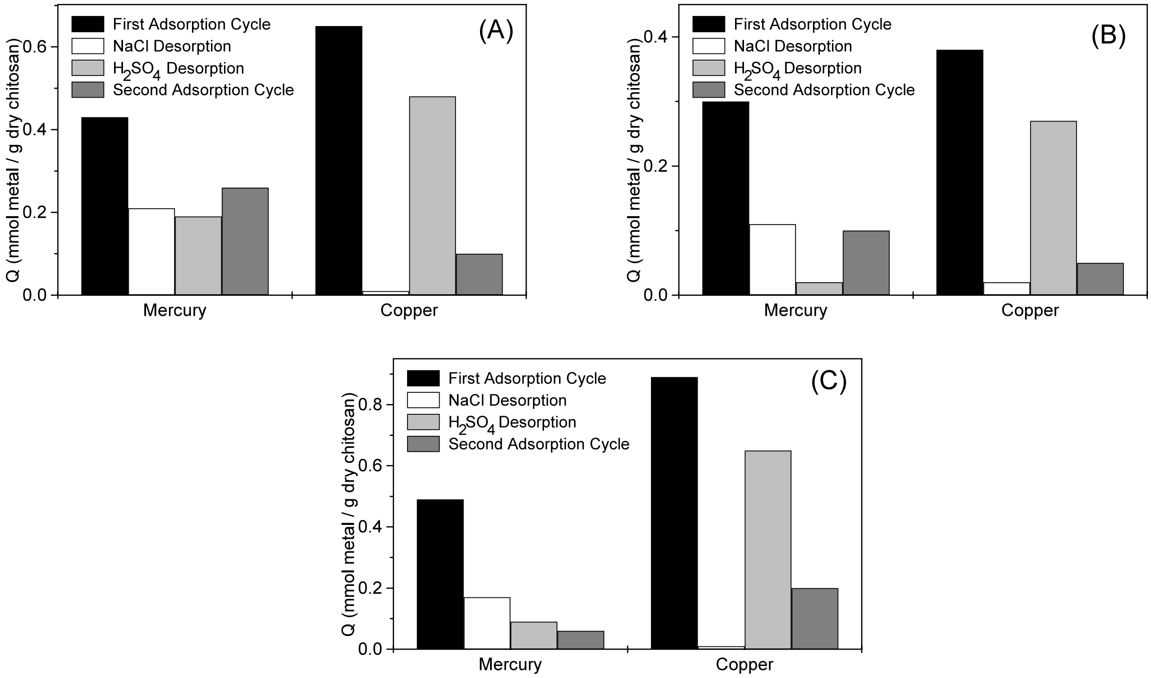

Fig. 5 (**A**), (**B**) and (**C**): Mercury and copper desorption on natural, glutaraldehyde-crosslinked and epichlorohydrin-crosslinked chitosan membranes, respectively

desorption of mercury and copper from raw, glutaraldehyde-crosslinked and epichlorohydrin-crosslinked chitosan membranes, respectively. The weak effect of NaCl on copper desorption and the possibility for chloride ions to form chloro-complexes may explain that this salt could be used for the selective separation of Cu and Hg (Vieira and Beppu 2006a, 2006b). In the first step, Hg ions were recovered by elution with NaCl solution; while Cu ions were desorbed with H_2SO_4 solution (copper desorption due to pH change). Two metal streams were obtained, containing mercury-rich and copper-rich solutions. The adsorption capacity at the next cycle was significantly reduced, probably due to a chemical modification caused by H_2SO_4 solution (Mukoma et al. 2004; Jijun et al. 2000). In this case, the hydroxonium competitive effect is probably more important than copper interaction with chitosan amino groups.

4 Conclusions

Chitosan membranes present more affinity for mercury ions than for copper ions and the crosslinking reaction increased the adsorption capacity for both metals. The competition in the binary mixture revealed a complex phenomenon. A standard behavior was not observed, as demonstrated by different values of $Q_{\max}$ obtained for mono-component systems compared to binary systems. The presence of copper ions in the mixture has a more significant impact on mercury adsorption than the presence of mercury ion considering copper sorption. The multi-component equilibrium models fitted well the experimental data, making possible to quantify the effect of one metal on the adsorption of the other one. Desorption results showed that it was possible to separate copper from mercury using a combination of desorption steps using successively NaCl and H_2SO_4 solutions for Hg and Cu recovery. These materials can mainly find application in the field of separation sciences.

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