



Chitosan selectivity for removing cadmium (II), copper (II), and lead (II) from aqueous phase: pH and organic matter effect

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ABSTRACT

The aim of this study was to investigate the selectivity of chitosan for cadmium, copper and lead in the presence and absence of natural organic matter (NOM) in different pH solutions.

Adsorption isotherms of one and three adsorbates at initial concentration of 5–100 mg/L were carried out in batch reactors at pH 4, 5, or 7 and 25 °C in reactive and clarified water. The chitosan employed had a MW of 107.8×10^3 g/mol and degree of acetylation (DA) of 33.7%.

The chitosan adsorption capacity at pH 4 in reactive water was 0.036, 0.016, 0.010 mmol/g for Pb^{2+} , Cd^{2+} , and Cu^{2+} , respectively, and it decreased for Pb^{2+} and Cd^{2+} in clarified water. Conversely, experiments carried out in clarified water showed that the cadmium adsorption capacity of chitosan was enhanced about three times by the presence of NOM at pH 7: an adsorption mechanism was proposed. Furthermore, it was found that the biosorbent selectivity, in both reactive and clarified water at pH 4, was as follows $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$.

Finally, the preliminary desorption experiments of Cd^{2+} conducted at pH 2 and 3 reported 68 and 44.8% of metal desorbed, which indicated that the adsorption mechanism occurred by electrostatic interactions and covalent bonds.

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1. Introduction

Discharges of effluents containing toxic compounds, even in low concentrations, have caused the pollution of soils, phreatic mantles, and water bearing stratum, deep aquifers, as well as continental and coastal waters. Wastewaters from mining, galvanoplastic, and foundry industries mainly contain heavy metals such as cadmium, chromium, copper, mercury, nickel, zinc, and lead. Cadmium and lead, specially, are heavy metals considered highly toxic due to the effects they cause to human health [1].

The processes currently used to remove these pollutants from water are chemical precipitation, oxidation–reduction, electrochemical deposition, filtering, ion exchange and adsorption. Adsorption is the most employed process because of its low cost and acceptable efficiency [2].

Chitin, poly-*N*-acetylglucosamine, is a natural polymer found in several sources such as crustaceans and fungal cell walls. Chitosan, poly *D*-glucosamine, is the deacetylated form of chitin that has a great variety of applications including biochemistry, phar-

macy, medicine, agricultural, as well as wastewater treatment [3].

Chitosan is a basic polymer, a feature given to it by the amino and hydroxyl groups present in its structure. Chitosan, being a base, forms salts with acids and originates polyelectrolytes with a solubility that is a function of the nature of the anion involved, deacetylation degree, polymer molecular weight, and temperature.

On the other hand, it is well known that the natural organic matter (NOM) consists of long molecules with a high molecular weight due to its functional groups, which contain carboxylics, phenolics, carbonyls and hydroxyls that may be connected to aliphatic or aromatic carbons [4]. The presence of these functional groups in the organic matter causes negative charges capable of forming complexes with metal ions present in solution, and these complexes might affect negatively or positively the adsorption capacity [4]. Ngah and Musa [3] reported that the adsorption of organic matter over chitosan takes place in the amino groups forming coordinated bonds, but to our knowledge just a few studies have been conducted to understand the roll of NOM in the removal and selectivity of metal ions (such as cadmium, copper, and lead) by this biosorbent. For instance, Yan and Bai [5] studied the adsorption capacity of lead onto chitosan hydrogels beads and reported that amine groups in chitosan were found to play the major role in the adsorption of lead

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ions or humic acids (HA), and when these two were simultaneously adsorbed their removal was significantly lower.

Therefore, the main objective of this research is to study the chitosan selectivity for removing cadmium, copper and lead from aqueous solutions in the presence and absence of NOM. In addition, based on the results, an adsorption mechanism is proposed.

2. Materials and methods

2.1. Materials

The biosorbent employed in this research was chitosan, which was prepared from chitin purified from lactic acid fermentation of shrimp heads (*Litopenaeus* sp.) according to a method reported by Cira et al. [6]. The chitin was used for the preparation of chitosan by homogeneous deacetylation as it is described by Ramírez-Coutiño et al. [7].

The clarified water used to study the NOM effect on the adsorption capacity was collected from a local water treatment plant, San Luis Potosi, Mexico (the physicochemical parameters are reported in Table 1). The standard solutions containing the heavy metals in study were prepared with $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ analytical grade.

2.2. Chitosan characterization

The degree of acetylation (DA) of chitosan was determined by ^1H nuclear magnetic resonance spectroscopy (^1H NMR), the spectra were recorded on a Bruker AC 200 spectrometer (200 MHz for ^1H). Chitosan samples were dissolved in a buffer of acetic acid (0.2 M)/ammonium acetate (0.15 M) and the average molecular weight (MW) was determined using a capillary viscometer. The parameters of Mark–Houwink–Kuhn–Sakurada employed were $\alpha = 0.85$ and $K = 1.38 \times 10^{-5} \text{ L/g}$ [8]. The DA of 33.7% and MW of $107.8 \times 10^3 \text{ g/mol}$ were determined by the methodology described above.

Chitosan was characterized by scanning electronic microscopy (SEM), infrared spectroscopy (IR), energy dispersive X-ray (EDX), and total organic carbon (TOC).

2.3. Chitosan solubility

The effect of pH on the chitosan solubility was determined in the following manner. Approximately 200 mg of chitosan was placed inside a Nylon mesh bag (150 μm aperture size). Then, these bags were introduced in an Erlenmeyer flask that contained 100 mL of reactive water previously set to a pH from 2 to 9 with 0.1N solution of HNO_3 or NaOH . The experiments were kept in

constant agitation for 24 h at 25 °C. After this period of time, the bags were removed from the flasks and dried in a stove at 90 °C for 12 h. Finally, the remnant total weight of each of the bags was obtained and the percentage of dissolved chitosan was computed.

2.4. Adsorption equilibrium data

The adsorption isotherms were carried out in a batch adsorber. A solution containing the metal and a mass of chitosan was added to an Erlenmeyer flask which served as an experimental batch adsorber. Next, the flask was submerged in a constant temperature bath, and through a magnetic bar cover with Teflon the solution in the flask was kept in constant agitation. The solution pH of these experiments was adjusted daily by adding HNO_3 or NaOH 0.1N until this was constant.

The adsorption isotherms were obtained under the following procedure: 250 mL of an aqueous solution of known metal concentration (0.018–0.178 mmol/L) and 0.25 g of chitosan were placed inside the batch adsorber. The chitosan mass was placed in a bag made of Teflon mesh before introducing it into the batch adsorber. The solution and chitosan were constantly stirred until equilibrium was reached: this occurred when the solution pH was constant and the concentration of two consecutive samples was the same. The samples were filtered by a 0.2- μm PTFE filter before the analysis.

The metal concentration was determined (average of four measurements) by flame Atomic Absorption Spectrophotometry (Analyst 400) and the amount of adsorbate removed by chitosan was calculated by a mass balance.

2.5. Desorption equilibrium data

The reversibility of the adsorption process was studied by conducting desorption experiments. Once the adsorption equilibrium was attained, the bag containing the chitosan was removed and rinsed with reactive water, set at the same pH as the solution used in the adsorption experiment, to remove metal residues that remained in the chitosan. Subsequently, the bag with chitosan was placed in reactive water previously set at pH 2 and 3. The solution pH was maintained constant by adding aliquots of 0.1N HNO_3 , and the experiment was constantly stirred for 48 h. Finally, the metal concentration was determined as described previously.

3. Results and discussion

3.1. Chitosan morphology

The chitosan morphology is observed in Fig. 1. It can be seen that the chitosan surface has a membrane aspect and does not present porosity, which indicates that it is likely not to have diffusion problems and thus the sorption process could be fast.

3.2. Effect of pH on chitosan solubility

Displayed in Fig. 2 are the experimental data of the chitosan solubility in HNO_3 . It is observed that at pH 2 the solubility is 11.86% and this diminishes as the pH of the solution increased, obtaining the minimum solubility at pH 6 (2.3%). The solubility increased again at pH values higher than 7, 5.6%, remaining constant at pH 8 and 9. At a pH between 2 and 3, the chitosan acquired a gel appearance and was difficult to handle, therefore the adsorption experiments were carried out at a pH between 4 and 7. At these pH

Table 1
Analysis of clarified water

Parameter	Value
pH	6.51
Conductivity ($\mu\text{S}/\text{cm}$)	196
Ca^{2+} (mequiv./L)	1.48
Mg^{2+} (mequiv./L)	0.37
Na^+ (mequiv./L)	0.1
K^+ (mequiv./L)	0.0
Cl^- (mequiv./L)	0.27
CO_3^{2-} (mequiv./L)	0.0
HCO_3^- (mequiv./L)	0.62
SO_4^{2-} (mequiv./L)	0.58
TOC (mg/L)	10.7
Hardness	92.76 mg/L CaCO_3
Cd, Pb and Cu	<L.D. ^a

^a L.D.: detection limited.

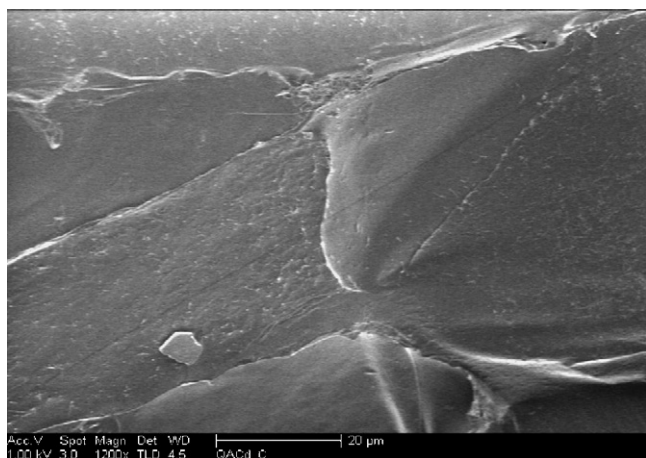


Fig. 1. Photomicrography of chitosan (augment 1200×).

values, the chitosan solubility was 3.82 and 2.56%, respectively, and remains in its original state as flakes.

3.3. Characterization by infrared spectroscopy

Infrared analyses were done on chitosan samples before and after being in contact with Cd²⁺ solution. These studies provide information regarding the functional groups and the bonds present in the biopolymer [9,10]. Fig. 3 shows the infrared spectrum of chitosan: the band at 3490 cm⁻¹ is due to the elongation of the N–H and O–H bonds, therefore, it can be assigned to several functional groups present in the sample as RNH₂ primary amines, R₂HN secondary amines, and alcohols. The band at 2854 cm⁻¹ is due the C–H (CH₃, CH₂) bond elongation, this band is characteristic of materials with saturated carbons or sp³. The band at 1660 cm⁻¹ is characteristic of the C=O bond of an amide, which was expected, since the chitosan was prepared from chitin by partial deacetylation. The band at 1640 cm⁻¹ is due to the flexion of the amine and amide N–H bond, plus the band observed at 1460 cm⁻¹ is caused by the bond flexion of methylene or groups of CH₂. Also the band around 1500 cm⁻¹ is due to the N–H bond flexion. The band at 1427 cm⁻¹ is due to the C–O–H bond flexion; this band generally appears very close to the CH₂ bands. The presence of primary, secondary and tertiary alcohols can be made out by means of the bands observed

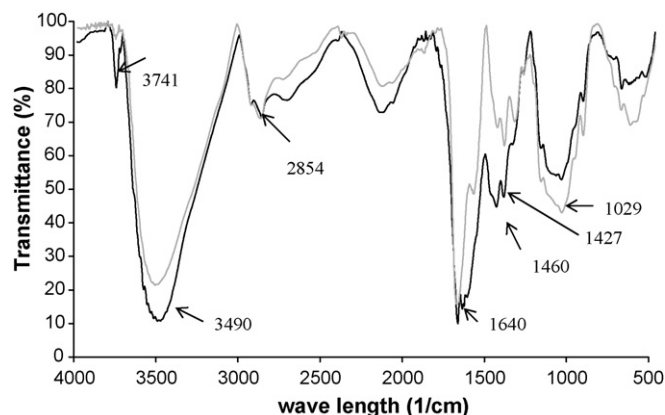


Fig. 3. IR spectrum of chitosan before and after being in contact with cadmium. Chitosan (dark line) and chitosan with cadmium (light line).

in the region from 1260 to 1000 cm⁻¹. Finally a 1029 cm⁻¹ band is related to the presence of a C–O elongation of a primary alcohol.

The differences between the IR spectra of chitosan before and after the cadmium was adsorbed can be observed in Fig. 3; similar results were obtained by Jin and Bai [10]. It is observed that the wide band at 3490 cm⁻¹ assigned to amines changed very much in intensity. This is because the vibration of the N–H bond is modified while forming a bond between the nitrogen (by its free pair of electrons) and the metal. Moreover the band at 1640 cm⁻¹ also assigned to the N–H bond decreased considerably in intensity and was displaced to 1590 cm⁻¹. It can also be notice that the band at 1500 cm⁻¹, related to N–H, reduced its intensity and moved at a minor wave length. There are several bands in the IR spectrum that neither present a reduction in their intensity nor change position: this indicates that the metal does not associate with the functional groups that generate these bands. Results from the IR spectrograph suggest that a coordination complex is formed between the chitosan and the metal with the participation of the amino and secondary alcohol functional groups. Hence, the complexes formed should be similar to the intermolecular complexes proposed by Debbaudt et al. [11], based on theoretical studies, where it is suggested that the metal predominantly associates with NH₂ and OH of secondary alcohols. On the other hand, since no participation of CH₂OH is observed it is difficult to prove that the latter intermolecular complexes could occur. Nevertheless, these experimental results do not discard the possibility that this could happen in a small proportion.

3.4. Adsorption isotherms of metal ions on chitosan

The experimental data of Cu²⁺, Cd²⁺ and Pb²⁺ adsorption isotherms were fitted by the Langmuir and Freundlich models:

$$q = \frac{q_m K C}{1 + K C} \tag{1}$$

$$q = K_F C^{1/n} \tag{2}$$

where C is the metal concentration at equilibrium (mmol/L), q is the amount adsorbed by chitosan (mmol/g), q_m and K are the Langmuir isotherm constants and K_F and n are the Freundlich isotherm constants. These constants were calculated by a least square method, and the average absolute percentage deviation (%D) was calculated as follows:

$$\%D = \left(\frac{1}{N} \sum_{i=1}^N \left| \frac{q_{exp} - q_{pred}}{q_{exp}} \right| \right) \times 100 \tag{3}$$

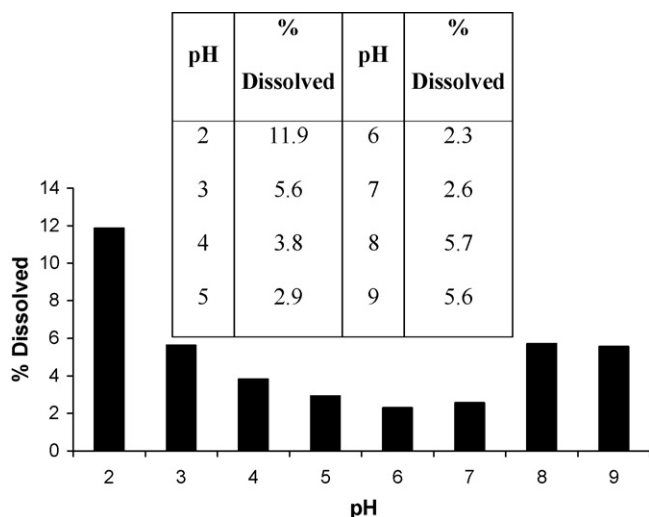


Fig. 2. Solubility of chitosan at different pH values.

Table 2
Parameters of Langmuir isotherm

Adsorbate	Dissolvent	pH	$q_{\max}K$ (L/g)	K (L/mmol)	% Deviation Langmuir	% Deviation Freundlich
Cd	Reactive	4	0.158	0.01	6.1	5.9
Cd	Clarified	4	0.055	0.30	15.4	19.9
Cd	Reactive	4	0.027	-1.12	38.0	47.8
Cd	Reactive	5	0.140	0.03	6.4	8.1
Cd	Reactive	7	0.635	7.89	14.4	4.9
Cd	Clarified	7	0.766	2.32	3.1	12.6
Pb	Reactive	4	0.174	7.43	34.4	32.7
Pb	Clarified	4	0.060	2.63	41.5	38.7
Cu	Reactive	4	0.821	12.7	26.7	30.2
Cu	Clarified	4	2.86	20.2	15.3	27.3

This table also includes the deviation percentage of the Freundlich isotherm model.

The results reported in Table 2 show that the %D varied from 3.1 to 41% for the Langmuir isotherm and from 5 to 47% for Freundlich isotherm. Although the %D indicates that the Langmuir model best fit the experimental data, it is also clear that the Freundlich model could also be appropriated. Based on these findings, it is important to emphasize that these two mathematical models fit reasonably well the experimental data (in concentration up to 0.7 mmol/L) and hence it is not possible to determine if the chitosan surface is cover by a mono or multi molecular layer of adsorbate.

3.5. pH effect on the cadmium adsorption isotherm

Adsorption experiments involving one and three metals were carried out to determine the chitosan adsorption capacity and its selectivity. These experiments were done in reactive and clarified water at different pH values.

Cadmium can react in solution with carbonates, phosphates, oxalates, arsenates, and cyanides depending on the pH of the solution, this element can also precipitate as hydroxide [12]. Cadmium is mainly found as Cd^{2+} at $pH \leq 8$, and from this value up to pH 9 $Cd(OH)^+$ ions are formed. At $pH > 9$ $Cd(OH)_2^0$ begins to form; at pH 10.6, 63% of the cadmium present is found as $Cd(OH)_2^0$ and the rest is present as $Cd(OH)^+$ and $Cd(OH)_3^-$; and at $pH > 13$ the $Cd(OH)_3^-$ anions predominate [13].

Fig. 4 compares the Cd^{2+} adsorption capacity of chitosan at pH 4, 5 and 7. It is observed that the maximum adsorption capacity occurs at pH 7, and this decreases as pH drops. The amount of

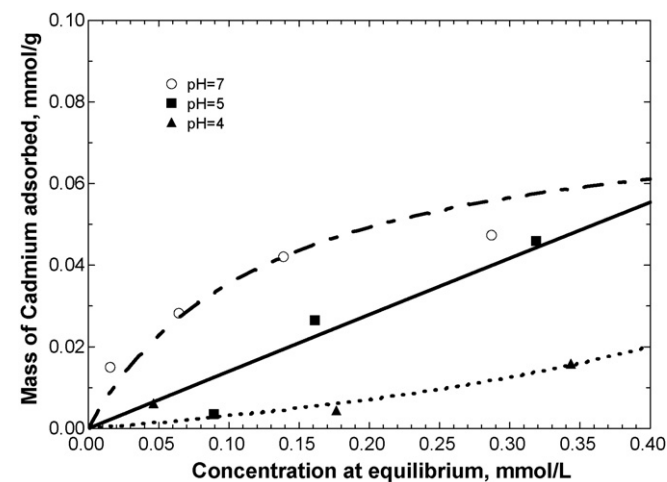


Fig. 4. Effect of pH on the adsorption isotherm of Cd(II) on chitosan in reactive water at 25 °C. The lines represent the Langmuir isotherm and the symbols the average concentration of replicates.

Cd^{2+} adsorbed at an equilibrium concentration of 0.36 mmol/L was 0.058, 0.051 and 0.016 mmol/g at pH 7, 5 and 4, respectively, which represents a decrease of 72% when pH drops from 7 to 4.

3.6. Chitosan selectivity for removing cadmium, lead, and copper

Chitosan selectivity for removing copper, lead, and cadmium in reactive water is shown in Fig. 5. These experiments were performed at pH 4 where according to the oxidation–reduction and speciation diagrams, these three metals exist in a divalent state. In order to verify that Cd^{2+} , Pb^{2+} , and Cu^{2+} were present as M^{2+} while in contact with chitosan, the oxidation–reduction potential was measured in a solution at pH 4. The potential recorded for Cd^{2+} , Pb^{2+} , and Cu^{2+} was 242, 228, and 234 mV, respectively, therefore according to the oxidation–reduction diagrams [14] these metals exist as Cd^{2+} , Pb^{2+} , and Cu^{2+} under these conditions.

This figure shows that for a concentration at equilibrium of 0.1 mmol/L, the mass adsorbed is 0.036, 0.016 and 0.01 mmol/g for Cu^{2+} , Cd^{2+} and Pb^{2+} , respectively, which indicates that the chitosan selectivity for removing heavy metals decreases in the following order: $Cu^{2+} > Cd^{2+} > Pb^{2+}$.

3.7. Effect of natural organic matter in the adsorption capacity of copper, cadmium, and lead

When NOM is present in the adsorption of heavy metals, the system becomes more complex. The interactions that may occur

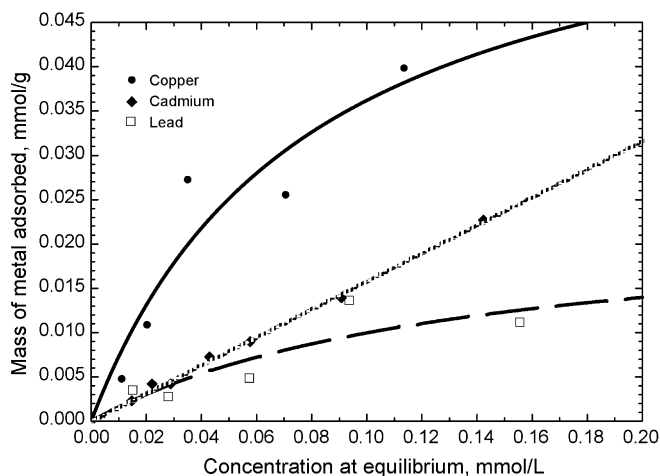


Fig. 5. Adsorption of different metals on chitosan in reactive water at pH 4 and 25 °C. The lines represent the Langmuir isotherm and the symbols the average concentration of replicates.

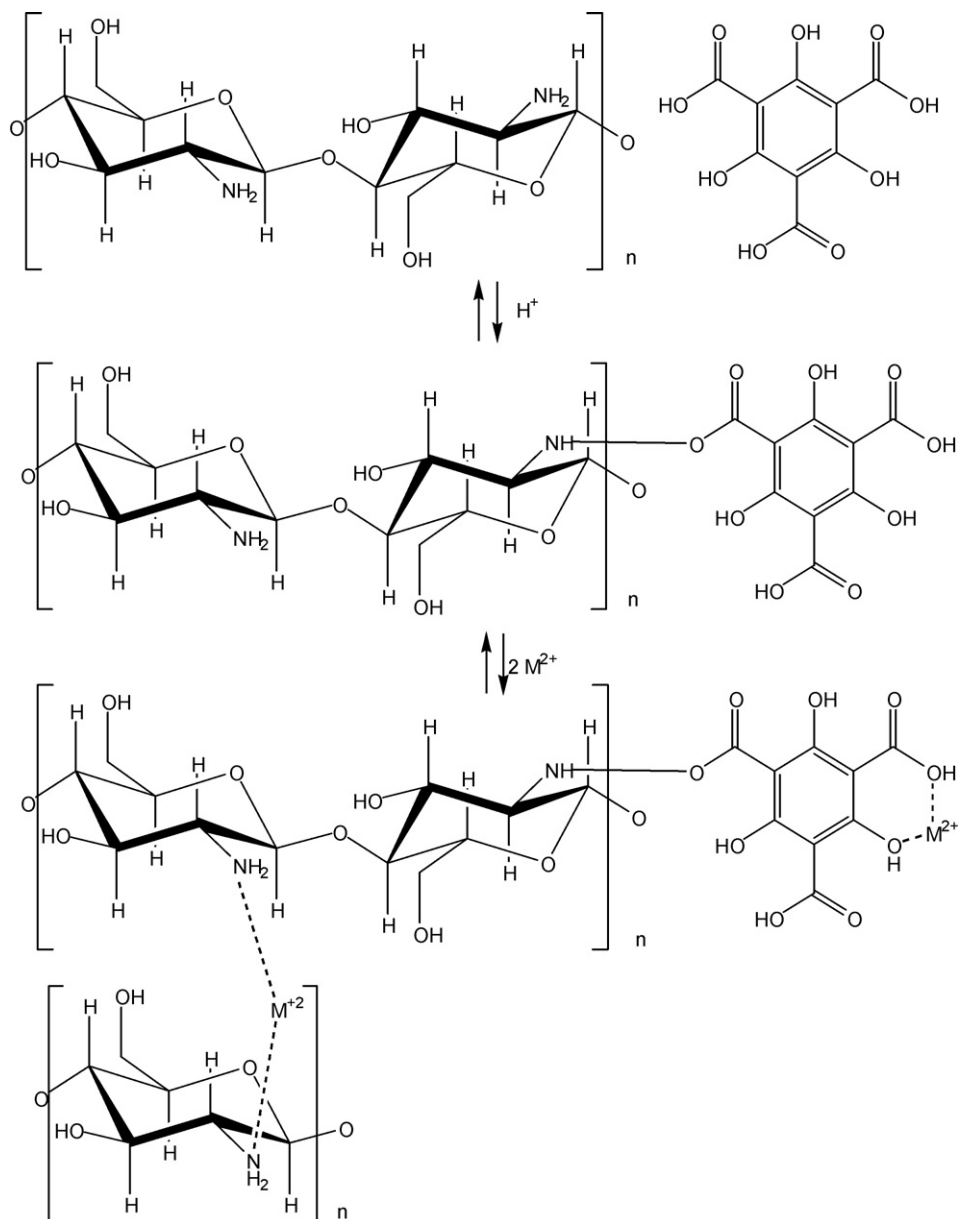


Fig. 6. Organic matter and metal adsorption mechanism on chitosan in a slightly acidic solution.

between the chitosan and the organic matter could be through a covalent bond since NOM contains functional groups of the carboxylic acid type (see Fig. 6). This could take place by forming amide bonds between the chitosan amino group and the carboxylic

acid group of the NOM. This equilibrium takes place very easily under slightly acid as well as basic conditions [15]. This would generate a tertiary type of complex where chitosan, organic matter, and metal ions participate.

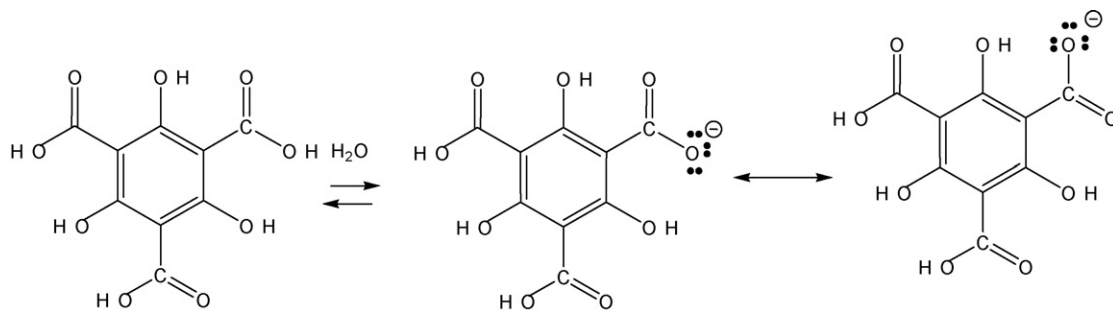


Fig. 7. Ionic structure of organic matter in solution.

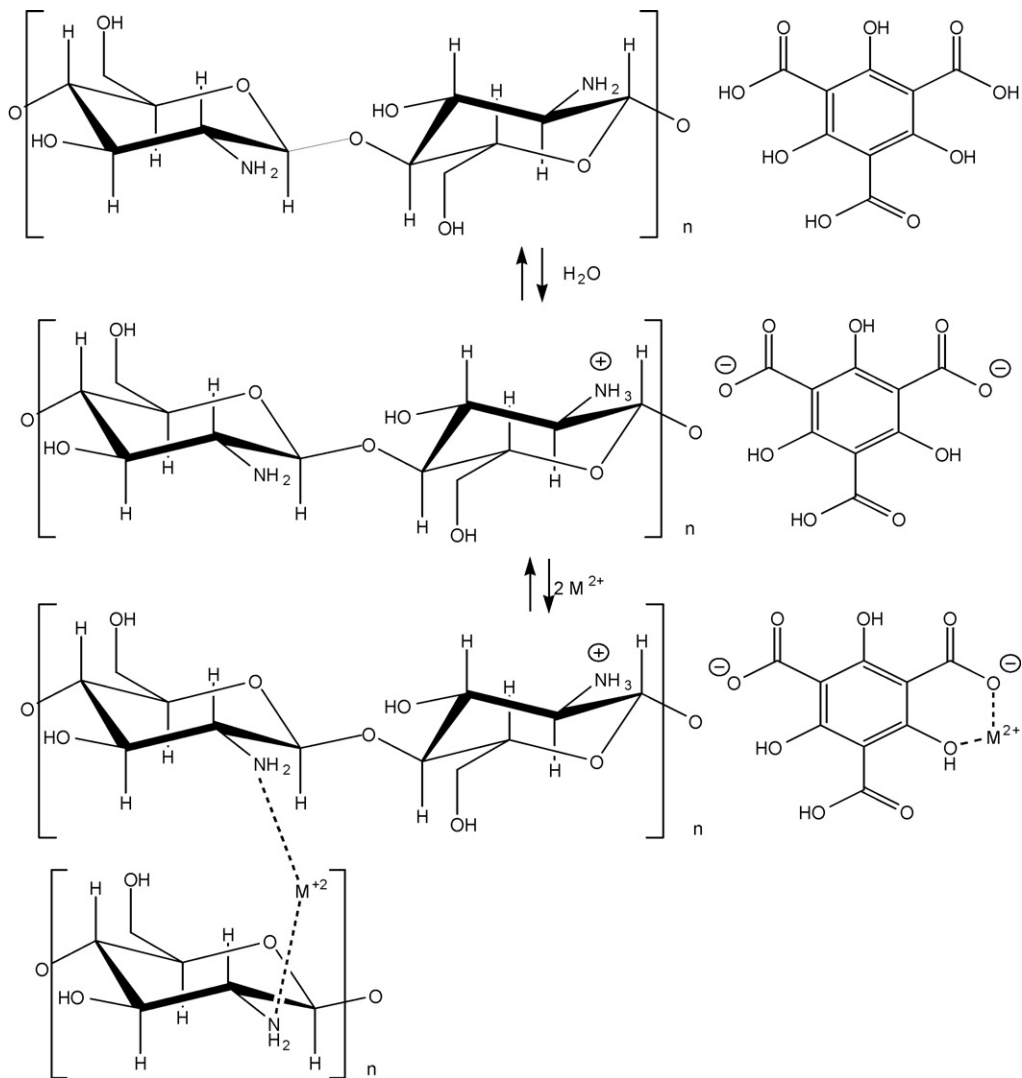


Fig. 8. Organic matter and metal interactions with chitosan in water.

Humic acids may be found in ionic form in aqueous solutions, since these produce a stabilized anion by resonance as shown in Fig. 7. Ionic type interactions could also exist between the organic matter and chitosan in totally neutral aqueous suspensions (see Fig. 8). Moreover, in the particular case of NOM, comprised of aromatic and ionic groups, its complexation with chitosan is favorable due to the hydrophilic and hydrophobic effects [16].

The chitosan adsorption capacity for organic matter was determined by obtaining the total organic carbon in chitosan and clarified water before and after being in contact among them. The TOC analysis of chitosan, prior and after being in contact with clarified water reported 86.6 and 90.7%, respectively: this represents an increase of 4.1%. While the same analysis in the clarified water reported 3% decrease in the TOC concentration after being in contact with chitosan: similar results were obtained by Ngah and Musa [3]. These results are in agreement with the mechanisms previously proposed.

The effect of the organic matter in the adsorption process was assessed by determining the Cd^{2+} adsorption isotherm at pH 7 and 25 °C, and the isotherms of Cu^{2+} , Cd^{2+} and Pb^{2+} at pH 4 and 25 °C, both in clarified water. Fig. 9 shows the effect of the NOM in the adsorption of Cd^{2+} . It is observed that at an equilibrium concentration of 0.44 mmol/L, the amount adsorbed by chitosan in reactive and clarified water was 0.06 and 0.18 mmol/g, respectively.

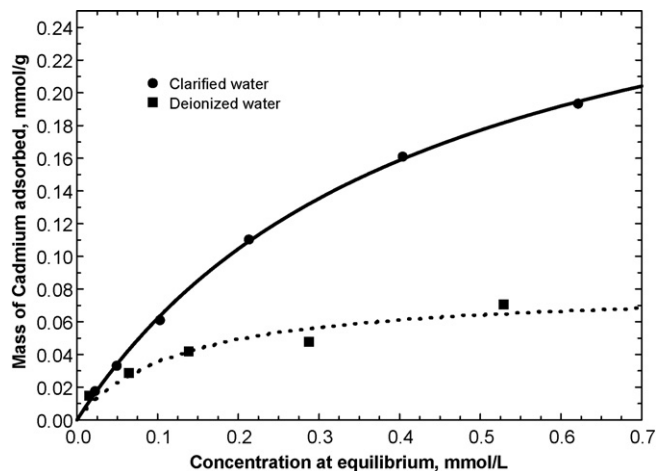


Fig. 9. Effect of the organic matter in the adsorption capacity of Cd^{2+} on chitosan pH 7 and 25 °C. The lines represent the Langmuir isotherm and the symbols the average concentration of replicates.

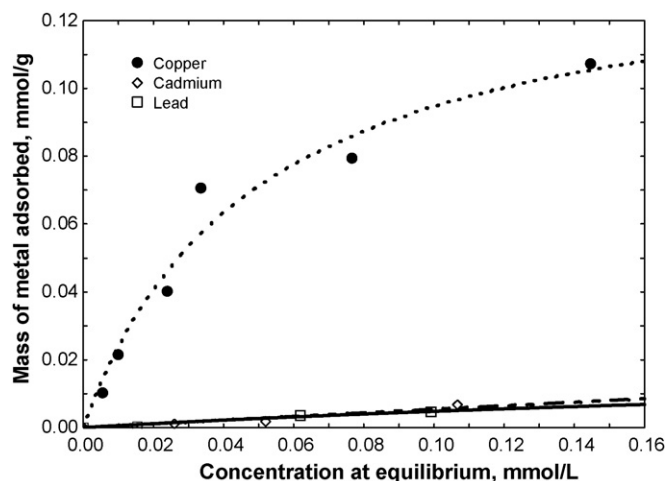


Fig. 10. Adsorption isotherms of different metals on chitosan in clarified water at pH 4 and 25 °C. The lines represent the Langmuir isotherm and the symbols the average concentration of replicates.

That is, the mass adsorbed of Cd^{2+} increased three times while the NOM was present in solution, which indicates that the presence of organic matter in solution enhanced the adsorption of cadmium as proposed in Figs. 7 and 8.

This same behavior is observed in Fig. 10 that shows the adsorption isotherms of the three metal ions in clarified water. The chitosan adsorption capacity for lead, cadmium, and copper was 0.01, 0.016 and 0.036 mmol/L in reactive water and 0.005, 0.006 and 0.1 mmol/g in clarified water, respectively. This means that the adsorption capacity decreased 50 and 63% for lead and cadmium, accordingly, and it increased 177% for copper. This behavior can be due to the existence of competition between metal ions and organic matter for active sites on chitosan, favoring adsorption of the most selective ion. It should be mentioned that, since natural water was used, besides the metal ions added to the clarified water there were other cations present (Table 1) such as Ca^{2+} , Mg^{2+} , Na^{+} and K^{+} that could compete for active sites on the chitosan and hence intervene in the removal of the metal ions studied herein.

3.8. Cadmium desorption from chitosan

The reversibility of the Cd^{2+} adsorption process on chitosan was studied at different concentrations of adsorbate at pH 2 and 3 in reactive water (see Table 3). The results showed a desorption of 68 and 40% of cadmium at pH 2 and 3, respectively. This indicated that the adsorption process is partially reversible and is likely to occur by two processes: (i) electrostatic interactions (physisorption) and (ii) covalent bonds (chemisorption). Moreover, it is observed that the desorption of Cd^{2+} is favored toward acid pH. The latest could be attributed to the protonation of NH_2 groups as described by the mechanism presented in Fig. 11.

Table 3

Amount of cadmium desorbed at different pH values

Experiment	Mass adsorbed at pH 7 (mmol/g)	Mass desorbed at pH 2 (mmol/g)	Mass desorbed at pH 3 (mmol/g)
a	0.015	0.008	0.006
b	0.028	0.013	0.008
c	0.042	0.025	0.014
d	0.047	0.038	0.021
e	0.071	0.057	0.032
f	0.100	0.082	0.043

Experiments a–f were conducted at different initial concentrations, constant pH, and 25 °C.

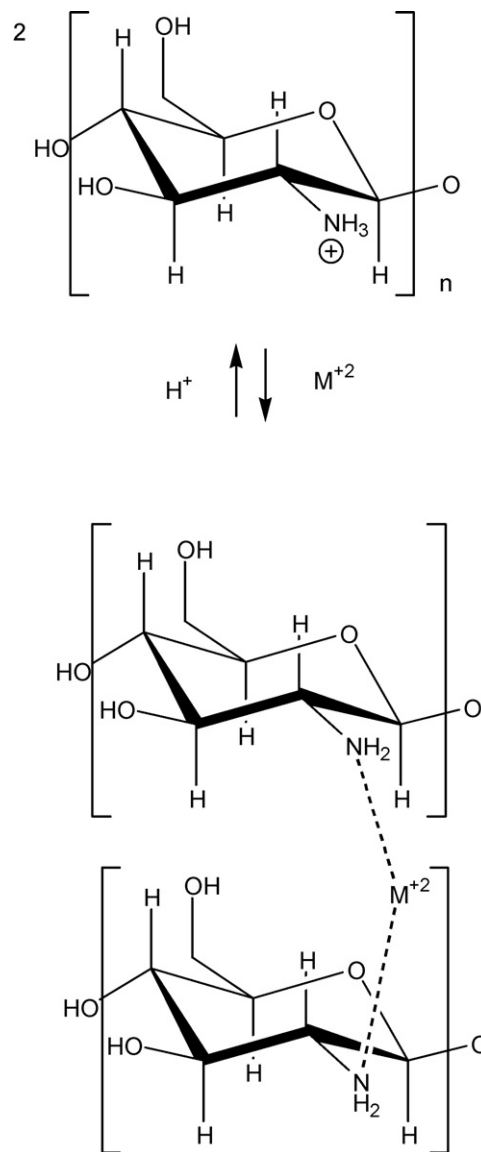


Fig. 11. Intermolecular complex of chitosan with metal cations in acidic solution.

3.9. Adsorption mechanism

The IR studies performed on chitosan previously loaded with cadmium indicated that the complexing main sites are the amines and secondary alcohol functional groups, since the nitrogen of the amino group and the oxygen of the alcohol have a pair of electrons that can add themselves to a proton or a cation by coordinated covalent bonds. The attraction of the electrons pair by the atom nucleus is stronger in the oxygen, and on the other hand nitrogen has a greater tendency to donate its pair of electrons to a metal ion to form a complex through a coordinated covalent bond [10]. This takes us to propose that the complexes between metal ions (M^{2+}) and chitosan are formed according to the mechanism illustrated in Fig. 12.

In this mechanism, the metal ions (M^{2+}) with empty orbitals function as a Lewis acid capable of accepting electron pairs. In contrast, the NH_2 and OH groups that have non-shared electron pairs function as Lewis bases donating their electrons pair.

This behavior depends on the solution pH. That is, if the adsorption system is in a neutral or slightly acid pH, the mechanism shown

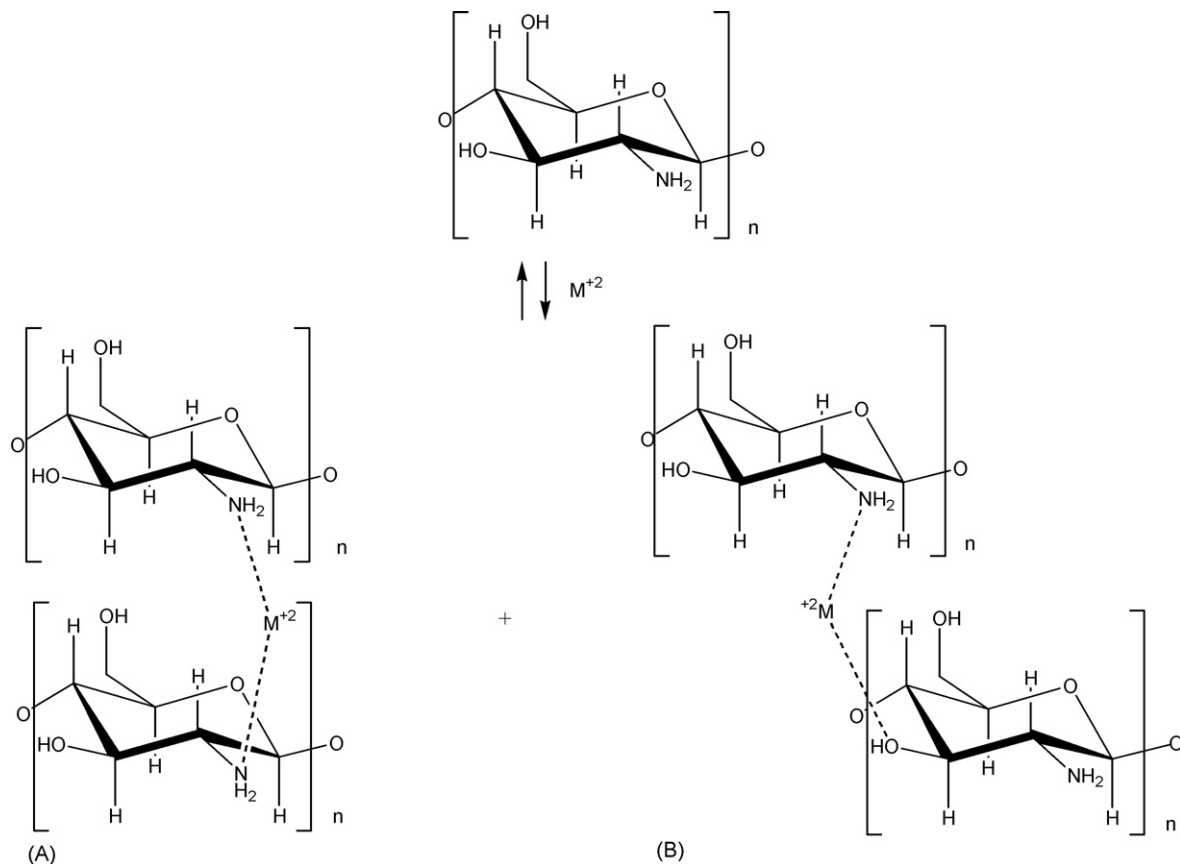


Fig. 12. Intermolecular complexes of chitosan with metal ions in a neutral or slightly acid pH.

in Fig. 12 will predominate. Nevertheless, when the adsorption system is in an acidic environment there are several Lewis acid–base type reactions. This mechanism is shown in Fig. 13. In this mechanism, there are acid–base type reactions between the amino group and the free orbital in the proton, but on the other hand the union strength of a metal ion with the nitrogen electron pair is greater than the strength of union of the complex formed between the nitrogen and the proton. Therefore, although in an acidic environment the amino group is found in a protonated form as RNH_3^+ , the proton could be replaced by an ion exchange process with a metal ion M^{2+} [10]. This process is shown in Fig. 11.

The adsorption process of metal ions on chitosan is controlled by the transport of these species in solution. Hence under acidic conditions the mobility of the adsorbate to the biosorbent surface is inhibited because the amino group (RNH_3^+) and the M^{2+} exhibit an electrostatic repulsion. This explains why metal adsorption capacity diminishes as the solution pH decreases.

3.10. Adsorption capacity comparison between chitosan and a commercially available activated carbon

Fig. 14 shows the Cd^{2+} adsorption isotherms on chitosan and granular activated carbon F-400 (Calgon Corporation) in reactive and clarified water at pH 7 and 25°C . It is observed that the GAC F-400 has a slightly higher adsorption capacity than that reported by chitosan: 0.059 and 0.054 mmol/g for the F-400 and chitosan, respectively, at an equilibrium concentration of 0.36 mmol/L.

The effect of NOM on the adsorption capacity in both adsorbents was also studied. Fig. 14 points out that chitosan has a higher adsorption capacity than the GAC F-400 in the presence of organic matter. At a concentration in the equilibrium of 0.36 mmol/L the

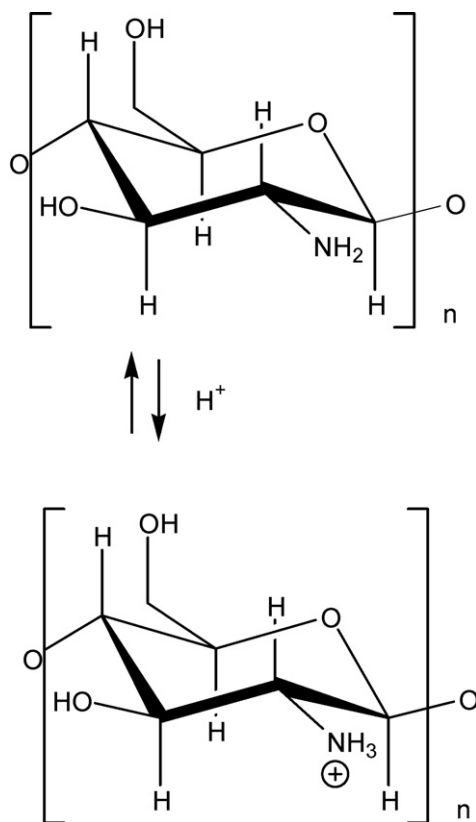


Fig. 13. Chitosan in acidic solution.

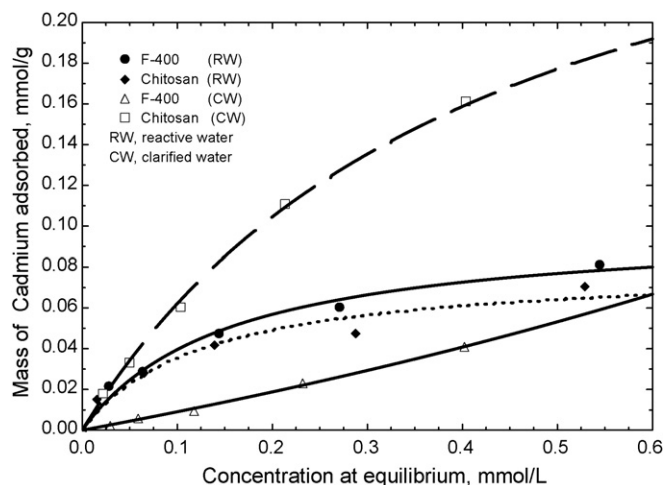


Fig. 14. Cadmium adsorption capacity between chitosan and GAC F-400 at pH 7 and 25 °C. The lines represent the Langmuir isotherm and the symbols the average concentration of replicates.

adsorption capacity was 0.14 and 0.04 mmol/g for chitosan and GAC F-400, respectively. This means a 2.6 times increase in the chitosan adsorption capacity and a 0.4 times decrease in adsorption capacity for GAC F-400 in the presence of organic matter. This notable decrease in the adsorption capacity of F-400 can be attributed to the obstruction of pores, which prevents the passage of metal ions inside the adsorbent where most of the surface area is available to sequester these species.

4. Conclusions

It is concluded that the chitosan used in this study is more soluble at $5 > \text{pH} > 7$. Furthermore the cadmium adsorption capacity of this biosorbent increases 3.6 times when the solution pH rises from 4 to 7. It was also found that the GAC F-400 has a slightly higher adsorption capacity than chitosan at pH 7 and 25 °C in reactive water. However, when NOM is present it enhances the cadmium adsorption capacity of chitosan about three times, on the contrary, the adsorption capacity of commercial GAC F-400 drops about 60%.

It was observed that the chitosan selectivity for cadmium, copper, and lead in both reactive and clarified water is as follows: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$. These three metals and NOM compete between each other for active sites on chitosan as illustrated in the mech-

anisms proposed. In addition, the amount of cadmium desorbed is function of the H^+ concentration: about 68% of cadmium is desorbed at pH 2, which suggests that the adsorption process of this contaminant is conducted by both electrostatic attraction (physisorption) and covalent interactions (chemisorption).

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