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Competitive adsorption of Cu(II) and Cd(II) ions by chitosan crosslinked with epichlorohydrin–triphosphate

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ABSTRACT

In this study, chitosan (CTS) was crosslinked with both epichlorohydrin (ECH) and triphosphate (TPP), by covalent and ionic crosslinking reactions, respectively. The resulting adsorbent (CTS–ECH–TPP) was characterized by SEM, CHN, EDS, FT-IR and TGA analyses, and tested for metal adsorption. The adsorbent was used in batch experiments to evaluate the adsorption of Cu(II) and Cd(II) ions in single and binary metal solutions. In single metal solutions the maximum adsorption capacities for Cu(II) and Cd(II) ions, obtained by Langmuir model, were 130.72 and 83.75 mg g^{-1}, respectively. Adsorption isotherms for binary solutions showed that the presence of Cu(II) decreased Cd(II) adsorption due to a significant competition effect, that is, the adsorbent was selective towards Cu(II) rather than Cd(II).

1. Introduction

Heavy metal contamination of the various water resources is of great concern given the toxic effect on humans as well as the biota present in the environment. The major sources of heavy metal pollutants are several industrial activities including mining, metal plating, oil refining, electronic device manufacturing, printing, and the production of chemicals, dyes and paints, pulp and paper, textiles, petrochemicals, leather, fertilizers and pesticides (Li and Bai, 2005; Srivastava et al., 2009).

The main techniques that have been widely used to remove toxic metals from industrial effluents are chemical precipitation, complexation, ion exchange, evaporation, electrodeposition, liquid–liquid extraction, membrane separation, advanced oxidation processes, electrolysis, reverse osmosis and biological treatment. However, these methods may be ineffective or expensive, especially when the heavy metal ions are present in the wastewater at low concentrations (Ngah et al., 2002; Justi et al., 2005; Chen et al., 2009; Popuri et al., 2009; Zhou et al., 2009a).

Adsorption is one of the most economical, effective and widely used methods for the removal of toxic metals from aqueous environments. The great advantage of this method over others is the low generation of residues, easy metal recovery and the possibility for the reuse of the adsorbent. Studies have been carried out to develop more effective and selective adsorbent materials, which are abundant in nature and require minimal processing in order to the decrease cost (Ng et al., 2003; Benassi et al., 2006; Vasconcelos et al., 2007).

The application of biopolymers as adsorbents is an emerging technique and is of interest in studies on the removal of metal ions from aqueous solutions. Special attention has been given to the biopolymer chitosan (CTS), which is usually obtained by alkaline deacetylation of chitin, a natural polysaccharide found in the exoskeletons of crustaceans such as shrimps, crabs, prawns and lobsters, which are waste products of the seafood processing industries (Arica et al., 2004; Ngah et al., 2004; Varma et al., 2004; Pedro et al., 2009).

CTS is widely regarded as a promising polymeric material of great scientific interest, due to its excellent properties, such as abundance, non-toxicity, hydrophilicity, biocompatibility, biodegradability, adsorption properties, antibacterial properties and wide application potential (Wu et al., 2001; Chiou and Li, 2003; Zhou et al., 2009b). The major limitation of CTS, however, is its solubility in most dilute mineral and organic acid solutions. Attempts have been made to improve its chemical stability under acidic conditions by chemical modification using crosslinking agents such as glutaraldehyde (GLA), epichlorohydrin (ECH), ethylene glycol diglycidyl ether (EGDE), genipin and triphosphate (TPP), leading to the formation of a three dimensional network. The chemical crosslinking reaction was found to be able to prevent the dissolution of CTS when metal sorption is performed in acidic solutions, as well as increase its capacity for the adsorption of metal ions (Li and Bai, 2005; Guibal, 2004; Ngah and Fatinathan, 2008; Vasconcelos et al., 2008; Muzzarelli, 2009).

Most of the studies concerning chitosan-metal bonding are conducted using single metal solutions. However, the presence of

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only one toxic metal ion is a rare situation both in natural water bodies and in wastewaters. In natural systems, numerous metal ions are often present and they compete for available adsorbent sites. It should also be noted that the presence of other metal ions can lead to synergism, antagonism or non-interaction. Thus, it is important to study the affinity of modified chitosan toward the adsorption of specific metal ions to investigate their removal from multi-component solutions (Vasconcelos et al., 2009).

The main objective of this study was to prepare chitosan crosslinked with epichlorohydrin via a covalent crosslinking reaction as well as triphosphate by ionic crosslinking reaction, to characterize the adsorbent by SEM, CHN, EDS, FT-IR and TGA analyses and investigate the adsorption of Cu(II) and Cd(II) ions in single and binary metal systems.

2. Experimental

2.1. Instrumentation

The scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed using a JEOL JSM-6390LV instrument. CHN elemental analysis was performed with a Carlo Erba CHNS-O-E1110 analyzer. Infrared (FT-IR) spectra were obtained with KBr pellets in the range of 2000–450 cm^{-1}, using a Perkin Elmer 2000 FT-IR spectrometer. Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA 50, with a heating rate of 10 °C min^{-1}, under nitrogen flow at a rate of 50 mL min^{-1}. The pH of the solutions was adjusted using a Corning pH/ion analyzer model 350. A Marconi MA 832 mini-shaker thermostatic bath was used in the adsorption and desorption experiments. The concentrations of Cu(II) and Cd(II) ions were determined by flame atomic absorption spectroscopy (FAAS) using a Varian SpectrAA 50 spectrometer equipped with an air–acetylene flame atomizer and a Hitachi hollow cathode lamp specific for each metal ion. The lamp was operated under the conditions recommended by the manufacture. Also, conventional values for the wavelength, slit width and burner height were applied. The aspiration rate was 6 mL min^{-1}. Quantitative analysis of a sample of freshwater was performed by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer SCIEX Elan 6000 spectrometer.

2.2. Materials and reagents

Chitosan was purchased from Purifarma (Brazil) with a degree of deacetylation of 90% and average molecular weight of 122.74 kDa. Epichlorohydrin was obtained from Synth (Brazil). Pentasodium triphosphate was purchased from Fluka (Switzerland). The working standard solutions of Cu(II) and Cd(II) ions were prepared using appropriate dilutions of stock solutions (1000 mg L^{-1}), which were obtained from dilutions of Fluka® (Sigma–Aldrich – Germany) ampoules ($CuCl_2$ and $CdCl_2$ in water, respectively). The following buffer solutions were used at a concentration of 0.1 mol L^{-1} to adjust the pH: chloroacetic/sodium chloroacetate (pH 2 and 3), acetic acid/sodium acetate (pH 4–6) and tris(hydroxymethyl)aminomethane adjusted with diluted HCl solution (pH 7–9). All solutions were prepared with distilled water. All reagents were of analytic grade and used without further purification.

2.3. Preparation of crosslinked chitosan

Chitosan was dissolved in 1% (v/v) acetic acid solution to produce a viscous solution with 1% (w/v) chitosan. A volume of 10 mL of 12.5 mol L^{-1} ECH was added to the chitosan solution and maintained at 60 °C for 2 h. The ECH/CTS molar ratio used was 1.0/2.0. Subsequently, 50 mL of 0.1 mol L^{-1} NaOH was added and the system was boiled for 3 h. Finally, 100 mL of 5% (w/v) TPP solution was added dropwise to the epichlorohydrin crosslinked chitosan solution under constant stirring. The product obtained was filtered, washed several times with distilled water and then dried in a vacuum.

2.4. Adsorption and desorption experiments

All experiments to investigate the adsorption (single and binary systems) of Cu(II) and Cd(II) ions onto the CTS–ECH–TPP adsorbent and the removal of metal ions added to a sample of water, as well as the subsequent desorption of the metals and reuse of the adsorbent, were carried out in batch tests, using a mini-shaker thermostatic bath at 25 °C and under constant stirring at 200 rpm.

The amount of metal ion adsorbed was calculated according to the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q is the amount of metal ions adsorbed by the CTS–ECH–TPP (mg g^{-1}), C_0 and C_e are the metal concentrations in the solution initially and after adsorption (mg L^{-1}), respectively, V is the volume of the solution (L) and m is the mass of adsorbent used (g).

2.4.1. Effect of pH

Samples (50.0 mg) of the CTS–ECH–TPP adsorbent were placed in a series of flasks containing 50.0 mL of a solution of each metal ion at an initial concentration of 50 mg L^{-1}, buffered within a pH range of 2–9. The buffer solutions were used to adjust the pH and as auxiliary complexing agents to prevent the precipitation of Cu(II) and Cd(II) ions. After 24 h, the final pH value was measured and aliquots of the solutions were removed and then diluted in volumetric flasks. The remaining concentrations of Cu(II) and Cd(II) ions were determined by FAAS at wavelengths of 324.8 and 228.8 nm, respectively.

2.4.2. Adsorption equilibrium isotherm (single and binary metal systems)

For the single metal ion adsorption experiments, 50.0 mg of CTS–ECH–TPP were placed in closed flasks containing 50.0 mL of Cu(II) or Cd(II) ion solutions, in various concentrations (10–400 mg L^{-1}) and buffered at optimum pH, while for the binary metal system, one metal concentration was varied from 20 to 400 mg L^{-1} and the concentration of the other metal was kept constant (10 or 100 mg L^{-1}). After 48 h, aliquots of the supernatant were removed and diluted in order to determine the remaining concentrations of metal ions by FAAS.

2.4.3. Removal of Cu(II) and Cd(II) ions added to a sample of lagoon water

Water samples were collected from a single point of Peri Lagoon (a freshwater body used as a source of potable water supply) located in Florianópolis, SC, Brazil and stored in polyethylene flasks. The samples were filtered through Schleicher and Schuell 0.45 μm membrane filters in order to remove particulate material and Cu(II) and Cd(II) ions were then added, resulting in a concentration of 10 mg L^{-1}. Aliquots of 50.0 mL of water containing the metal ions were placed in contact with different amounts of adsorbent (25.0–200.0 mg) for a period of 48 h. After this period, aliquots were removed and then diluted in volumetric flasks. The remaining concentrations of metal ions were determined by FAAS.

2.4.4. Desorption and reuse studies

For the desorption studies, 20.0 mg of CTS–ECH–TPP were added to 50.0 mL of 25 mg L^{-1} Cu(II) or Cd(II) ion solutions, buffered at optimum pH and kept under stirring for 48 h. The

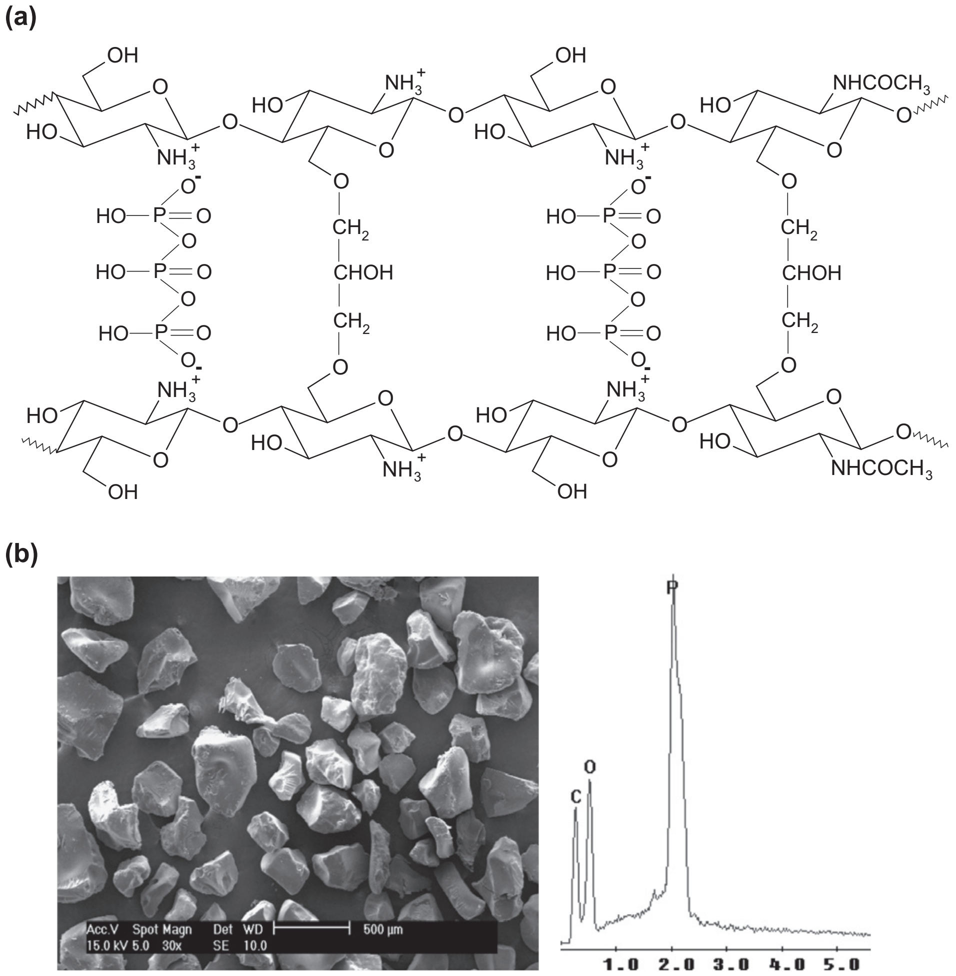

Fig. 1. Structure (a) and SEM micrograph (b) of CTS–ECH–TPP.

M^{2+}-CTS–ECH–TPP complex was collected by filtration using 0.45 µm membrane filters and washed several times with distilled water to remove any unabsorbed metal ions. The amount of Cu(II) and Cd(II) ions adsorbed per gram of CTS–ECH–TPP was determined from the metal ion concentration remaining in each solution. The adsorbent samples containing each metal ion were placed in contact with 50.0 mL of HNO_3 (pH 1.0) and EDTA (pH 4.5) solutions, at different concentrations and maintained under stirring for 3 h. The amount of metal ions desorbed was then determined by FAAS. The adsorbent was finally collected from the solution by filtration, washed with distilled water, and then reused in the next cycle of adsorption/desorption. The adsorption/desorption experiments were conducted for five cycles.

The percentage of desorption was calculated from the following expression:

$$\text{Desorption } (\%) = \frac{\text{amount of metal ions desorbed}}{\text{amount of metal ions adsorbed}} \times 100 \qquad (2)$$

3. Results and discussion

3.1. Characterization of CTS–ECH–TPP

Fig. 1a shows the structure of modified chitosan, initially using the crosslinking agent epichlorohydrin, followed by the introduction of phosphate groups from the ionic interaction between the NH_3^+ groups of chitosan and the negatively charged groups of the triphosphate.

The CTS–ECH–TPP particle size was 100–150 µm, obtained using appropriate sieves, and the particles did not show a well-defined shape in the SEM analysis (Fig. 1b).

The C, H and N values for the CTS composition were 39.43%, 8.41% and 7.30%, respectively, and for the CTS–ECH–TPP adsorbent they were 29.00%, 7.44% and 4.78%, respectively. The semi-quantitative results obtained from the EDS revealed an atomic percentage of phosphorus in the new adsorbent of 4.46%. It was observed that there was a decrease in the percentage of C, H and N atoms and the presence of P atoms after the chitosan modification.

The FT-IR spectra for the CTS, TPP and CTS–ECH–TPP samples are shown in Fig. 2. The CTS–ECH–TPP spectrum (Fig. 2c) showed a new peak at 1554 cm^{-1}, which can be attributed to the ionic interaction between the positively charged amino groups of the crosslinked chitosan and the negatively charged groups of the triphosphate (Lee et al., 2001; Moura et al., 2009). In addition, peaks at 1647, 1385 and 1081 cm^{-1} representing C=O stretching, C—H deformation and C—O stretching, respectively, were present in the chitosan spectrum (Fig. 2a) and peaks at 1225, 891 and 516 cm^{-1}, corresponding P=O stretching and deformation, were present in the TPP spectrum (Fig. 2b).

The TGA thermograms for the CTS, TPP and CTS–ECH–TPP samples are shown in Fig. 3. The thermogravimetric profiles reveal that the mass loss occurs in two stages. The first stage at around 64–110 °C, with a mass loss of 2–10%, is related mainly to the loss of

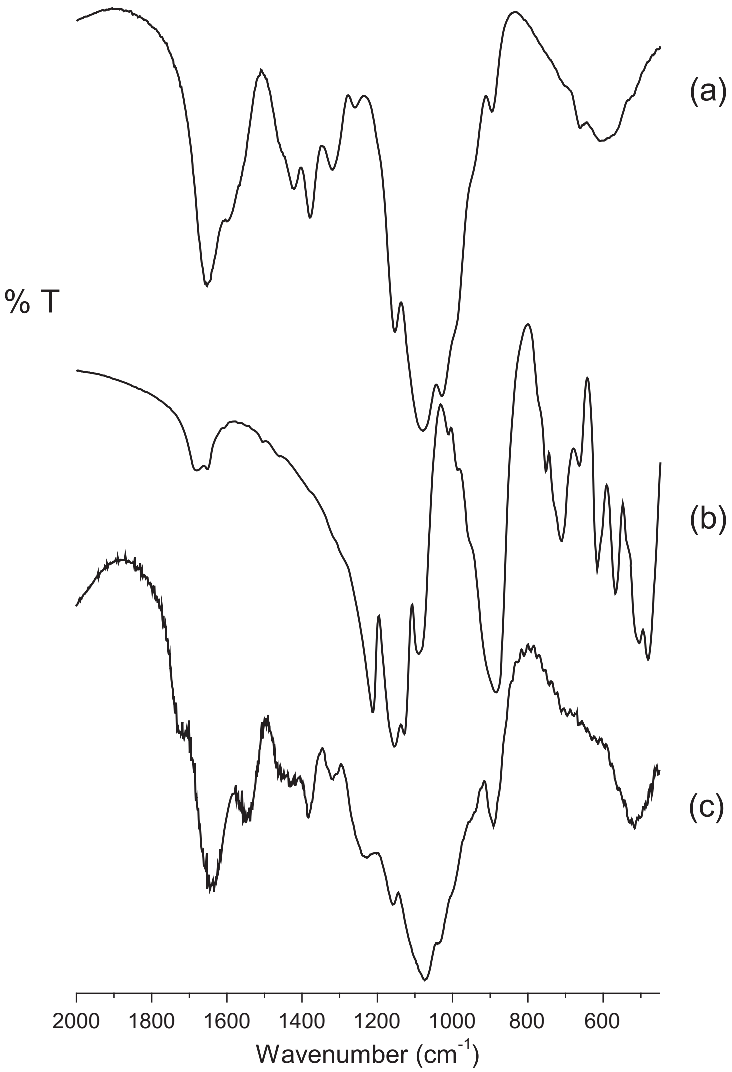

Fig. 2. FT-IR spectra of: (a) CTS, (b) TPP and (c) CTS–ECH–TPP, using KBr pellets in the range of 2000–450 cm^{-1}.

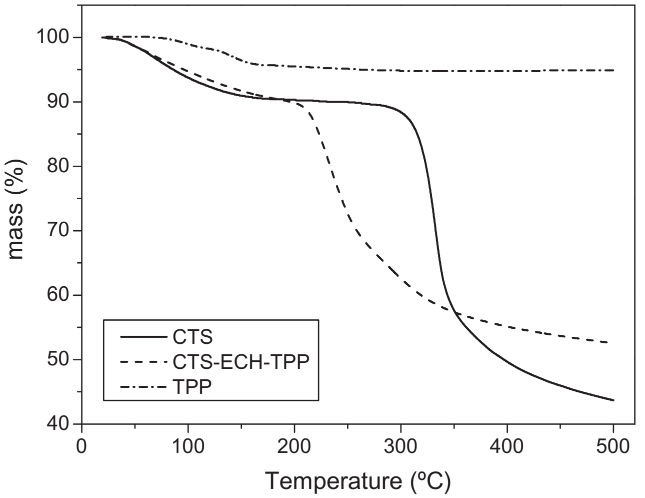

Fig. 3. TGA thermograms of CTS, TPP and CTS–ECH–TPP. The samples were analyzed under nitrogen flow at a rate of 50 mL min^{-1} and at a heating rate of 10 °C min^{-1}.

water physically adsorbed on the surface of the materials. The second stage showed that the degradation temperature for CTS was 332.2 °C with a mass loss of 49.7%, while the degradation of CTS–ECH–TPP was observed at 231.6 °C with a mass loss of 37.8%.

The degradation temperature for CTS–ECH–TPP is lower than that of the unmodified chitosan, which indicates that the adsorbent is less thermally stable than chitosan. The decrease in CTS–ECH–TPP stability, when compared to the original polymer, can be attributed to the ionic interaction between the NH_3^+ groups of chitosan and the negatively charged groups of the triphosphate, as well as the reduction in intramolecular and intermolecular interactions involving the hydrogen bonds present in the pure chitosan, since the molecules of epichlorohydrin and triphosphate occupy a considerable space between the polymer chains.

The characterization results confirmed that the formation of the adsorbent (CTS–ECH–TPP) occurred successfully.

3.2. Effect of pH

The pH of the aqueous solution is an important parameter in adsorption processes. In this study, the effect of pH on the adsorption of Cu(II) and Cd(II) ions onto CTS–ECH–TPP was studied in the pH range of 2–9.

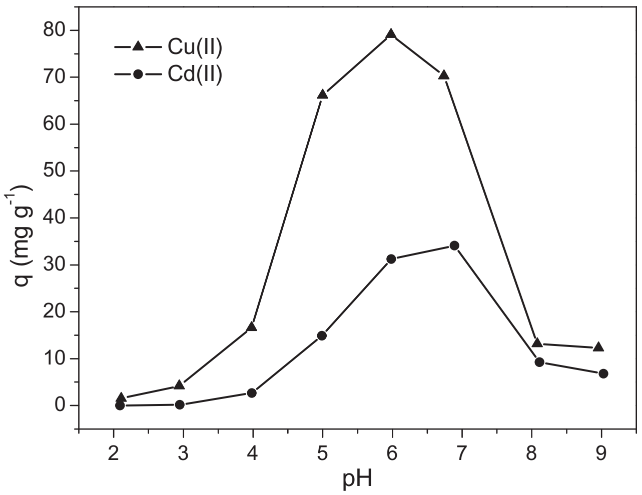

Fig. 4. Effect of pH on adsorption of Cu(II) and Cd(II) ions by CTS–ECH–TPP. Volume = 50.0 mL; [Cu^{2+} or Cd^{2+}] = 50 mg L^{-1}; adsorbent mass = 50.0 mg; temperature = 25 °C; stirring = 200 rpm.

Fig. 4 shows the effect of pH on the adsorption of Cu(II) and Cd(II) ions by CTS–ECH–TPP. It was observed that the amount of Cu(II) ions adsorbed increases with solution pH up to almost pH 6.0 and then decreases with increasing pH. A similar pattern was observed for Cd(II) ions, but the maximum amount adsorbed was reached at pH 7.0.

At acid pH, the adsorbent surface will be completely covered with hydronium ions which compete strongly with metal ions for adsorption sites. With an increase in pH, the concentration of H_3O^+ ions decreases, facilitating the adsorption of metal ions by the adsorbent (Gupta and Bhattacharyya, 2006). At basic pH, there is a disruption of electrostatic interactions and hydrogen bonds between the phosphate groups of the triphosphate and the amino groups of the chitosan. The triphosphate complexed with the metal ions then moves to the solution and the amount of adsorption decreases.

3.3. Adsorption equilibrium isotherm (single and binary metal systems)

Fig. 5(a and b) shows the adsorption equilibrium isotherms obtained for the adsorption of Cu(II) and Cd(II) ions by CTS–ECH–TPP in single and binary metal systems. In this figure the relationship between the amount of metal ion adsorbed on the adsorbent surface and the metal ion concentration of the aqueous phase at equilibrium can be observed. This relationship showed that the amount adsorbed increased with the equilibrium concentration of the metal ion in solution, progressively reaching saturation of the adsorbent.

3.3.1. Langmuir isotherm

The Langmuir model assumes that the adsorbent surface has sites of identical energy and that each adsorbate molecule is located at a single site; hence, it predicts the formation of a monolayer of the adsorbate on the adsorbent surface (McKay, 1996). This equation (Eq. (3)) is preferentially used in studies on adsorption in solution, where q_e and C_e are the amount adsorbed and the adsorbate concentration in solution, respectively, both at equilibrium, K_L is the Langmuir constant and q_m is the maximum adsorption capacity of the monolayer formed on the adsorbent

$$q_e = \frac{K_L C_e q_m}{1 + K_L C_e} \tag{3}$$

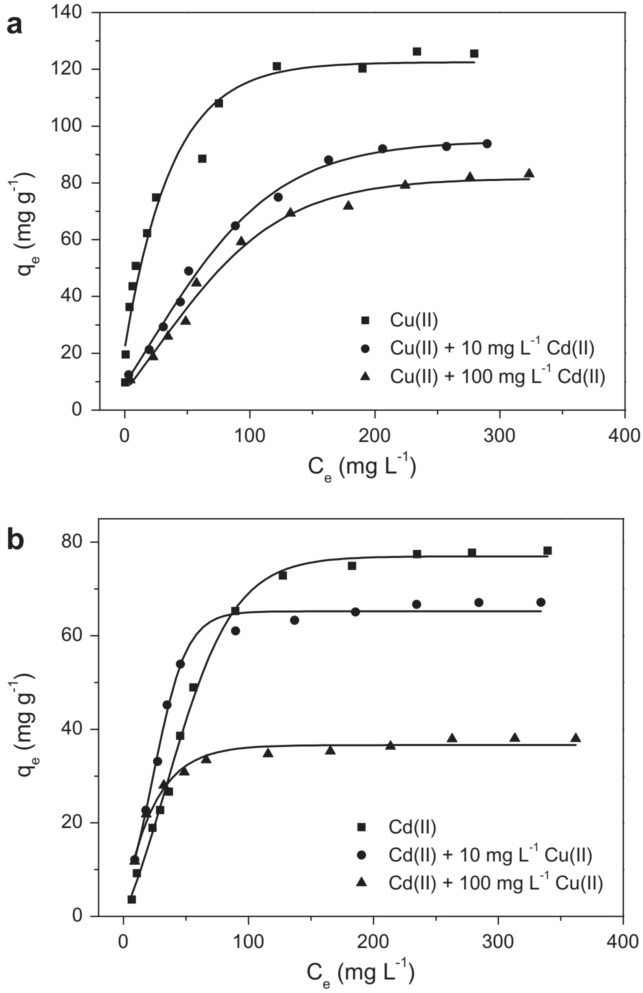

Fig. 5. Adsorption isotherm of Cu(II) (a) and Cd(II) (b) ions onto CTS–ECH–TPP in single and binary metal systems. Volume = 50.0 mL; [Cu^{2+} or Cd^{2+}] = 10–400 mg L^{-1}; pH 6.0 for Cu(II) and 7.0 for Cd(II); adsorbent mass = 50.0 mg; contact time 48 h; temperature = 25 °C; stirring = 200 rpm.

The linear form of the Langmuir isotherm, represented by Eq. (4), is employed to determine the q_m and K_L values from the angular and linear coefficients obtained by plotting C_e/q_e as a function of C_e, which are given in Table 1

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{4}$$

The Langmuir constant (K_L) is used to calculate R_L, a dimensionless separation factor given by Eq. (5)

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

where C_0 is the initial metal concentration (mg L^{-1}). The R_L values indicate whether the adsorption is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Ngah et al., 2002; Futalan et al., 2011). The R_L values calculated are given in Table 1.

3.3.2. Freundlich isotherm

The Freundlich isotherm is an empirical equation and is one of the most widely used isotherms for the description of multi-site adsorption. Mathematically, it is expressed by

$$q_e = K_F C_e^{1/n} \tag{6}$$

Table 1
Adsorption isotherm parameters for adsorption of Cu(II) and Cd(II) ions onto CTS–ECH–TPP in single and binary metal systems.

Metal ions	Cu(II)	Cu(II) + 10 mg L^{-1} Cd(II)	Cu(II) + 100 mg L^{-1} Cd(II)
Langmuir			
q_m (mg g^{-1})	130.72	118.62	101.23
K_L (L mg^{-1})	8.44×10^{-2}	1.45×10^{-2}	1.46×10^{-2}
R_L	0.372–0.029	0.775–0.147	0.773–0.146
R^2	0.998	0.993	0.998
%*D*	13.10	8.12	10.56
Freundlich			
K_F (mg g^{-1})	20.76	3.40	2.55
n	2.64	1.57	1.52
R^2	0.986	0.970	0.969
%*D*	16.16	13.63	15.42
Metal ions	Cd(II)	Cd(II) + 10 mg L^{-1} Cu(II)	Cd(II) + 100 mg L^{-1} Cu(II)
Langmuir			
q_m (mg g^{-1})	83.75	70.72	39.49
K_L (L mg^{-1})	3.91×10^{-2}	6.26×10^{-2}	6.86×10^{-2}
R_L	0.561–0.060	0.444–0.038	0.422–0.035
R^2	0.997	0.999	0.999
%*D*	15.29	6.21	10.83
Freundlich			
K_F (mg g^{-1})	1.21	2.72	4.34
n	1.14	1.35	1.96
R^2	0.978	0.933	0.929
%*D*	33.70	54.68	52.40

Table 2
Maximum adsorption capacity of various chitosan samples modified for adsorption of Cu(II) and Cd(II) ions reported in the literature.

Adsorbent	q_m (mg g^{-1})		References
	Cu(II)	Cd(II)	
Chitosan microspheres	80.71	–	Ngah et al. (2002)
Chitosan crosslinked with EGDE	45.94	–	Ngah et al. (2002)
Chitosan crosslinked with GLA	59.67	–	Ngah et al. (2002)
Chitosan crosslinked with ECH	62.47	–	Ngah et al. (2002)
Chitosan modified with Reactive Blue 2 dye	57.0	–	Vasconcelos et al. (2007)
Chitosan modified with H_2fmbme complexing agent	113.6	–	Vasconcelos et al. (2008)
Chitosan–tripolyphosphate chelating resin	200	–	Lee et al. (2001)
Chitosan–alginate	–	6.6	Gotoh et al. (2004)
Chitosan modified with sulphoxine chelant agent	–	32.9	Vitali et al. (2008)
Chitosan modified with Reactive Orange 16 dye	107.3	90.3	Vasconcelos et al. (2009)
Chitosan modified with BPMAMFF complexing agent	109	38.5	Justi et al. (2005)
Chitosan crosslinked with ECH–TPP	130.72	83.75	Present study

Eq. (6) can also be expressed in the linearized logarithmic form as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

where K_F and *n* are the Freundlich isotherm constants indicating the adsorption capacity and adsorption intensity, respectively (Ngah et al., 2004; Febrianto et al., 2009). The results calculated for the Freundlich isotherm constants are given in Table 1.

The most appropriate isotherm model to interpret the adsorption of metal ions by CTS–ECH–TPP was selected based on the highest values for the average absolute percentage deviation (%*D*) and correlation coefficient (R^2) obtained.

The %*D* values were calculated as follows:

$$\%D = \left(\frac{1}{N} \sum_{i=1}^{N} \left| \frac{q_{e,\exp} - q_{e,\mathrm{calc}}}{q_{e,\exp}} \right| \right) \times 100 \tag{8}$$

where $q_{e,\exp}$ and $q_{e,\mathrm{calc}}$ are the experimental and calculated amounts adsorbed, respectively, and *N* is the number of experimental points.

The results for the adsorption isotherm parameters related to the adsorption of Cu(II) and Cd(II) ions onto CTS–ECH–TPP in single and binary metal systems are given in Table 1.

On analyzing the values of %*D* and R^2 obtained using the Langmuir and Freundlich isotherm models, it can be observed that the Langmuir equation provided the best fit for the experimental data. Thus, this isotherm model was used to interpret the adsorption of metal ions by the CTS–ECH–TPP adsorbent.

The maximum adsorption capacities (q_m) for Cu(II) and Cd(II) ion adsorption onto other modified chitosan adsorbents, preparation under different conditions, reported in the literature, are compared in Table 2. It can be seen that the q_m value varies considerably for different adsorbents and that, by comparison, the CTS–ECH–TPP system exhibits a good capacity to adsorb Cu(II) and Cd(II) ions from aqueous solutions.

The R_L values at concentrations of 20–400 mg L^{-1} are in the range of $0 < R_L < 1$, which indicates that the adsorption of Cu(II) and Cd(II) ions onto CTS–ECH–TPP in single and binary metal systems is favorable.

According to the results presented in Table 1 and Fig. 5a, it can be observed that on increasing the concentration of Cd(II) ions the amount of Cu(II) ions adsorbed from the Cu(II)/Cd(II) binary solutions was lower in relation to the single metal solution. With the addition of 10 mg L^{-1} Cd(II) ions there was a 9.2% reduction in the amount of Cu(II) ions adsorbed, while with the addition of 100 mg L^{-1} Cd(II) ions there was a 22.8% decrease in the amount of Cu(II) ions adsorbed.

In Fig. 5b, it can be noted that on increasing the concentration of Cu(II) ions in the binary solutions the amount of Cd(II) ions adsorbed decreased. In the binary solution with 10 mg L^{-1} Cu(II) ions added there was a reduction of 14.9% and with 100 mg L^{-1} Cu(II) ions there was a reduction of 52.7% in the amount of Cd(II) ions adsorbed, in relation to the single metal solution.

These results revealed that the presence of Cu(II) ions had a stronger influence on the adsorption of Cd(II) than the presence of Cd(II) ions on the adsorption of Cu(II). Through the values for the maximum adsorption capacity (q_m) obtained in the experiments with binary systems Cu(II) + 100 mg L^{-1} Cd(II) and Cd(II) + 100 mg L^{-1} Cu(II) it was observed that the adsorption of Cu(II) ions was around 2.6 times higher than that of Cd(II) ions. This indicates that the affinity of the adsorbent for adsorption of the metal ions followed the order of Cu(II) $\gg$ Cd(II). These results are in agreement with those of the single metal solutions, which showed higher adsorption of Cu(II) ions when compared to Cd(II) ions.

According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, the oxygen atoms of the triphosphate groups added to the chitosan can be classified as hard bases. These atoms coordinate preferentially with metal ions classified as hard acids. In this regard, Cu(II) is classified as an intermediate acid, while the Cd(II) ion is a soft acid due to its high polarizability and large atomic radius (Martell and Hancock, 1996). This explains why the adsorbent had a lower affinity for Cd(II). Furthermore, a comparison of the properties of the metals studied, such as ionic radius (0.73 Å $Cu^{2+} <$ 0.95 Å Cd^{2+}), hydrated ionic radius (4.19 Å $Cu^{2+} <$ 4.26 Å Cd^{2+}) and electronegativity (1.90 $Cu^{2+} >$ 1.69 Cd^{2+}), explains the affinity of the adsorbent for Cu(II) being higher than for Cd(II). According to Vasconcelos et al. (2009), this high adsorption of Cu(II) ions is a consequence of its paramagnetic nature, high electronegativity, coordination geometry and Jahn–Teller distortion which occurs when the Cu(II) is bound to the CTS–ECH–TPP.

Table 3
Concentration of elements present in the sample of freshwater collected from Peri Lagoon determined by ICP-MS.

Element	Concentration (μg L^{-1})
Na	2395
Mg	816
K	645
Si	615
Sr	62.4
Ba	22.2
Zn	10.4
Cu	UDL
Cd	UDL

UDL = Under Detection Limit (18 ng L^{-1} for Cu and 2 ng L^{-1} for Cd).

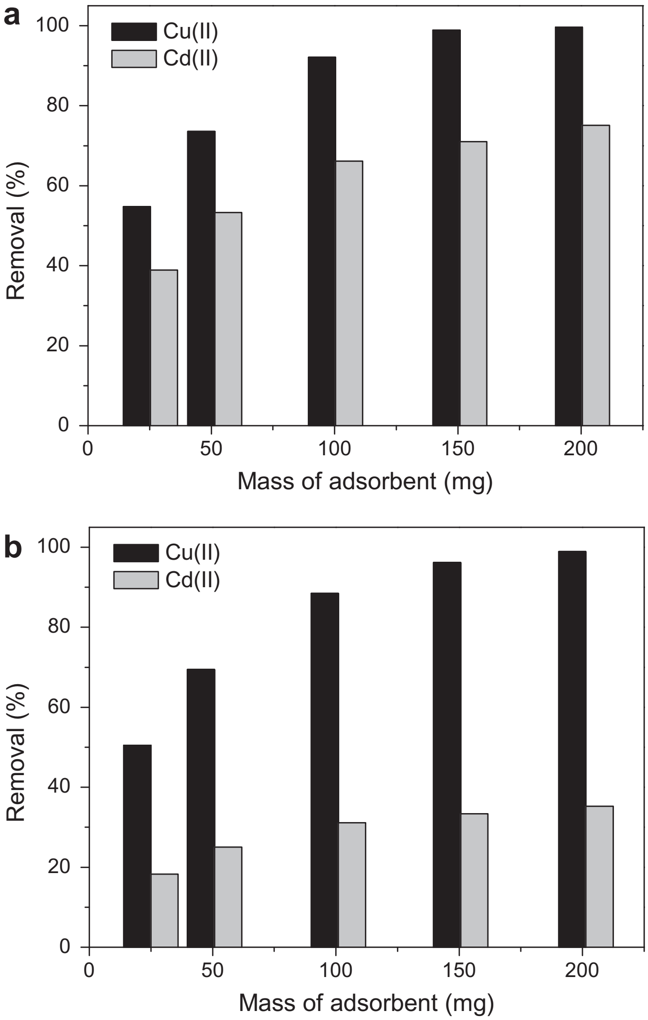

Fig. 6. Removal of Cu(II) and Cd(II) ions added to a freshwater sample through adsorption onto CTS–ECH–TPP. (a) Single metal solutions and (b) binary metal solutions. Volume = 50.0 mL; [Cu^{2+} or Cd^{2+}] added = 10 mg L^{-1}; adsorbent mass = 25.0–200.0 mg; contact time 48 h; temperature = 25 °C; stirring = 200 rpm.

Table 4
Percentages of Cu(II) and Cd(II) ion desorption from M^{2+}-CTS–ECH–TPP complex.

Eluent	Concentration (mol L^{-1})	Desorption (%)	
		Cu(II)	Cd(II)
HNO_3	0.1	87.9	88.5
HNO_3	1	88.7	89.9
EDTA	0.1	87.6	88.2
EDTA	0.01	84.9	88.0
EDTA	0.001	64.0	86.5

3.4. Removal of Cu(II) and Cd(II) ions added to the lagoon water sample

After performing the adsorption studies, the adsorbent was tested in the removal of Cu(II) and Cd(II) ions added to a sample of freshwater collected from Peri Lagoon located in Florianópolis, SC, Brazil. The initial pH of the sample was 7.2. Qualitative analysis of the sample performed by ICP-MS revealed the presence of the elements Na, Mg, K, Si, Sr, Ba and Zn and the absence of detectable amounts of Cu(II) and Cd(II) ions using this method (Table 3).

The values for the percentage removal of Cu(II) and Cd(II) ions as a function of the mass of CTS–ECH–TPP are shown in Fig. 6, where Fig. 6a shows the removal of metal ions from single metal solutions and Fig. 6b from binary metal solutions.

In Fig. 6a it can be noted that of the metal ions studied, across the whole range of adsorbent masses used, the Cu(II) ion had the highest removal values. It was found that 200 mg of CTS–ECH–TPP was able to remove approximately 100% of the Cu(II) and 75% of the Cd(II) added to the freshwater sample, indicating a greater affinity of the adsorbent for Cu(II) ions.

In Fig. 6b there is a sharp decrease in the removal of Cd(II) ions, as also observed on the competitive adsorption isotherm. Furthermore, across the whole range of adsorbent masses used, the order of the affinity of CTS–ECH–TPP for the metal ions was the same as that obtained from the competitive adsorption isotherm, i.e., Cu(II) $\gg$ Cd(II).

3.5. Desorption and reuse studies

Desorption studies are important to investigate the possibility for the recovery of metals adsorbed on the adsorbent surface, as well as for the regeneration of the adsorbent for subsequent reuse.

In this study, HNO_3 and EDTA solutions, at different concentrations, were used as eluents. To protonate the acid sites of the adsorbent and elute the metal to the solution HNO_3 was used, while EDTA has a sufficiently high complexation constant for Cu(II) and Cd(II) to allow the almost complete removal of the adsorbed ions.

The values for the percentage of Cu(II) and Cd(II) ions desorbed for each eluent are listed in Table 4. The highest desorption values for Cu(II) and Cd(II) ions (88.7% and 89.9%, respectively) were obtained using a 1 mol L^{-1} HNO_3 solution. The 0.1 mol L^{-1} HNO_3 and EDTA solutions also provided good desorption results (around 88%).

After optimization of the eluent and its corresponding concentration, the adsorption/desorption cycles were repeated five times as shown in Fig. 7. In this figure it can be observed that there was a decrease of 14.6% in the amount of Cu(II) ions adsorbed from the first to second cycle, but from this cycle onward the amount adsorbed remained practically constant. In the case of Cd(II) ions it was found that the amount adsorbed was little changed after five cycles. Therefore, the CTS–ECH–TPP adsorbent could be reused for the adsorption of Cu(II) and Cd(II) ions from aqueous solutions.

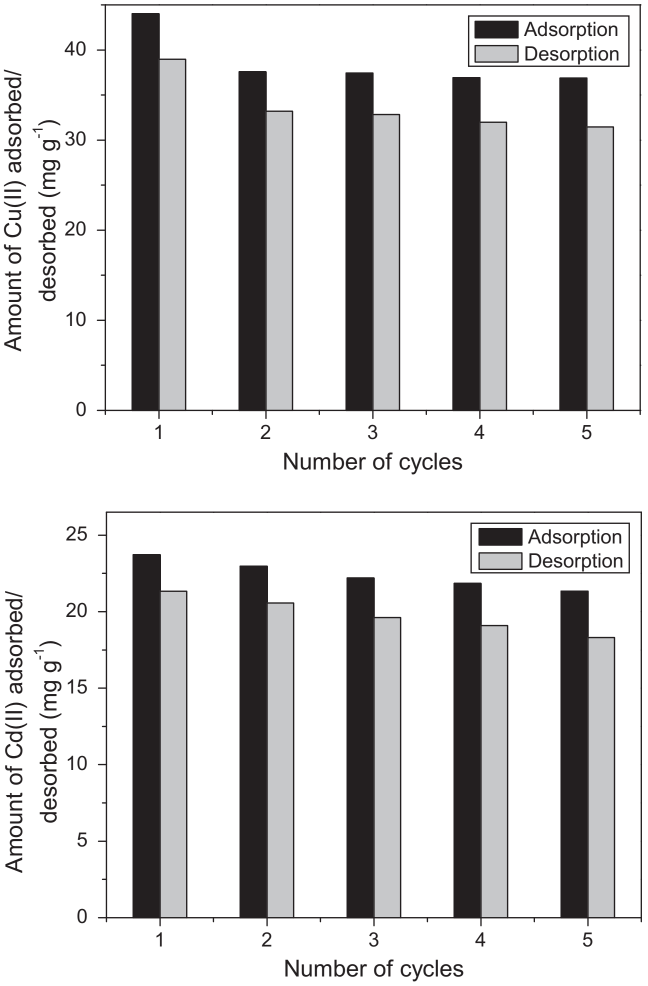

Fig. 7. Adsorption and desorption cycles: adsorption – volume = 50.0 mL; [Cu^{2+} or Cd^{2+}] = 25 mg L^{-1}; pH 6.0 for Cu(II) and 7.0 for Cd(II); adsorbent mass = 20.0 mg; contact time 48 h; temperature = 25 °C; stirring = 200 rpm. Desorption – volume = 50.0 mL of 1 mol L^{-1} HNO_3; contact time 3 h; temperature = 25 °C; stirring = 200 rpm.

4. Conclusions

Techniques such as SEM, CHN, EDS, FT-IR and TGA, used for the characterization of CTS–ECH–TPP, confirmed that the formation of the adsorbent occurred successfully. The equilibrium adsorption data for Cu(II) and Cd(II) in single solutions revealed higher maximum adsorption capacity for Cu(II) when compared with Cd(II). In binary solutions, the presence of Cu(II) had a stronger influence on cadmium adsorption than the presence of Cd(II) on copper adsorption. The adsorbent showed stronger interaction with Cu(II) than Cd(II), suggesting that this material can be used in separation and pre-concentration processes and in the treatment of industrial effluents containing Cu(II) and/or Cd(II) ions.

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