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Chemically modified natural cotton fiber: a low-cost biosorbent for the removal of the Cu(II), Zn(II), Cd(II), and Pb(II) from natural water

Álisson Gomes Paulino, Adriana Jesus da Cunha, Rení Ventura da Silva Alfaya, Antonio Alberto da Silva Alfaya*

Departamento de Química, Centro de Ciências Exatas, Universidade Estadual de Londrina, CP 6001, 86051-990, Londrina, Paraná, Brazil
Tel. +55 04333714811; Fax: +55 04333714276; email: alfaya@uel.br

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ABSTRACT

In this work, the removal of Cu(II), Zn(II), Cd(II), and Pb(II) ions from aqueous solution by natural cotton fiber modified with citric acid (NCFCA) is reported, using both batch and continuous systems. Specifically, kinetics and adsorption isotherms have been determined considering the effect of contact time, pH, and heavy metals concentration. Adsorption isotherms show that the experimental maximum adsorption capacity of Cu(II), Zn(II), Cd(II), and Pb(II) were 6.12, 4.53, 8.22, and 21.62 mg g^{-1}, respectively, at 25°C and pH 5. Furthermore, breakthrough curves were obtained for the adsorption of heavy metals using a fixed bed column packed with NCFCA at pH 5, flow rate = 2.5 mL min^{-1} and 1.0×10^{-4} mol L^{-1} of metals concentration. The Thomas model has been used for data fitting of adsorption competitions of continuous experiments and for determining the design parameters that are useful to characterize the performance of the packed bed column. The natural water real samples were treated with the fixed bed column packed with NCFCA, and the results of the analyses of the percolated samples show that the biosorbent is efficient for the removal of heavy metals that are present in low concentrations in the samples.

Keywords: Cotton fiber; Adsorption; Heavy metals; Fixed-bed; Kinetics; Wastewater treatment

1. Introduction

Heavy metal contamination of various water resources is of great concern because of their toxic effect to human beings, other animals and the environment. The major sources of heavy metal pollutants such as Cu(II), Zn(II), Cd(II), and Pb(II) are from industrial and agricultural activities [1]. Heavy metals are not biodegradable and tend to be accumulated in living tissues, causing various diseases and disorders; therefore, they must be removed before discharge to natural resources [2]. Thus, the removal of heavy metals has particular importance from the ecotoxicological viewpoint.

Copper is an essential trace element for human health and plays an important role in carbohydrate and lipid metabolism and in the maintenance of heart and blood vessel activity [3]. However, an excessive amount of copper in the body can be toxic. Acute symptoms from excessive ingested copper include

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*Corresponding author.

salivation, epigastric pain, nausea, vomiting, diarrhea, intravascular hemolytic anemia, acute hepatic and renal failure, shock, and coma.

Zinc is a common metal found in effluents of a large number of industries. This metal is an essential element for life and is a micronutrient in trace amounts [4]. Acute symptoms from excessive ingested zinc include depression, lethargy, neurologic signs such as seizures and ataxia, and increased thirst [5].

Lead and cadmium are the most problematic heavy metals in regard to environmental pollution. Acute symptoms from excessive ingestion include brain problems, kidney damage, renal disorder and Itai–Itai [5].

The chemical precipitation process has been traditionally employed for heavy metal removal from industrial wastewater. However, adsorption and ion-exchange methods have been evaluated as promising techniques. In the context of the removal heavy metals at low cost from wastewaters many studies have been focused on the investigation of agricultural by-products and livestock waste [6–9].

Cellulose constitutes the most abundant and renewable polymer resource available worldwide. It is estimated that by photosynthesis, 10^{11}–10^{12} tons of cellulose are synthesized annually in a relatively pure form, for example, in the seed hairs of the cotton plant, but more often are combined with lignin and hemicelluloses in the cell wall of woody plants [10]. Unmodified cellulose has a low heavy metal adsorption capacity as well as variable physical stability. Therefore, chemical modification of cellulose is carried out to achieve adequate structural durability and efficient adsorption capacity for heavy metal ions [11]. Cellulose is relatively inert because the hydroxyl groups, which are responsible for the majority of the reactions with organic or inorganic reagents, are involved in inter- and intra-molecular hydrogen bonds [12]. Natural cotton fiber is a cheap material, with few studies in the literature about surface chemical modification with organic reagents to increase its adsorption capacity for heavy metals in aqueous solution [3,13–17].

The present work describes the preparation of thermochemically esterified natural cotton fiber with citric acid to produce a biosorbent for the removal of heavy metals. The extraction of Cu(II), Zn(II), Cd(II), and Pb(II) were investigated under batch method and on the column packed with NCFCA.

2. Materials and methods

2.1. Materials

The natural cotton fiber was gracefully donated by the Cooperativa Central de Algodão de Ibiporã (Coceal), Paraná State, Brazil. The natural cotton fiber is of long type with 10 m of diameter and 12–15 cm of length. All reagents used in this study were of analytical grade. The water used was Milli-Q_{plus} quality.

2.2. Surface modification of natural cotton fiber

The natural cotton fibers were washed with water and dried at 60°C. Then, 200 g of this material was dispersed in 1.5 L of a NaOH 0.5 mol L^{-1} solution, and the mixture was left for 1 h at 100°C. The fibers were filtered and washed with HCl 0.01 mol L^{-1} solution and then with water. The cotton fibers were dried at 60°C and denominated natural cotton fiber treated, NCFT.

About 4.0 g of NCFT were dispersed in 150 mL of a citric acid 1.0 mol L^{-1} solution and the resulting mixture was left for 0.5 h at room temperature. Then, the mixture was placed at 60°C for 24 h and finally to 125°C for 2 h. The material was washed with water and dried again at 60°C and was denominated natural cotton fiber modified with citric acid (NCFCA).

2.3. Characterization

2.3.1. Physical measurements

The sample used for the scanning electron microscopy analysis was dispersed on a double-faced tape adhered on a brass support and coated with a film of graphite on a low-voltage sputtering Balzers MED 020 apparatus. The images were made with a JEOL JSM 6360LV microscope.

The infrared spectra of NCFT and NCFCA were obtained with KBr pellets (2 wt.%), and the equipment used was a Shimadzu FT-IR 8300 spectrophotometer with 4 cm^{-1} resolution and after 200 scans.

2.4. Determination of the point of zero charge (PZC)

The PZC for the NCFCA was determined by the processes described previously in the literature for organic materials [18–20].

2.5. Adsorption studies

2.5.1. pH variation

The maximum adsorption capacity was determined by batch method at pH values varying between 1 and 6, shaking the suspension for 1 h at a temperature of 25 ± 1°C. The desired pH was adjusted with NaOH or HCl solutions. In a typical experiment, 200 mg of the NCFCA was suspended in 50 mL of the cation solution $1.0 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}$ at the desired pH. At different periods of time, aliquots of supernatant were withdrawn for metal analysis. The amount of metal adsorbed on the adsorbent surface (q_e) was calculated by applying the equation

$$q_e = (q_i - q_s)/m \tag{1}$$

where q_i and q_s are the initial and the amount (mg) of the metal ion which remained in solution after adsorption procedure, respectively, and m is the mass (g) of the solid in each flask. The metal ions were analyzed by an inductively coupled plasma (ICP-AES) spectrometer E-Thermo Jarrell Ash ICAP 61.

2.5.2. Batch adsorption

The NCFCA adsorption capacity for individual metals was studied at the pH 5.0 using the batch procedure. For this determination, about 200 mg of the adsorbent were immersed in 50 mL of the metal solutions, whose concentrations varied between 1.0×10^{-5} and $1.0 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}$. The mixtures were shaken in a thermostated water batch with constant speed for 1 h. After the prescribed contact time, the aliquots of supernatant withdrawn were analyzed as stated in Section 2.5.1.

2.5.3. Sorption kinetics

In order to consider the kinetic effects, the linear pseudo-first-order equation and pseudo-second-order equation were used [21,22].

2.5.4. Adsorption isotherms

Solutions of Cu(II), Zn(II), Cd(II), and Pb(II) ions at different concentrations were prepared, ranging from 1.0×10^{-5} to $1.0 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}$ at pH 5.0. Afterwards, 50 mL of metal solutions was individually used and agitated with 200 mg of NCFCA in an orbital shaker for 1 h. After the allotted contact time had passed, aliquots of supernatant withdrawn and were analyzed as stated in Section 2.5.1.

2.5.5. Studies of adsorption in fixed-bed column

The experimental module included a glass column with 0.5 cm internal diameter and 35 cm height connected with a peristaltic pump and a thermostatic bath. The bed was packed distributing 2 g of NCFCA (dry base) along the column. The material was maintained in contact with water for 12 h to complete the hydration process. Then, the residual water was drained, and the height was fixed in 18.5 cm. The material was washed with water using continuous flow for 12 h in order to have the bed accommodation. After this procedure, the heavy metals solution (Cu (II), Zn(II), Cd(II), and Pb(II) mixed with the concentration of $1.0 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}$ of each metal ion) was fed to the column by peristaltic pump. The pH feed solution was adjusted to 5.0 with a solution of HCl. The thermostatic bath was used to keep the feed solutions and the system at a constant temperature of $25 \pm 1^{\circ}\text{C}$. The feed flow rate used was $2.5\,\text{mL}\,\text{min}^{-1}$. Samples of metallic ions solution were collected at the column outlet at different time intervals and have been analyzed for metal concentrations by using the ICP-AES equipment. The samples were collected until the system reached a steady state (column exhaustion).

3. Results and discussion

3.1. Preparation of the biosorbent

The treatment of the natural cotton fiber with a NaOH solution with heat was necessary to remove lignin, resins, and natural fats. This treatment allows the fibers to become white, hydrophilic and makes possible for the chemical surface modification with citric acid. Fig. 1 shows in a schematic form the process of incorporation of the citric acid on the surface of NCFT.

The natural cotton fiber is primarily composed of cellulose that has a large number of hydroxyl groups, forming inter- and intra- molecular hydrogen bonds [23]. Thermic treatment of citric acid promotes the formation of citric anhydride and it reacts with the hydroxyl groups of cellulose producing carboxylate groups on the fiber [3]. The high mechanical and chemical stability of the NCFCA is due to the cellulose structure with its hydrogen bonds that are not easily broken.

3.2. IR spectra

The FTIR spectra before and after chemical modification on the cotton fiber are shown in Fig. 2. Comparing the FTIR spectrum of NCFCA (curve B) with the NCFT (curve A), it can be seen that there was a new characteristic stretching vibration absorption band of carbonyl group at $1{,}735\,\text{cm}^{-1}$ due to citric acid esterification on the fiber surface.

As shown in Fig. 2, the spectra display a number of absorption bands, indicating the complex nature of the material examined. The FTIR spectroscopic analysis indicated broadbands at $3{,}420\,\text{cm}^{-1}$, representing bonded –OH groups. The bands observed at

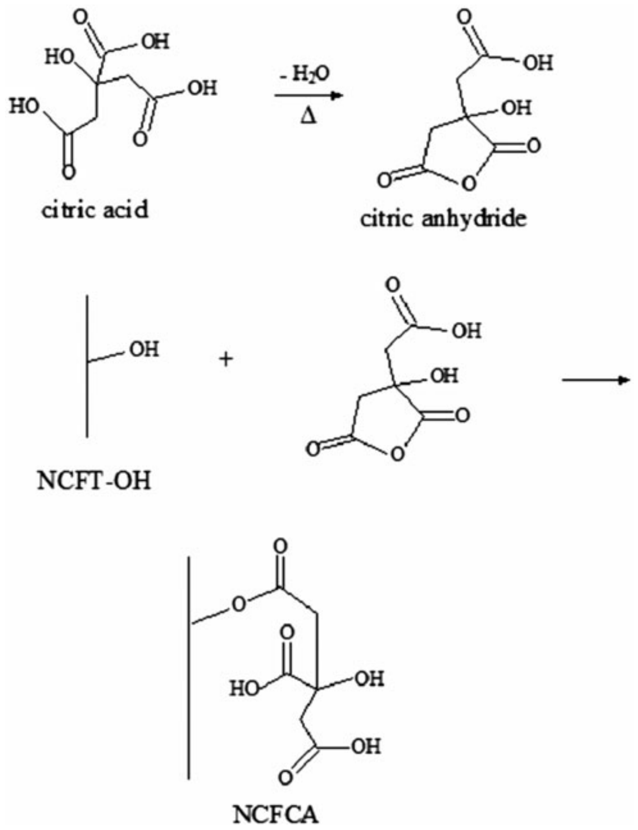

Fig. 1. Schematic representation of the preparation of NCFCA.

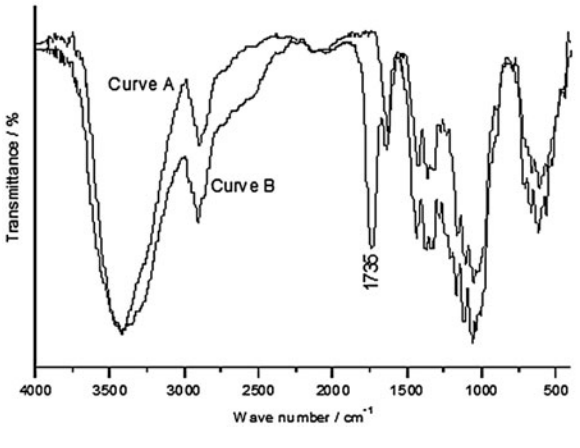

Fig. 2. IR spectra of NCFT (curve A) and NCFCA (curve B).

about 2,915–2,848 cm^{-1} could be assigned to the aliphatic –C–H group. The band around 1,631 cm^{-1} corresponds to the –C–O– stretch. Symmetric bending of $–CH_3$ is observed to shift to 1,434 and 1,345 cm^{-1}. The band observed at 1,141 cm^{-1} could be assigned to C-O stretching of ether groups.

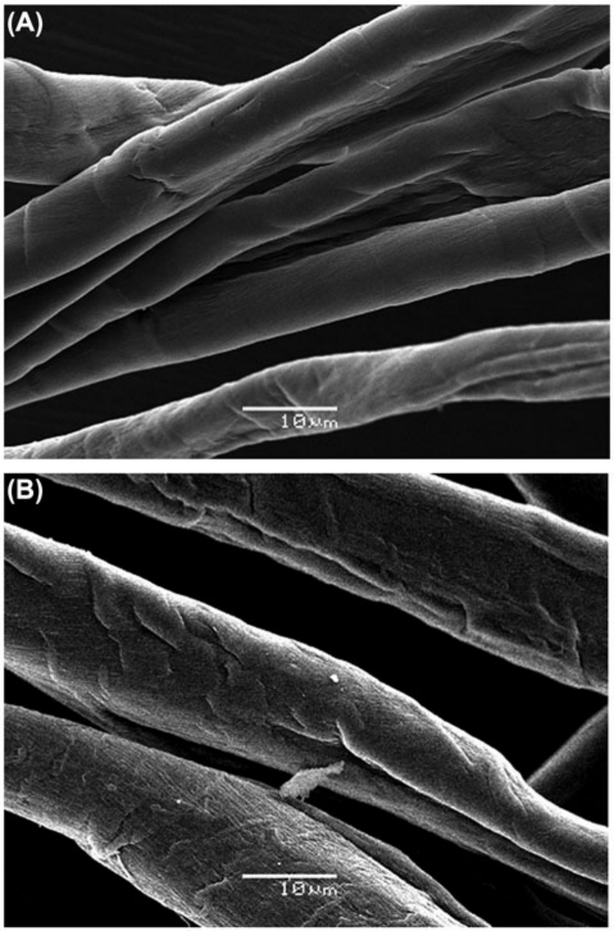

Fig. 3. SEM image of NCFCA (A) and NCFT (B).

3.3. Surface morphology

The SEM images of NCFT and NCFCA are shown in Fig. 3. The image of NCFCA (Fig. 3(A)) shows a smooth surface due to chemical reaction of esterification with citric acid and –OH groups available on the surface of cotton fiber without destruction the structure of cotton fibers. The image of NCFT (Fig. 3(B)) shows small fractures on fiber surface caused by the process of removing natural fats and resins using a NaOH solution, and those fractures are promoted by the rupture of the intermolecular interactions between cellulose fibrils.

3.4. Adsorption studies

3.4.1. pH variation

Fig. 4 shows the initial pH variation of the solution with the adsorption capacity of metal ions by NCFCA. The adsorption of metal ion was lowest at the initial pH 1.0 until pH 2.5. When $\mathrm{pH} < 3$, the nonionic form

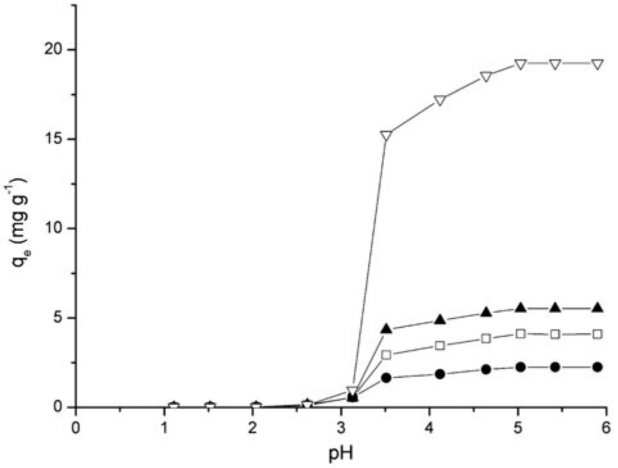

Fig. 4. Variation of the adsorption capacity of Cu(II) (□), Zn(II) (●), Cd(II) (▲), and Pb(II) (▽) with the change pH solution by NCFCA.

of carboxyl group, –COOH, was represented, metal ion adsorption was small because of the absence of electrostatic interaction. When pH > 3, carboxyl group was turned into $–COO^-$, ion adsorption was increased, but the adsorption capacity of metal ions was not significantly altered in the pH range 4–6. For the reasons stated previously, pH 5.0 was selected for the other experiments.

The acid sites on NCFCA are of the carboxylic group type. The determined value of the pzc for the biosorbent was 3.2 [18–20]. This value is highly consistent with the behavior shown in Fig. 4. For pH values above 3.2, the acid groups are negatively charged increasing the adsorption of metal ions due to electrostatic interaction between species. For pH values lower than 3.2, the site with the proton acid is not electrostatic charged and thus present a very small adsorption.

3.4.2. *Effect of contact time*

Fig. 5 illustrates the time required for metal ions adsorption with NCFCA. The adsorption rate of metal ions was very quick during the initial stage of the adsorption process. After a very fast adsorption, the value gradually increased with time and reached adsorption equilibrium at about 10 min.

3.4.3. *Influence of initial metal concentration*

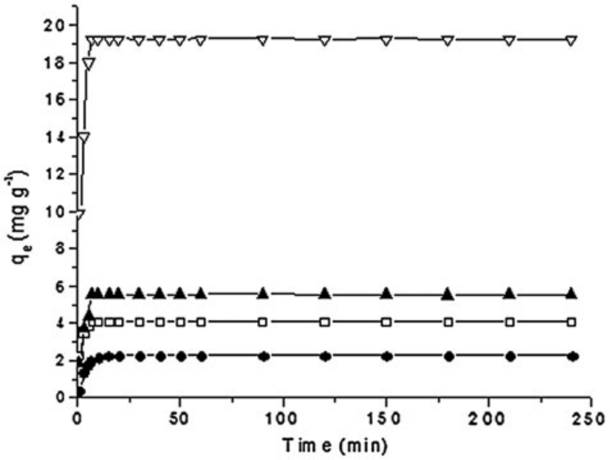

Fig. 5. Effect of contact time on adsorption capacity of Cu (II) (□), Zn(II) (●), Cd(II) (▲), and Pb(II) (▽) by NCFCA, with concentration of 1.0 × 10–4 mol L^{-1}.

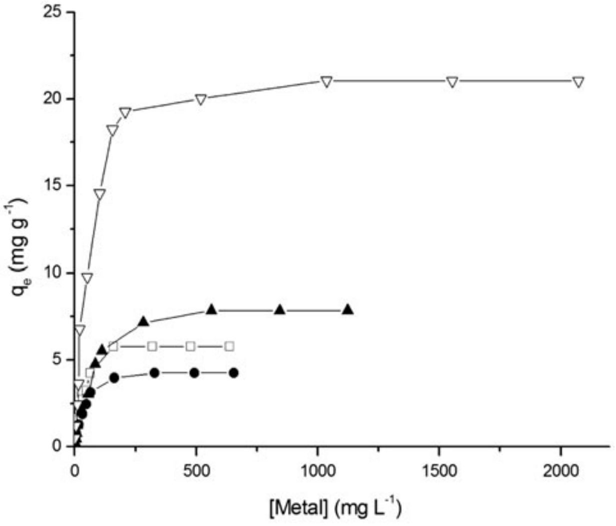

Fig. 6. Influence of initial concentration of Cu(II) (□), Zn (II) (●), Cd(II) (▲), and Pb(II) (▽) on adsorption by NCFCA with 1 h of contact time and pH 5.0.

The influence of initial metal concentration on adsorption capacity by NCFCA was shown in Fig. 6. The metal ion concentration studied was in the range of 1.0×10^{-5}–1.0×10^{-2} mol L^{-1} at pH 5.0 and 1 h of contact time. The value of adsorption obtained was 5.79, 4.26, 7.86, and 20.7 mg g^{-1} for Cu(II), Zn(II), Cd (II), and Pb(II), respectively.

With the data in Fig. 6, the Langmuir equation was employed to study the sorption isotherm of the metal ions Cu(II), Zn(II), Cd(II), and Pb(II).

The Langmuir equation is based on the assumption that maximum adsorption corresponds to the saturated monolayer of sorbate molecule on the sorbent surface that the energy of adsorption is constant and that there is no transmigration of sorbate in the plane of the surface.

Table 1
Langmuir parameters and linear coefficients

Parameter/ion	Cu	Zn	Cd	Pb
b (L mg^{-1})	0.034 ± 0.001	0.022 ± 0.002	0.023 ± 0.001	0.028 ± 0.002
Q_m (mg g^{-1})	6.12 ± 0.08	4.53 ± 0.06	8.22 ± 0.09	21.62 ± 0.18
Q_m (mmol g^{-1})	0.096 ± 0.001	0.069 ± 0.001	0.073 ± 0.001	0.104 ± 0.001
R^2	0.9994	0.9996	0.9998	0.9997

The linear Langmuir equation [23] was shown as follows:

$$C_e/q_e = 1/(bQ_m) + C_e/Q_m \tag{2}$$

where C_e (mg L^{-1}) is the concentration of the metallic ions solution at equilibrium, Q_m is the maximum adsorbed capacity and represents a practical limiting adsorption capacity when the adsorbent surface is fully covered with monolayer adsorbate molecules and b is Langmuir constant. The Q_m value can be obtained from the slope ($1/Q_m$) of the linear plot of C_e/q_e vs. C_e. The parameters of the Langmuir model are presented in Table 1.

3.4.4. *Adsorption kinetics*

3.4.4.1. Pseudo-first-order model. The adsorption kinetics data of metallic ions were analyzed using the Lagergren rate equation [24]. The linearized form of the pseudo-first-order equation [22] is illustrated by:

$$\log(q_e - q_t) = \log q_e(k'_1/2.303)t \tag{3}$$

where q_e and q_t are the amounts of metallic ions adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k'_1 is the Lagergren rate constant of first-order adsorption time (min^{-1}). Values of q_e and k'_1 were calculated from the slope and intercept of plot of $\log(q_e - q_t)$ vs. t (figure not shown). The R^2 values of the pseudo-first-order model (0.09–0.17) found are significantly lower than pseudo-second-order model. Based on these results, it can be concluded that the adsorption of metallic ions on NCFCA did not fit a pseudo-first-order kinetic model and suggests that the pseudo-first-order model was not suitable for modeling the adsorption of metallic ions on NCFCA.

3.4.4.2. Pseudo-second-order model. A pseudo-second-order model can be used to describe the sorption kinetics. The linearized form of the pseudo-second-order equation [22] is illustrated by:

$$t/q_t = 1/k'_2 q_e^2 + t/q_e \tag{4}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the solute amounts adsorbed per unit mass of adsorbent at equilibrium time, t is the time (min), and k'_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). The equilibrium constants of pseudo-second-order model, k'_2 and q_e can be obtained by plotting t/q_t vs. t (Fig. 7). This model is more likely to predict kinetic behavior of adsorption of metallic ions on NCFCA. The linear plot of t/q_t vs. t (Fig. 7) showed R^2 value greater than 0.999 as can be seen in Table 2. In addition, the theoretical $q_{e,\text{cal}}$ value is closer to the experimental $q_{e,\text{exp}}$ value. Considering these results, it can be said that pseudo-second-order kinetic model provided a good correlation for the adsorption of metallic ions on NCFCA in contrast to pseudo-first-order model.

3.5. *Continuous process*

The dynamic behavior of a packed bed column is described in terms of the breakthrough curve. Typical experimental breakthrough curves for Cu(II), Zn(II),

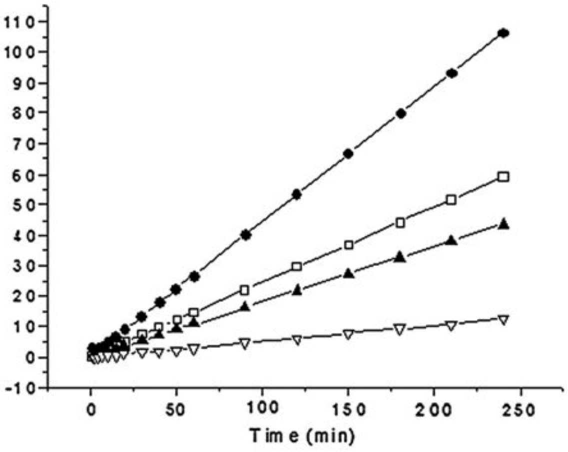

Fig. 7. Pseudo-second-order kinetic plot for the adsorption of Cu(II) (□), Zn(II) (●), Cd(II) (▲), and Pb(II) (▽) by NCFCA.

Table 2
Pseudo-second-order adsorption rate constant and calculated and experimental q_e values for metallic ions adsorption

Pseudo-second-order kinetic model				
Parameter/ion	Cu	Zn	Cd	Pb
k'_2 (g mg^{-1} min^{-1})	1.592 ± 0.005	0.366 ± 0.003	0.357 ± 0.004	0.204 ± 0.002
$q_{e,\mathrm{cal}}$ (mg g^{-1})	4.06 ± 0.02	2.27 ± 0.02	5.54 ± 0.02	19.26 ± 0.02
$q_{e,\mathrm{exp}}$ (mg g^{-1})	4.06 ± 0.03	2.25 ± 0.03	5.52 ± 0.04	19.25 ± 0.04
R^2	0.9999	0.9997	0.9999	0.9999

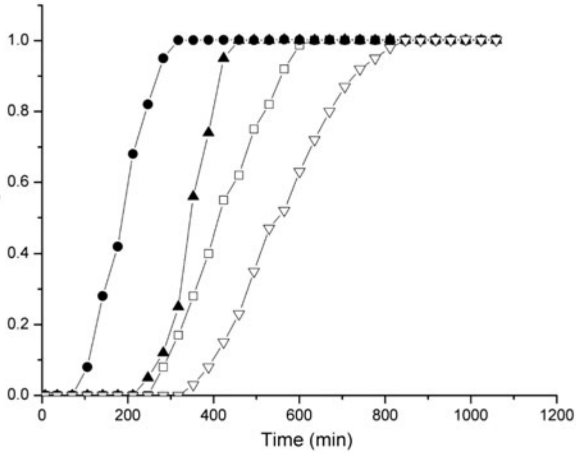

Fig. 8. Experimental breakthrough curves for Cu(II) (□), Zn(II) (●), Cd(II) (▲), and Pb(II) (∇) ions adsorbed on NCFCA in the concentration = 1.0 × 10–4 mol L^1, pH 5.0, 25°C, and flow rate = 2.5 mL min^{-1}.

Cd(II), and Pb(II) in competition conditions are represented in Fig. 8. The experiments were conducted using one solution with all metallic ions in the same concentration, 1.0×10^{-4} mol L^{-1} and flow rate of 2.5 mL min^{-1} at pH 5.0. The maximum adsorption capacity can be calculated using the following equation:

$$q_e = (C_o - C)/mV \tag{5}$$

where q_e is the amount of metallic ion on biosorbent (mg g^{-1}), C_o and C are the initial and final concentration, respectively, (mg L^{-1}), m is the mass of biosorbent (g) in the column, and V is the volume of the solution (L). Table 3 shows the values of maximum adsorption capacity of the metallic ions in continuous process in competitive conditions. The order of saturation of the bed was Zn < Cu < Cd < Pb in those experimental conditions.

The theoretical analyses of fixed-bed experiment in metallic ion adsorption were based on Thomas and Yoon–Nelson models.

Table 3
Values of the maximum capacity adsorption of metallic ions on NCFCA in column in competitions conditions. The concentration is 1.0 x 10^{-4} mol L^{-1}, pH 5.0, mass 2.039 g and flow rate 2.5 mL L^{-1}

Metallic ion	Maximum capacity adsorption (mg g^{-1})
Zn^{2+}	0.525 ± 0.002
Cu^{2+}	1.376 ± 0.003
Cd^{2+}	2.199 ± 0.005
Pb^{2+}	5.914 ± 0.007

The Thomas model assumes a Langmuir model of adsorption/desorption process and that no axial dispersion was derived with adsorption so that the rate of the driving force obeyed second-order reversible reaction kinetics [22,25].

$$C_t/C_o = 1/1 + \exp((k_{\mathrm{Th}/f})(q_{\mathrm{Th}}m - C_oV_BN)) \tag{6}$$

where k_{Th} (mL min^{-1} mg^{-1}) is the Thomas rate constant, q_{Th} (mg g^{-1}) is the theoretical saturated adsorption capacity in Thomas model, f (mL min^{-1}) is the flow rate of the effluent, m (g) is the mass of the adsorbent, V_B (mL) is the effluent volume, C_o (mg mL^{-1}) is the influent metallic ions concentration, C_t (mg mL^{-1}) is the effluent concentration at time t, and N is the bed volume number. The value of C_t/C_o is the ratio of effluent and influent metallic ions concentrations at a certain time.

The Yoon–Nelson model is a relatively simple model which assumes that the rate of decrease in the probability of adsorption for each adsorbate ion was proportional to the probability of adsorbate sorption and the probability of adsorbate breakthrough on the adsorbent [26].

$$\ln(C_t/C_o - C_t) = k_{\mathrm{YN}}nN - k_{\mathrm{YN}\tau} \tag{7}$$

where k_{YN} (min^{-1}) is the Yoon–Nelson rate constant, n (min) is the time-BV Scale factor, N is the bed volume number, τ is the time required for 50% adsorbate breakthrough (min), C_o (mg L^{-1}) is the influent ion concentration, C_t (mg L^{-1}) is the effluent concentration at time t.

The simulated results by aforementioned models were all listed in Table 4. According to the correlation coefficients of the linear form for the two models, a more accurate prediction could be made on the adsorption process in fixed-bed systems by the Thomas model. The accordance of the experimental data (Fig. 8) with the Thomas model also indicated that the adsorption behavior of metallic ions was a Langmuir-type adsorption and followed pseudo-second-order kinetics, which was fully consistent with the analyses in the bath studies.

In general, the breakthrough curves obtained in this study represent a normal adsorption curve with an observed typical S-shape and its characteristics and concentration gradient change significantly with respect to the feed concentration, flow rate, and pH. To characterize the performance of NCFCA-packed bed column, several key parameters obtained from the breakthrough curve data have been determined. Specifically, the mass transfer zone (MTZ) is one of the parameters frequently used to determine the effective height of the adsorption column [27,28]. This parameter is defined as the length of adsorbing zone in the column and can be calculated from:

$$\mathrm{MTZ} = L(t_e - t_b/t_e) \tag{8}$$

where L is the bed height in cm, t_b is the time required to reach the breakthrough point, and t_e is the time to reach the exhaustion point, respectively. Typically, the breakthrough is determined when the effluent concentration reaches 5% of the influent concentration, while the exhaustion of packed bed column is reached when the effluent concentration is equal to 95% of the influent concentration [28]. So the Thomas model has been used for the calculation of MTZ taking account that t_b (i.e. $C/C_o = 0.05$) and t_e (i.e. $C/C_o = 0.95$) are given by [27]:

$$t_b = (q_{\mathrm{bed}} W_{\mathrm{bed}}/QC_o) - (\ln\,(19)/k_{\mathrm{Th}} C_o) \tag{9}$$

$$t_e = (q_{\mathrm{bed}} W_{\mathrm{bed}}/QC_o) + (\ln\,(19)/k_{\mathrm{Th}}\ C_o) \tag{10}$$

where Q is the flow rate in the column, (mL $\min^{-1}$), q_{bed} is the maximum metal adsorption capacity of the column, (mg g^{-1}) and W_{bed} is the mass of the bed in g. For favorable separations, the breakthrough curves would be a step function and, as a consequence, a high value of t_b is desirable. The column performance was also characterized by calculating the ratio of the

Table 4
The parameters in fixed-bed experiments for adsorption on various metallic ions

Thomas model				Yoon–Nelson model			Breakthrough parameters			
Ion	k_{TH} (mL mg^{-1} $\min^{-1}$)	q_{TH} (mg g^{-1})	R^2	K_{YN} ($\min^{-1}$)	τ (min)	R^2	t_b (min)	t_e (min)	MTZ (cm)	R_q
Cu	4.723 ± 0.003	2.16 ± 0.04	0.9293	0.034 ± 0.001	273 ± 0.5	0.9056	287 ± 0.5	620 ± 0.5	9.94 ± 0.02	0.353 ± 0.006
Zn	7.032 ± 0.005	0.96 ± 0.02	0.9896	0.046 ± 0.002	120 ± 0.5	0.9232	100 ± 0.5	270 ± 0.5	11.65 ± 0.03	0.212 ± 0.008
Cd	4.205 ± 0.007	3.17 ± 0.03	0.9926	0.047 ± 0.001	230 ± 0.5	0.9356	253 ± 0.5	450 ± 0.5	8.10 ± 0.03	0.386 ± 0.005
Pb	1.257 ± 0.002	9.13 ± 0.05	0.9689	0.026 ± 0.002	359 ± 0.5	0.9217	387 ± 0.5	830 ± 0.5	9.87 ± 0.02	0.422 ± 0.006

Table 5
ICP results of natural water real samples before and after treatment with the NCFCA in fixed-bed

Sample	Ions	C_{initial} (mg L^{-1})	C_{final} (mg L^{-1})	Removal ratio (%)
1	Cu	1.05 ± 0.02	nd	100.0
	Zn	0.89 ± 0.01	nd	100.0
	Cd	1.15 ± 0.01	0.04 ± 0.01	96.5
	Pb	0.79 ± 0.02	nd	100.0
2	Cu	0.99 ± 0.01	nd	100.0
	Zn	1.13 ± 0.02	0.03 ± 0.01	97.3
	Cd	0.87 ± 0.01	nd	100.0
	Pb	1.06 ± 0.02	nd	100.0
3	Cu	1.02 ± 0.02	nd	100.0
	Zn	1.17 ± 0.02	0.07 ± 0.01	94.0
	Cd	0.92 ± 0.01	nd	100.0
	Pb	1.01 ± 0.01	nd	100.0
4	Cu	1.02 ± 0.01	nd	100.0
	Zn	0.86 ± 0.02	nd	100.0
	Cd	1.06 ± 0.01	nd	100.0
	Pb	1.14 ± 0.02	0.01 ± 0.01	99.1
5	Cu	1.06 ± 0.01	nd	100.0
	Zn	0.75 ± 0.01	nd	100.0
	Cd	1.02 ± 0.01	nd	100.0
	Pb	1.04 ± 0.01	nd	100.0
6	Cu	0.36 ± 0.01	nd	100.0
	Zn	0.85 ± 0.01	nd	100.0
	Cd	1.26 ± 0.02	0.01 ± 0.01	99.2
	Pb	1.08 ± 0.01	nd	100.0
7	Cu	0.76 ± 0.01	nd	100.0
	Zn	0.96 ± 0.01	nd	100.0
	Cd	0.22 ± 0.01	nd	100.0
	Pb	0.32 ± 0.01	nd	100.0
8	Cu	1.36 ± 0.02	nd	100.0
	Zn	1.84 ± 0.02	0.01 ± 0.01	99.5
	Cd	0.32 ± 0.01	nd	100.0
	Pb	0.18 ± 0.01	nd	100.0
9	Cu	0.18 ± 0.01	nd	100.0
	Zn	0.22 ± 0.01	nd	100.0
	Cd	0.12 ± 0.01	nd	100.0
	Pb	0.24 ± 0.01	nd	100.0
10	Cu	0.13 ± 0.01	nd	100.0
	Zn	1.54 ± 0.01	0.01 ± 0.01	99.4
	Cd	1.76 ± 0.01	nd	100.0
	Pb	0.92 ± 0.01	nd	100.0

nd = not detected.

maximum adsorption capacity of heavy metals obtained in adsorption isotherm at batch conditions (Q_m) to the adsorption capacity of the packed bed column (q_{Th}) determined using the Thomas model where:

$$R_q = q_{\text{Th}}/Q_m \tag{11}$$

This parameter is useful to compare the adsorption performance of NCFCA in both batch and continuous competition conditions and can be used to estimate the filter material usage rate. Thus, the breakthrough and exhaustion times, MTZ and R_q, are summarized in Table 4.

3.5.1. Effect of column reuse

In order to investigate the stability and potential recyclability of the column, 75 extraction–elution cycles were carried out. The column was stored in water between adsorption/desorption cycles. The desorption cycle was carried out by 0.001 mol L^{-1} HCl solution through the bed in the downward direction at a flow rate of 3.5 mL min^{-1} and following with water at pH 4.0 for 15 min. The regenerations were carried in the counter-current mode, that is, in the downflow mode. Counter-current operation generally reduces regeneration cost and regenerant volume and increases effluent quality [29–31]. Elution efficiency (%) was calculated by dividing the total adsorption capacity in the second run by the total adsorption capacity in the first run. The regenerated NCFCA showed uptake capacity comparable with the fresh one over 75 cycles with standard deviation of ±2.5%.

3.6. Application of the NCFCA studied for natural water treatment

The ten real samples from natural water of Igapó I, II, and III lakes in Londrina city were analyzed by ICP technique after filtration. The results before and after treatment are given in Table 5. It is seen that the NCFCA displays high removal efficiency toward Cu (II), Zn(II), Cd(II), and Pb(II) ions.

4. Conclusions

In this paper, adsorption of Cu(II), Zn(II), Cd(II), and Pb(II) ions from aqueous solution by NCFCA in both batch and continuous competitions conditions has been studied. Our results indicate that NCFCA is a acidic material that can be used as adsorbent for metallic ions removal from aqueous solutions. Specifically, kinetics experiments indicate that Cu(II), Zn(II), Cd(II), and Pb(II) ions adsorption is fast and may occur in the external surface of NCFCA. Furthermore, adsorption isotherms show that the experimental maximum adsorption capacity of the Cu(II), Zn(II), Cd(II), and Pb(II) ions is 6.12, 4.53, 8.22, and 21.62 mg g^{-1}, respectively, at 25°C and pH 5 and that chemisorption may play an essential role in the process. For batch experiments, the pseudo-second-order kinetic and Langmuir isotherm are the most appropriate models for fitting metallic ions adsorption data. In the continuous system using a packed column, breakthrough curves were obtained for metallic ions in competition conditions. The Thomas model has shown an appropriate performance in the modeling of Cu(II), Zn(II), Cd(II), and Pb(II) breakthrough curves obtained at operating conditions tested in this study. Finally, the material in the fixed-bed can be used for the removal of the metallic ions in real samples of natural waters in low concentrations.

Symbols

b — Langmuir constant
C — final concentration, (mg L^{-1})
C_e — equilibrium metal ions concentration, ppm (mg L^{-1})
C_o — initial metal ions concentration, ppm (mg L^{-1})
C_t — effluent concentration at time t, (mg mL^{-1})
f — flow rate of the effluent, (mL min^{-1})
k_1' — pseudo-first-order rate constant (min^{-1})
k_2' — pseudo-second-order rate constant (mg g^{-1} min^{-1})
k_{Th} — rate constant, (mL min^{-1} mg^{-1})
k_{YN} — –Nelson rate constant, (min^{-1})
L — bed height, (cm)
m — amount of adsorbent added in g
MTZ — mass transfer zone
N — bed volume number, (mL)
n — BV scale factor (min)
NCFCA — natural cotton fiber modified
NCFT — natural cotton fiber treated
PZC — point of zero charge
Q — flow rate in column, (mL min^{-1})
Q_m — maximum adsorption capacity (mg g^{-1})
q_{bed} — maximum metal adsorption capacity, (mg g^{-1})
q_e — amount of adsorbed per g of adsorbent at equilibrium, (mg g^{-1})
q_i — initial amount of the metal ion, (mg)
q_s — amount of the metal ion remained in solution, (mg)
q_t — amount of the metal ions adsorbed at equilibrium at time t
q_{Th} — theoretical saturated adsorption capacity in Thomas model, (mg g^{-1})
R^2 — linear regression coefficient
R_q — parameter to compare the adsorption performance in both batch and continuous competitions conditions
t — time, (min)
t_e — time to reach the exhaustion point, (min)
t_b — time required to reach the breakthrough point, (min)
τ — time required for 50% adsorbate breakthrough, (min)
V — volume of the solution, (L)
V_B — effluent volume, (mL)
W_{bed} — mass of the bed, (g)

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