Journal of Hazardous Materials 162 (2009) 270–280

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Pecan nutshell as biosorbent to remove Cu(II), Mn(II) and Pb(II) from aqueous solutions

Julio C.P. Vaghetti, Eder C. Lima*, Betina Royer, Bruna M. da Cunha, Natali F. Cardoso, Jorge L. Brasil, Silvio L.P. Dias

Instituto de Química, Universidade Federal do Rio Grande do Sul (UFRGS), Av. Bento Gonçalves 9500, Caixa Postal 15003, CEP 91501-970, Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:
Received 12 January 2008
Received in revised form 6 May 2008
Accepted 8 May 2008
Available online 15 May 2008

Keywords:
Pecan nutshell
Non-linear fitting
Adsorption kinetic
Divalent metallic ion
Biosorption

ABSTRACT

In the present study we reported for the first time the feasibility of pecan nutshell (PNS, *Carya illinoensis*) as an alternative biosorbent to remove Cu(II), Mn(II) and Pb(II) metallic ions from aqueous solutions. The ability of PNS to remove the metallic ions was investigated by using batch biosorption procedure. The effects such as, pH, biosorbent dosage on the adsorption capacities of PNS were studied. Four kinetic models were tested, being the adsorption kinetics better fitted to fractionary-order kinetic model. Besides that, the kinetic data were also fitted to intra-particle diffusion model, presenting three linear regions, indicating that the kinetics of adsorption should follow multiple sorption rates. The equilibrium data were fitted to Langmuir, Freundlich, Sips and Redlich–Peterson isotherm models. Taking into account a statistical error function, the data were best fitted to Sips isotherm model. The maximum biosorption capacities of PNS were 1.35, 1.78 and 0.946 mmol g^{-1} for Cu(II), Mn(II) and Pb(II), respectively.

1. Introduction

Industrial activity is responsible to generate large volume of effluents containing hazardous species [1]. The species with the most toxicological relevance presented on the industrial effluents are the heavy metals and semimetals [1,2], which are not biodegraded by action of the time, being bioaccumulated [2]. In this way, the removal of toxic species from aqueous effluents before being disposed in the environment is required [3].

The conventional methods used to remove toxic metals from aqueous effluents include membrane filtration [4,5], chemical precipitation [5], ion exchange [6], adsorption on activated carbon [7], and silica [8–11]. In the major part of the cases the use of these methods in the remediation processes is precluded due to high costs involved [12]. In this context, in the last years several works reporting the use of alternative low cost adsorbents for toxic metal removal from aqueous solutions has been reported [12,13].

The biosorbent is a natural origin adsorbent such as microorganism [14], residuals of agricultural activities [15,16], wastes of food industries [17,18] that are available in large amounts, mainly at the proximities of the contaminated aqueous effluent, presenting low cost. Therefore the adsorption process for removal of toxic species from the aqueous effluents becomes very attractive from the economical point of view [12,13].

Pecans tree [*Carya illinoensis* (Wangenh.) C. Koch], native from North America, belong to the Juglandaceae family which also includes walnuts (*Juglans* sp.) [19]. In the south of Brazil there are extended plantation areas of the walnut tree, which were introduced by North-American immigrants in 1870 [20]. The kernel of pecan nut is largely consumed in Brazil [20], however the nutshell is a brown by-product of difficult biodegradation. Due to the need to find new and inexpensive adsorbents for metal removal, and also to diminish the large amounts of pecan nutshell (PNS), in this work is presented an application of the use of pecan nutshell as a biosorbent for successful removal of Cu(II), Mn(II) and Pb(II) metallic ions from aqueous solutions.

2. Materials and methods

2.1. Biosorbent material

Pecan walnuts were acquired at local market in Porto Alegre, RS, Brazil. The weight of each nut ranged within 5–10 g. The nutshell corresponds to approximately 49% of the walnut. About 500 g of pecan nutshell was washed with distilled water and subsequently it was boiled in 6.0 L of water during 2 h, in order to remove the water soluble phenolic compounds present in the nutshell [19–21] and avoid its releases to water solutions during the adsorption

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* Corresponding author. Fax: +55 51 3308 7304.
E-mail addresses: eder.lima@ufrgs.br, profederlima@gmail.com (E.C. Lima).

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doi:10.1016/j.jhazmat.2008.05.039

Table 1
Physical and chemical properties of the PNS biosorbent

Elemental analysis for PNS	
C (%)	48.72
H (%)	12.17
N (%)	1.39
Organic matter (%)	97.61
Carboxylic groups (mmol g^{-1})	1.04
Phenolic groups (mmol g^{-1})	1.11
Protein (%)	1.50
Total fiber (%)	38.3
Ashes content (%)	1.09
Mineral composition of PNS	
Na (%)	0.114
K (%)	0.127
Ca (%)	0.124
Mg (%)	0.087
P (%)	0.287
Fe (%)	0.073
Al (%)	0.098
Mn (%)	0.036
Zn (%)	0.0047
Cu (%)	0.0020

experiments. Subsequently, the pecan nutshell was washed with distilled water, dried at 70 °C in an air-supplied oven for 8 h. After that, the pecan nutshell was grounded in a Wiley mill and subsequently sieved. The fraction of biosorbent with diameter of particles lower than 250 μm was used. The apparent density of the powder PNS was 1.30 g cm^{-3}, and it presented an intense brown coloration that was assigned to polyphenols and tannins [19,21].

The PNS biosorbent was characterized by FTIR using a Shimadzu FTIR, model 8300 (Kyoto, Japan). The spectrum was obtained with a resolution of 4 cm^{-1}, with 100 cumulative scans.

The biosorbent was analyzed by scanning electron microscopy (SEM) in JEOL microscope, model JEOL JSM 6060, using an acceleration voltage of 20 kV and magnification ranging from 100 to 20,000 fold.

For determination of major mineral components of the PNS biosorbent, a digestion procedure using nitric acid and hydrogen peroxide, as described elsewhere [22], was employed. The mineral composition of the PNS biosorbent present in the digest of the biomass was determined by flame atomic absorption spectrometry using an Analyst 200 spectrometer (PerkinElmer).

The elemental analysis of the PNS adsorbent was carried out on a CHN PerkinElmer M CHNS/O Analyzer, Model 2400, after degassing treatment at 150 °C. The analyses were made in triplicate.

The fiber contents of PNS natural adsorbent was evaluated as described elsewhere [23].

The physical and chemical properties of the natural adsorbent are presented in Table 1.

2.2. Metallic ion solutions and its determination

Stock standard solutions of metals Cu(II), Mn(II) and Pb(II), containing 5000 mg L^{-1} of each element, were prepared from $CuSO_4{\cdot}5H_2O$, $MnSO_4$, $Pb(NO_3)_2$ analytical grade, furnished by Vetec (Rio de Janeiro, Brazil), by dissolving suitable amounts of these metal salts in distilled waster. Working metal solutions from 10.00 to 1000.0 mg L^{-1} were prepared from suitable serial dilution of the stock solutions. The pH adjustments of the solutions were made with aliquots of 1.0 mol L^{-1} of HCl and NaOH, utilizing a pH/mV hand-held meter handylab 1 Schott (Mainz, Germany) provided with combined glass electrode model Blue-Line 23.

The metal ions were measured by a PerkinElmer Flame Atomic Absorption Spectrometer model Analyst 200 using air-acetylene flame (10.0:2.5 L min^{-1}). Hollow cathode lamps of Cu ($\lambda = 324.75$ nm), Mn ($\lambda = 279.48$ nm) and Pb ($\lambda = 217.00$ nm) of the same manufacturer, were used as radiation sources.

2.3. Batch biosorption experiments

Aliquots of 20.00 mL of 10.00–1000.0 mg L^{-1} of Cu(II), Mn(II) and Pb(II) were added to conical plastic tubes (117 mm height, 30 mm diameter) containing 20.0–300.0 mg of PNS. The flasks were capped, and placed horizontally in a Tecnal shaker model TE-240 (Piracicaba, SP, Brazil), and the system was agitated for 5–360 min. Afterwards, in order to separate the adsorbent from the aqueous solutions, the flasks were centrifuged using Fanem centrifuge (São Paulo, SP, Brazil) and aliquots of 1–5 mL the supernatant were properly diluted to 20.0–100.0 mL in calibrated flasks using water. The metallic ions final concentrations were determined by FAAS.

The amount of adsorbate uptaken by the biosorbent is given by Eq. (1).

$$q = \frac{(C_o - C_f)V}{m} \tag{1}$$

where q is the amount of metallic ion uptaken by the biosorbent (mg g^{-1}); C_o is the initial metallic ion concentration put in contact with the adsorbent (mg L^{-1}), C_f is the metallic ion concentrations (mg L^{-1}) after the batch adsorption procedure, V is the volume of metallic ion solution (L) put in contact with the adsorbent and m is the mass (g) of adsorbent.

2.4. Statistical evaluation of the kinetic and isotherm parameters

In this work, the kinetic and equilibrium models were fitted employing the non-linear fitting method, using the non-linear fitting facilities of the software Microcal Origin 7.0.

In addition, the model was also evaluated by percentage error function [3,11], which measures the differences (%) in the amount of the metallic metal ion uptaken by the adsorbent predicted by the models and the actual q measured experimentally.

$$F_{\text{error}}(\%) = 100 \times \sqrt{\sum_{i}^{p} \left(\frac{q_{i\,\text{model}} - q_{i\,\text{experimental}}}{q_{i\,\text{experimental}}} \right)^2 \cdot \left(\frac{1}{p-1} \right)} \tag{2}$$

where $q_{i\,\text{model}}$ is each value of q predicted by the fitted model and $q_{i\,\text{experimental}}$ is each value of q measured experimentally, and p is the number of experiments performed.

3. Results and discussion

3.1. Characterization of the biosorbent

Fig. 1 shows the FTIR vibrational spectra of pecan nutshell. The wide band with maxima at 3405 cm^{-1} was assigned to the stretching of O—H group of macromolecular association [24], the band at 2925 cm^{-1} was assigned to stretching of $-CH_2-$ bond of methylene groups and the weak band at 2854 cm^{-1} [24] was assigned to –CH– bond of methyne group presented in the PNS structure [18,24]. The sharp band observed at 1708 cm^{-1} was assigned to a C=O bond of carboxylic acid that is usually present in fiber materials containing pectin [17,18]. The strong peak that appears at 1622 cm^{-1} is C=O stretching vibration of a carboxylic acid that exists in with intermolecular hydrogen bond [17,18,24]. The sharp peak observed at 1510 cm^{-1} is assigned to C=C ring stretch of aromatic rings [24]. In addition the band of 1458 cm^{-1} confirms the presence of C=C of aromatic rings [24]. Several bands ranging from 1319 to 1051 cm^{-1} refer to C—O bonding of phenols [16]. This splitting pattern is characteristic of several different C—O bonding of different phenols,

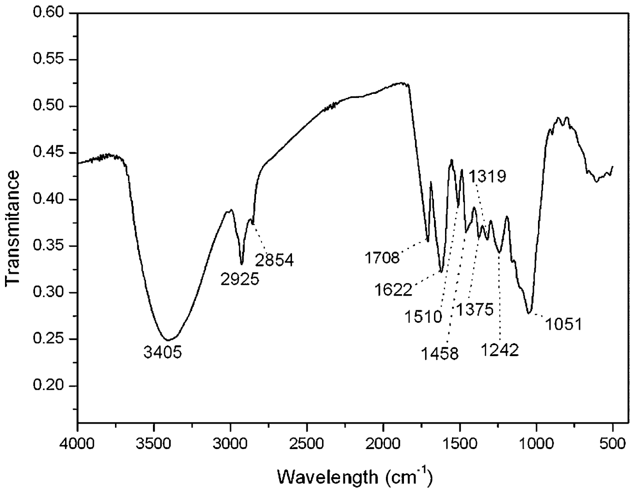


Fig. 1. FTIR spectrum of pecan nutshell biosorbent.

indicating that pecan nutshell is rich on tannins, as already reported [19,21]. From these results, it can be inferred that the metallic ions would bond to pecan nutshell natural adsorbent through interaction with the active groups OH of phenolic groups, as well as the COOH of carboxylic acids [17,18]. The FTIR data are also corroborated by the elemental analysis, CHN contents, carboxylic groups and phenolic groups presented on the biosorbent (Table 1).

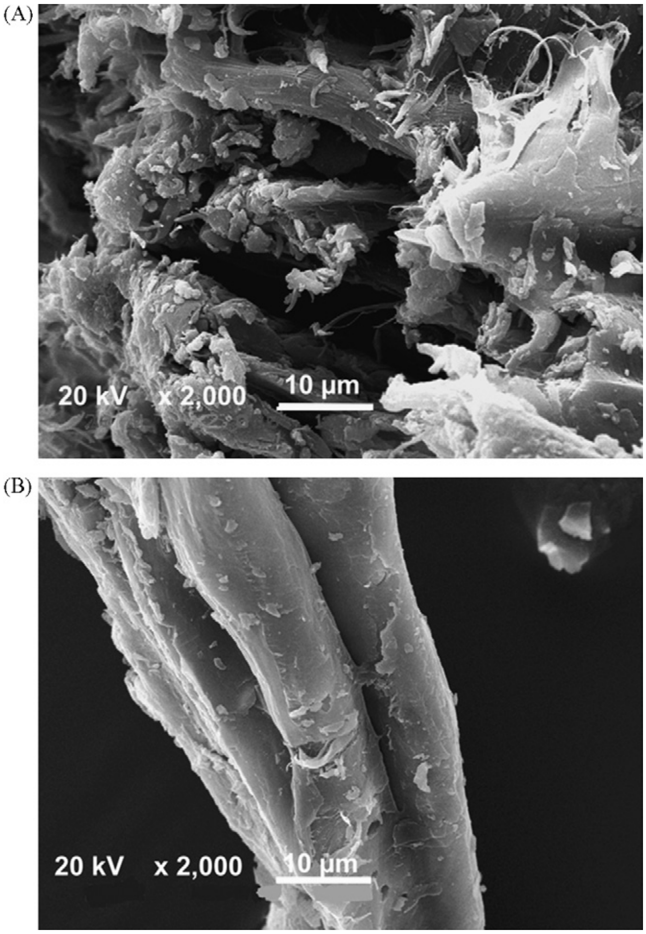


Fig. 2. Scanning electron microscopy of PNS biosorbent: (A) transversal view of fiber 2000×; (B) longitudinal view of fiber 2000×.

Scanning electron micrographies of the PNS are shown in Fig. 2. The fiber material presents a compact surface with some fissures in its structure, mainly at the cross section of the PNS fiber (Fig. 2A). On the other hand, at the longitudinal disposal of the fiber, few fissures can be observed (Fig. 2B).

3.2. *Effects of acidity on adsorption*

One of the most important factors in adsorption studies is the effect of the acidity of the medium. Different adsorbates being adsorbed at diverse adsorbents will present divergent ranges of suitable pH region for adsorption. The acidity of the medium affects the metal adsorption because hydrogen ions could compete with metallic ions to the active sites of the biosorbent. The effects of initial pH on adsorption capacity of Cu(II), Mn(II) and Pb(II) ions using PNS were evaluated within the pH range of 2–8 (Fig. 3, at left). As can be seen, the maximum of biosorption for Cu(II), Mn(II) and Pb(II) took place at pH values ranging from 5 to 6.0. These optimum acidities were in agreement with previous works [11]. For these metallic ions the biosorption increased from 2.0 to 5.0, and it reached a plateau up to pH 6.0. For pH values higher than 6.5 the amount of adsorbates uptaken by the biosorbent was decreased. A possible explanation to this observation can be attributed that at lower pH values, the dissociation of the carboxylic acids of the biosorbent leading to the formation of carboxylate groups will be precluded, since the pK_a of carboxylic acids ranges from 3.8 to 5.0 [25]. Therefore, an increase in the pH value from 2.0 to 5.0 will lead to a remarkable increase in the amount of metallic ion biosorbed. At pH values ranging from 6.5 to 8.0, the hydrolysis of metallic ions could take place [26], leading to a decrease of biosorption process, as already observed for others biosorbents containing carboxylic acids [17,18] as well as for organically modified silica gel [3,11].

In order to continue this work, for all the metallic ions, the pH value was fixed at 5.5 throughout this work.

3.3. *Biosorbent dosage*

The study of natural biosorbent dosages for removal of Cu(II), Mn(II) and Pb(II) from aqueous solution was carried-out at different adsorbent doses (1.0–15.0 g L^{-1}) using 100.0 mg L^{-1} of the metallic ion solutions. It was observed that quantitative removals of the metallic ions were attained for biosorbent dosages of at least 4.0 g L^{-1} for Pb(II) and 5.0 g L^{-1} for Cu(II) and Mn(II) (see Fig. 3 at right). For biosorbent dosages higher than these values, the metallic ions removal remained almost constant. Increases in the percentage of metallic ions removal with biosorbent dosages could be attributed to increases in the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption. On the other hand, the increase in the biosorbent dosage promotes a remarkable decrease in the amount of metallic ion uptaken per gram of adsorbent (q_e) (see Fig. 3, at right). The decrease in q_e value may be due to the concentration gradient between adsorbate and biosorbent with increasing biomass concentration causing a decrease in amount of metallic ion adsorbed per gram of biomass [27]. This can be explained on the basis of initial concentration gradient between the solid adsorbent and the bulk liquid. For a fixed volume of adsorbate solution and for a fixed initial adsorbate concentration, the initial concentration gradient between the adsorbent and the adsorbate solution gets increased with the decrease of initial metallic ion concentration. For a fixed volume of metallic ion solution and initial metallic ion concentration, the initial concentration gradient between the adsorption vacant sites present on the solid adsorbent and the concentration of adsorbate in the solution gets decreased with increasing adsorbent mass, leading to a decrease in q_e value, as already reported

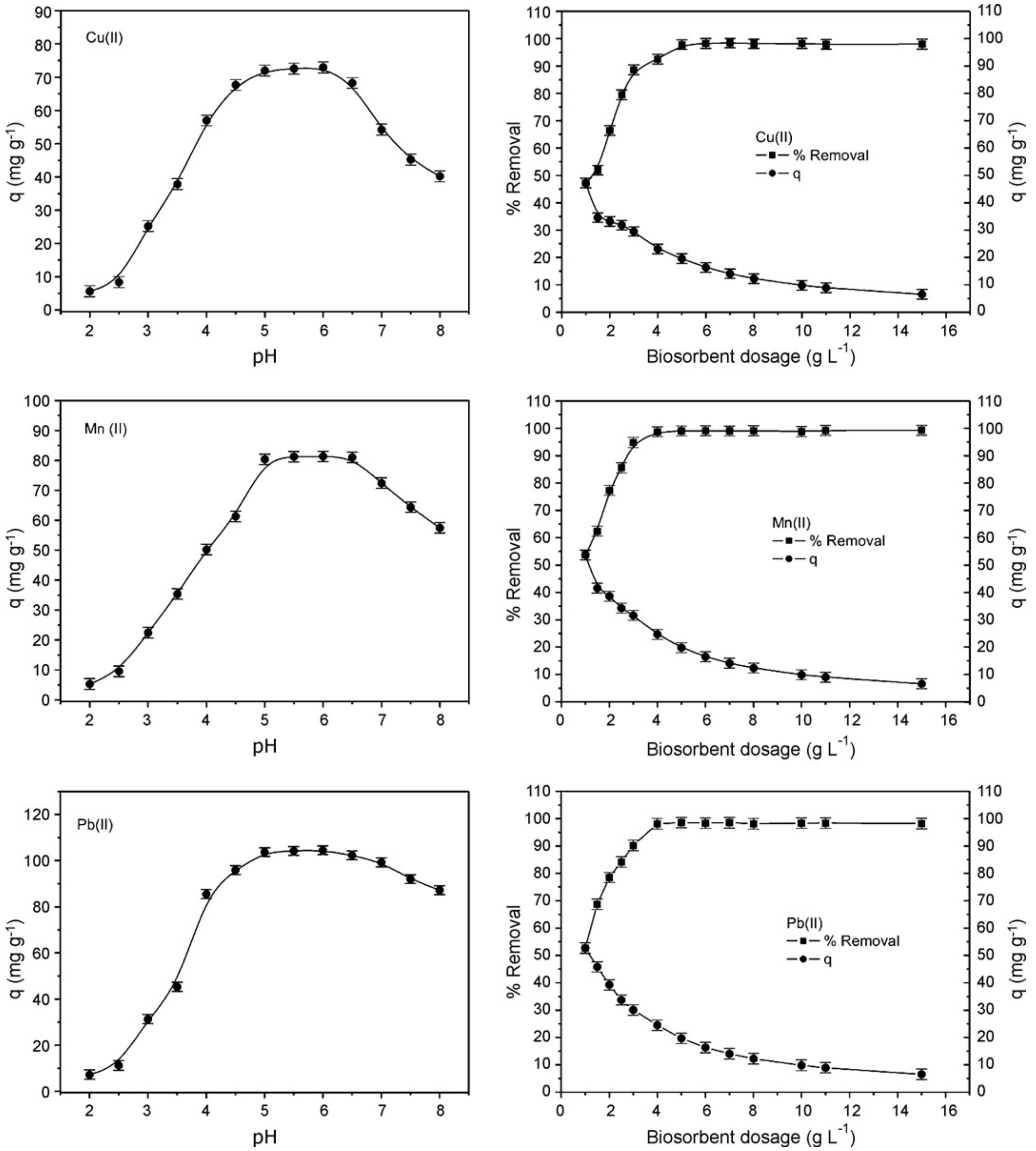


Fig. 3. Left: Effect of pH on the metallic ion adsorption ($100\,mg\,L^{-1}$). Right: Effect of PNS biosorbent dosage on the metallic ions ($100\,mg\,L^{-1}$) removal from aqueous effluents and on the amount of metallic ion adsorbed.

[27]. In this sense, the biosorbent dosage was fixed at $4.0\,g\,L^{-1}$ for Pb(II) and $5.0\,g\,L^{-1}$ for Cu(II) and Mn(II) to continue this work.

3.4. Kinetic studies

Adsorption kinetic study is important in treatment of aqueous effluents as it provides valuable information on the reaction pathways and in the mechanism of adsorption reactions.

Many kinetic models were developed in order to find intrinsic kinetic adsorption constants. Traditionally, the kinetics of metal ions adsorption is described following the expressions originally given by Largegren [28]. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_f(q_e - q_t) \tag{3}$$

where q_t is the amount of adsorbate adsorbed at time t ($mg\,g^{-1}$), q_e is the adsorption capacity in the equilibrium ($mg\,g^{-1}$), k_f is the pseudo-first-order rate constant (min^{-1}), and t is the contact time (min). The integration of Eq. (3) with initial conditions, $q_t = 0$ at $t = 0$, and $q_t = q_t$ at $t = t$ leads to:

$$\ln(q_e - q_t) = \ln(q_e) - k_f t \tag{4}$$

After rearranging this equation in a non-linear form the pseudo-first-order kinetic equation is:

$$q_t = q_e[1 - \exp(-k_f t)] \tag{5}$$

In addition, a pseudo-second-order equation [29] based on adsorption equilibrium capacity may be expressed in the form:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_s(q_e - q_t)^2 \tag{6}$$

where k_s is the pseudo-second-order rate constant ($g\,mg^{-1}\,min^{-1}$). The integration of Eq. (6) with initial conditions, $q_t = 0$ at $t = 0$, and $q_t = q_t$ at $t = t$ leads to:

$$q_t = \frac{k_s q_e^2 t}{1 + q_e k_s t} \tag{7}$$

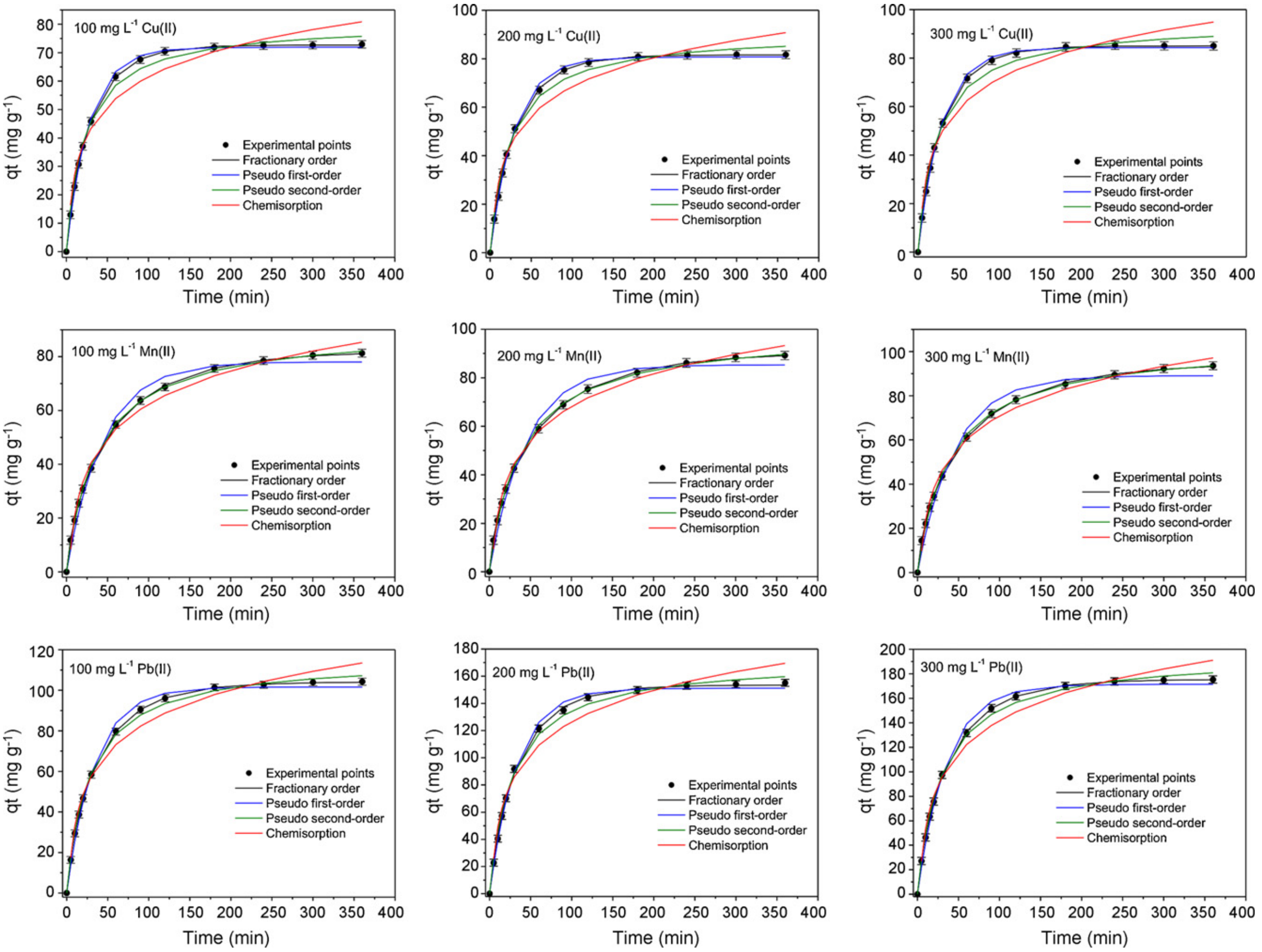


Fig. 4. Non-linear kinetic models for the adsorption of Cu(II), Mn(II) and Pb(II) using PNS as biosorbent.

The initial sorption rate (h_o, expressed in mg g^{-1} min^{-1}) can be obtained when t approaches to zero.

$$h_o = k_s q_e^2 \tag{8}$$

The Elovich equation is for general application to chemisorption kinetics [30]. The equation has been applied satisfactorily to some chemisorption processes and has been found to cover a wide range of slow adsorption rates. The same equation is often valid for systems in which the adsorbing surface is heterogeneous, and is formulated as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{9}$$

Integrating this equation for the boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ for $t = t$, it gives:

$$q_t = \left(\frac{1}{\beta}\right) \ln(t - t_o) - \left(\frac{1}{\beta}\right) \ln(t_o) \tag{10}$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is related to the extent of surface coverage and the activation energy involved in chemisorption (g mg^{-1}) and $t_o = 1/\alpha\beta$.

If t is much larger than to, the kinetic equation can be simplified as

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t) \tag{11}$$

Despite the pseudo-first and pseudo-second-order kinetic models being used for most adsorption kinetic works, determination of some kinetic parameters, as possible changes of the adsorption rates in function of the initial concentration and the adsorption time, as well as the determination of fractionary kinetic orders, still lacks in the kinetic adsorption models reported in the literature. In this way, an alternative fractionary kinetic equation proposed by Avrami [31,32] was described previously [31,32]. The adsorption should be visualized now using Avrami's exponential function, which is an adaptation of kinetic thermal decomposition modeling [31,32].

$$\alpha = 1 - \exp[-(k_{AV} t)]^n \tag{12}$$

where α is adsorption fraction (q_t/q_e) at time t, k_{AV} is the Avrami kinetic constant (min^{-1}), and n is a fractionary reaction order which can be related, to the adsorption mechanism [33,34].

By inputting the α in Eq. (12), the Avrami kinetic equation could be written as:

$$q_t = q_e\{1 - \exp[-(k_{AV} t)]^n\} \tag{13}$$

For describing the adsorption of Cu(II), Mn(II) and Pb(II) on PNS biosorbent the four kinetic models depicted above were fitted (Fig. 4). The kinetic parameters of the fitted models were presented on Table 2.

As can be seen, the Avrami fractionary kinetic order was suitably fitted, presenting low error function values [3,11,16] and also high R^2 values, for the three initial concentration levels of the metallic ions employed. How lower is the error function, lower will be the difference of the q calculated by the model from the q experimentally

Table 2

Kinetic parameters for Cu(II), Mn(II) and Pb(II) using PNS as biosorbent

	C_o (mg L^{-1})								
	Cu(II)			Mn(II)			Pb(II)		
	100.0	200.0	300.0	100.0	200.0	300.0	100.0	200.0	300.0
Fractionary order									
k_{AV} (min^{-1})	0.0337	0.0318	0.0328	0.0185	0.0179	0.0173	0.02623	0.02795	0.02524
q_e (mg g^{-1})	72.6	81.5	85.0	82.2	90.7	95.2	104.1	153.5	175.5
n	0.892	0.903	0.920	0.774	0.752	0.743	0.830	0.881	0.842
R^2	0.9999	0.9996	0.9998	0.9999	0.9999	0.9999	0.9999	0.9991	0.9999
F_{error} (%)	1.10	1.78	1.60	0.91	1.56	0.87	2.26	3.26	1.40
Pseudo-first order									
k_f (min^{-1})	0.0354	0.0334	0.0341	0.0223	0.0223	0.0218	0.0291	0.0300	0.0278
q_e (mg g^{-1})	71.9	80.7	84.3	78.1	85.3	89.1	101.6	151.2	171.4
R^2	0.9983	0.9983	0.9989	0.9899	0.9874	0.9865	0.9948	0.9970	0.9955
F_{error} (%)	3.83	3.61	28.98	11.67	12.37	13.64	6.78	3.60	6.84
Pseudo-second order									
k_s (g mg^{-1} min^{-1})	5.50×10^{-4}	4.50×10^{-4}	4.40×10^{-4}	2.80×10^{-4}	2.60×10^{-4}	2.40×10^{-4}	3.00×10^{-4}	2.10×10^{-4}	1.70×10^{-4}
q_e (mg g^{-1})	80.5	90.9	94.8	90.9	99.3	103.9	115.7	172.1	196.0
h_o (mg g^{-1} min^{-1})	3.56	3.72	3.96	2.31	2.56	2.59	4.01	6.22	6.53
R^2	0.9938	0.9937	0.9926	0.9995	0.9994	0.9989	0.9980	0.9962	0.9976
F_{error} (%)	5.26	6.04	41.40	3.66	4.00	5.88	2.59	6.02	2.77
Chemisorption									
α (mg g^{-1} min^{-1})	8.92	9.05	9.69	5.74	6.34	6.58	9.76	14.4	15.5
β (g mg^{-1})	0.0663	0.0577	0.0555	0.0556	0.0510	0.0489	0.04453	0.02971	0.02606
R^2	0.9635	0.9655	0.9624	0.9916	0.9932	0.9926	0.98079	0.9757	0.9807
F_{error} (%)	11.61	11.45	51.49	10.06	9.52	10.85	7.09	9.62	7.52
Intra-particle diffusion									
k_i (mg g^{-1} $min^{-0.5}$)	2.81	2.34	2.21	2.48	2.83	2.89	4.96	3.61	4.53

Conditions: Temperature was fixed at 25 °C, pH 5.5 biosorbent dosage 4.0 g L^{-1} for Pb(II) and 5.0 g L^{-1} for Cu(II) and Mn(II).

measured. It should be stressed that only the analysis of R^2 values to establishment of a given model is not enough, because the error function evaluates the differences associated with each individual point fitted by the model in relation to each experimental point measured. On the other hand the R^2 value measures the differences associated of each individual point in relation to the average fitted curve [3,11,16]. As an example, the differences of the R^2 and the F_{error} values could be visualized for Cu(II) pseudo-first-order kinetic model for the three levels of concentration (see Table 2). The R^2 values obtained were 0.9983, 0.9983 and 0.9989 for 100, 200 and 300 mg L^{-1} of initial concentration of Cu(II), respectively. The F_{error} values were, 3.83, 3.61 and 28.98%, respectively. It should be stressed that although the best R^2 value obtained with the most concentrated solution of Cu(II) (300 mg L^{-1}) leaded to the higher error (28.98%), conversely, with the lower initial concentrations of Cu(II), the value of R^2 were little bit worse, but with much better values of error function (percentage of error lower than 3.85%). These results reinforce the need of using a statistical error function to better evaluate the adsorption models, as previously reported [3,11,16].

Additionally, it was verified that the q_e values found in the fractionary order were in good agreement with the experimental q_e values. These results indicate that the fractionary-order kinetic model should be taken into account for explaining the adsorption process of Cu(II), Mn(II) and Pb(II) uptaken by the PNS biosorbent.

By analyzing the values of the kinetic parameters depicted on Table 2, it should be mentioned that the k_{AV} values are much better for evaluation of the kinetic process than the pseudo-second-order kinetic constant (k_s), since the values of the Avrami's constant does not depend on the initial concentration of the adsorbate, since its unit is min^{-1}. On the other hand, the k_s values strongly depend on the initial concentration, since its units is g mg^{-1} min^{-1}. Observing the data reported in Table 2, the percentage of variation of k_{AV} was lower than 6.6% for the three metallic ions using three different initial concentration levels. On the other hand, the percentage of variation of k_s was up to 43.3%, when the initial concentration levels of the metallic ions were increased from 100.0 to 300.0 mg L^{-1}. Therefore, the fractionary kinetic model provides a constant rate parameter which is much better for comparison of different kinetic constants, using several adsorbates and adsorbents.

Taking into account that the kinetic results fitted very well to the fractionary kinetic model for the three metallic ions, and fairly good to pseudo-first-order for Cu(II) and Pb(II) and pseudo-second-order kinetic models for Mn(II) (see Table 2 and Fig. 4), the intra-particle diffusion model [33], was plotted in order to verify the influence of mass transfer resistance on the binding of Cu(II), Mn(II) and Pb(II) to the PNS biosorbent (see Table 2 and Fig. 5).

The possibility of intra-particle diffusion resistance affecting adsorption was explored using the intra-particle diffusion model as [33,34]:

$$q_t = k_{id}\sqrt{t} + C \tag{14}$$

where k_{id} is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$), and C is a constant related with the thickness of boundary layer (mg g^{-1}).

Thus, the intra-particle diffusion constant, k_i (mg g^{-1} $min^{-0.5}$), can be obtained from the slope of the plot of q_t (uptake at any time, mg g^{-1}) versus the square root of time (Fig. 5). If this plot passes through the origin, then intra-particle diffusion is the rate controlling step. Fig. 5 shows the plots of q_t versus $t^{1/2}$, with multi-linearity for the three metallic ions chosen, which implies that the adsorption process involves more than one kinetic stage (or sorption rates) [34].

For instance, the PNS exhibited three stages, which can be attributed to each linear portion of the figure. The first linear portion was attributed to the diffusional process of metallic ions to the PNS biosorbent surface [34]; hence, was the fastest sorption stage. This result is corroborated by the fractionary-order kinetic model. The second portion, ascribed to intra-particle diffusion, was a delayed process. The third stage may be regarded as the diffusion

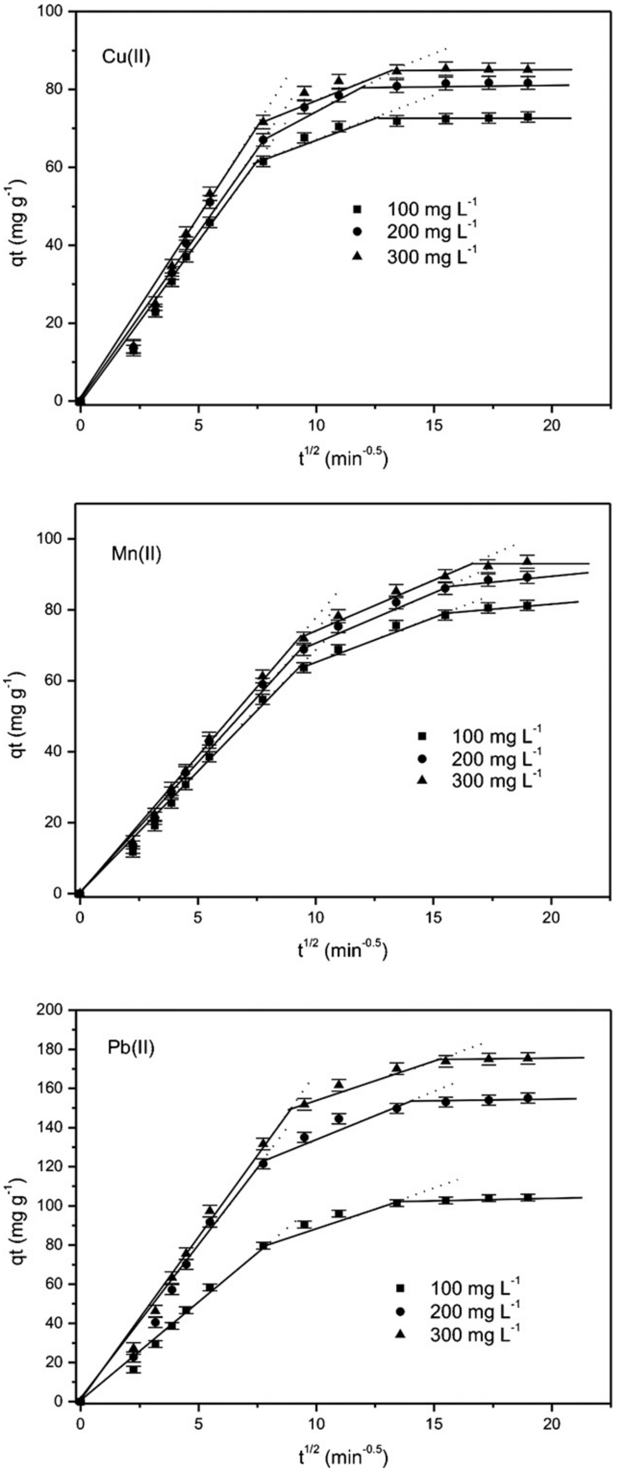


Fig. 5. Intra-particle diffusion kinetic model for the adsorption of Cu(II), Mn(II) and Pb(II).

through smaller pores, which is followed by the establishment of equilibrium [34].

3.5. Desorption experiments

Desorption experiments were carried-out in order to verify the possible mechanism of adsorption of Cu(II), Mn(II) and Pb(II) on PNS. Batch desorption studies were carried out by agitating 20.0 mL of 100.0 mg L^{-1} metallic ion solutions with 100.0 mg of PNS (biosorbent dosage of 5.0 g L^{-1}) for 300 min. The remaining liquid phase was separated from the solid phase, and the metallic loaded adsorbents, were firstly washed with water for removing non-adsorbed metallic ions. Then, metallic loaded biosorbents were agitated with 20.0 ml of aqueous solutions (0.050–1.00 mol L^{-1} HCl; 0.050–1.00 mol L^{-1} HNO_3; 0.010–0.50 mol L^{-1} KCl; and 0.050–0.15 mol L^{-1} NaOH) up to 1 h (see Table 3). It was observed that NaOH did not promote any remarkable removal of the metallic ions loaded biosorbents after 1 h of contact time. In addition, the desorption experiments carried-out with KCl promoted a slightly regeneration of the metal loaded PNS biosorbent (<25%, see Table 3). The best recovery results were achieved by using HCl ($\geq$95.5) and HNO_3 ($\geq$97.5). These results indicate that the metallic ions should interact with the carboxylic acid and phenolic groups present of the PNS biosorbent, as described in Scheme 1.

In the first step, the acidity of the medium should be adjusted by keeping the pH ranging from 5.0 to 6.0, in order to the release of H^+ from the PNS biosorbent. In the second step, the metal uptake by the PNS fiber took place. In the third step, the release metallic ions from the loaded biosorbents occur by addition of HNO_3 and/or HCl, regenerating the biosorbent.

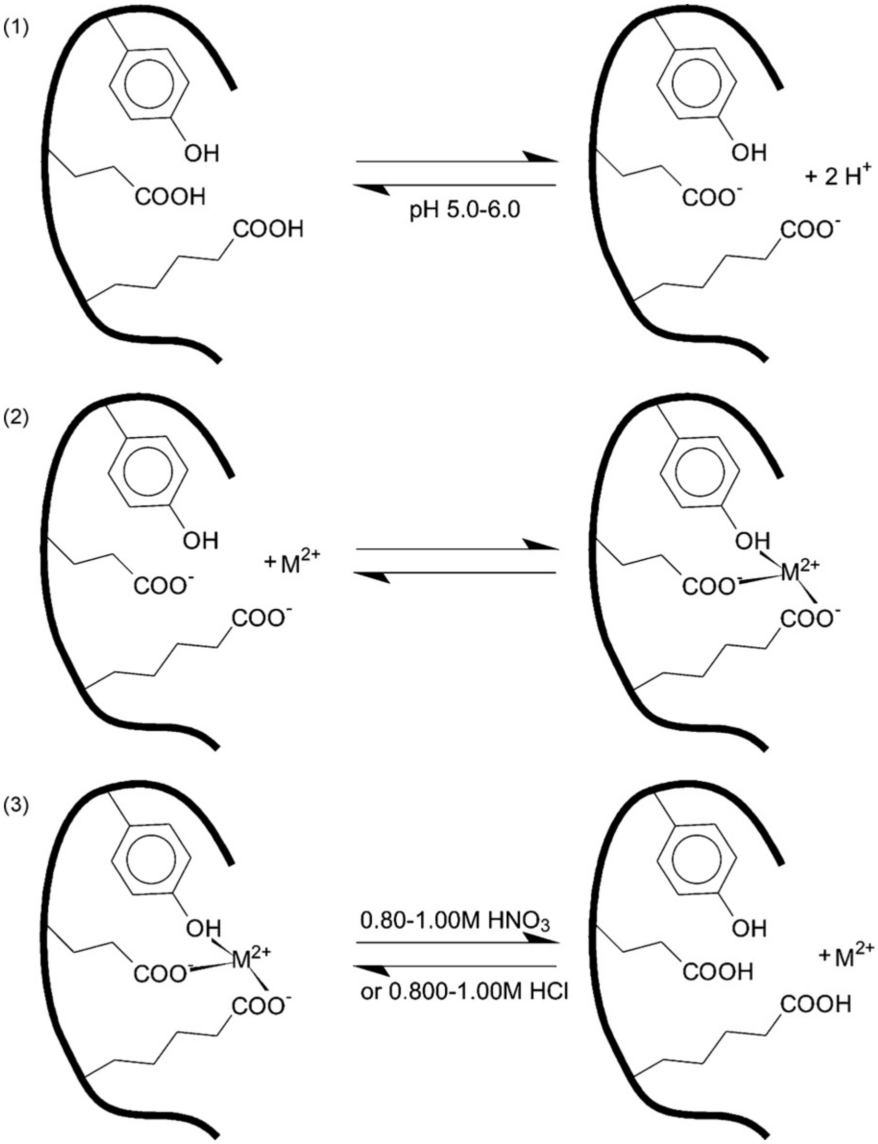
In order to verify the reutilization of the regenerated biosorbent, it was again employed for metal uptake in a new cycle of adsorption. It was observed that the adsorption capacity was about 75% of the original biosorbent, for the three chosen metallic ions, indicating that PNS could be a good alternative adsorbent for Cu(II), Mn(II) and Pb(II) removal from aqueous solution.

3.6. Equilibrium studies

An adsorption isotherm describes the relationship between the amount of adsorbate uptaken by the adsorbent and the adsorbate concentration remaining in solution. There are many equations for analyzing experimental adsorption equilibrium data. The equation parameters of these equilibrium models often provide some insight into the adsorption mechanism, the surface properties and affinity

Table 3
Desorption of Cu(II), Mn(II) and Pb(II) from PNS

Eluent	% removal		
	Cu(II)	Mn(II)	Pb(II)
HCl (mol L^{-1})			
0.050	28.36	36.78	33.65
0.10	40.36	45.36	47.89
0.25	50.98	70.25	70.25
0.50	66.36	77.36	80.26
0.80	84.45	93.65	97.85
1.00	95.56	97.68	99.36
HNO_3 (mol L^{-1})			
0.050	37.87	42.36	36.98
0.10	45.69	49.56	55.24
0.25	58.74	79.56	78.98
0.50	70.25	83.25	93.25
0.80	95.26	98.56	98.85
1.00	97.53	98.67	99.00
NaOH (mol L^{-1})			
0.050	0.01	0.11	0.02
0.10	0.32	0.42	0.14
0.15	1.24	0.75	2.50
KCl (mol L^{-1})			
0.05	12.57	8.54	11.7
0.10	16.36	10.23	16.87
0.25	19.25	14.56	20.57
0.50	30.27	19.32	24.52



Scheme 1. Mechanism of adsorption and desorption of divalent cations by PNS.

of the adsorbent. In this work, the Langmuir, Freundlich, Sips and Redlich–Peterson isotherm models were tested.

3.6.1. Langmuir isotherm model

The Langmuir isotherm is based on the following assumptions [35]:

- adsorbates are chemically adsorbed at a fixed number of well-defined sites;
- each site can only hold one adsorbate specie;
- all sites are energetically equivalent;
- there are no interactions between the adsorbate species.

The Langmuir isotherm equation is:

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \qquad (15)$$

where C_e is the supernatant concentration after the equilibrium of the system (mg L^{-1}), K_L the Langmuir affinity constant (L mg^{-1}), and Q_{max} is the maximum adsorption capacity of the material (mg g^{-1}) assuming a monolayer of adsorbate uptaken by the adsorbent.

3.6.2. Freundlich isotherm

Freundlich isotherm model is an exponential equation and therefore assumes that the concentration of adsorbate on the adsorbent surface increases with the adsorbate concentration. Theoretically, using this expression, an infinite amount of adsorption can occur [36]. The equation is widely applied in heterogeneous systems.

The Freundlich isotherm equation is:

$$q_e = K_f {C_e}^{1/n_F} \qquad (16)$$

where K_F is the Freundlich constant related with adsorption capacity [mg g^{-1}(mg L^{-1})$^{-1/n_F}$] and n_F is the Freundlich exponent (dimensionless).

3.6.3. Sips isotherm model

This model is empirical and it consists of the combination of the Langmuir and Freundlich isotherm type models. The Sips model

Table 4
Isotherm parameters for Cu(II), Mn(II) and Pb(II) biosorption, using PNS as biosorbent

	Cu(II)	Mn(II)	Pb(II)
Langmuir			
$Q_{\max}$ (mg g^{-1})	91.2	103.8	211.7
K_L (L mg^{-1})	0.0400	0.0313	0.0177
R^2	0.9206	0.9532	0.9698
F_{error} (%)	14.93	13.46	26.96
Freudlich			
K_F (mg g^{-1} (mg L^{-1})$^{-1/n_F}$)	36.6	35.3	45.6
n_F	7.30	6.20	4.43
R^2	0.5751	0.6598	0.7677
F_{error} (%)	39.00	40.87	76.92
Sips			
$Q_{\max}$ (mg g^{-1})	85.9	98.0	195.9
K_S ((mg L^{-1})$^{-1/n_S}$)	0.00304	0.00416	0.00197
n_S	0.573	0.644	0.6456
R^2	0.9942	0.9960	0.9982
F_{error} (%)	2.14	2.40	1.53
Redlich–Peterson			
K_{RP} (L g^{-1})	3.65	3.25	3.76
a_{RP} (mg L^{-1})$^{-g}$	0.0400	0.0313	0.0177
g	1.00	1.00	1.00
R^2	0.9206	0.9532	0.9698
F_{error} (%)	14.93	13.46	26.97

Conditions: Temperature was fixed at 25 °C, contact time was fixed at 5 h, pH was fixed at 5.5, and biosorbent dosage of 4.0 g L^{-1} for Pb(II) and 5.0 g L^{-1} for Cu(II) and Mn(II).

takes the following form [37]:

$$q_e = \frac{Q_{\max} K_S C_e^{1/n_S}}{1 + K_S C_e^{1/n_S}} \tag{17}$$

where K_S is the Sips constant related with affinity constant (mg L^{-1})$^{-1/n_S}$ and $Q_{\max}$ is the Sips maximum adsorption capacity (mg g^{-1}), n_S is the Sips exponent (dimensionless).

At low adsorbate concentrations it effectively reduces to a Freundlich isotherm, while at high adsorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm.

3.6.4. *Redlich–Peterson isotherm model*

This is an empirical equation that describes an equilibrium isotherm [38].

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{g}} \quad \text{where } g \leq 1 \tag{18}$$

where K_{RP} and a_{RP} are Redlich–Peterson constants, with the respective units: L g^{-1} and (mg L^{-1})$^{-g}$ and g is the Redlich–Peterson exponent (dimensionless), whose value should be ≤1. This equation reduces to a linear isotherm in the case of low surface coverage ($g = 0$) and to a Langmuir isotherm when $g = 1$.

The isotherms of adsorption of Cu(II), Mn(II) and Pb(II) on PNS adsorbent were performed, using the best experimental conditions described previously (see Fig. 6).

The data of the fitted models are presented on Table 4. Based on the F_{error} values, the best isotherm model fitted was the Sips for the three metal ions, that presented the lowest values for F_{error}, which means that the q fitted by the isotherm model were close to the q measured experimentally. The differences of the F_{error} values among the Sips and the other isotherm models were very remarkable, indicating that Langmuir, Freundlich and Redlich–Peterson isotherm models were not suitably fitted for Cu(II), Mn(II) and Pb(II).

3.7. *Comparison of different adsorbents for Cu(II), Mn(II) and Pb(II) adsorption*

In Table 5 was presented a comparison of several adsorbents employed for Cu(II), Mn(II) and Pb(II) adsorption. As can be seen from Table 5, the PNS biosorbent employed in this work presented very high adsorption capacities for the chosen adsorbates when

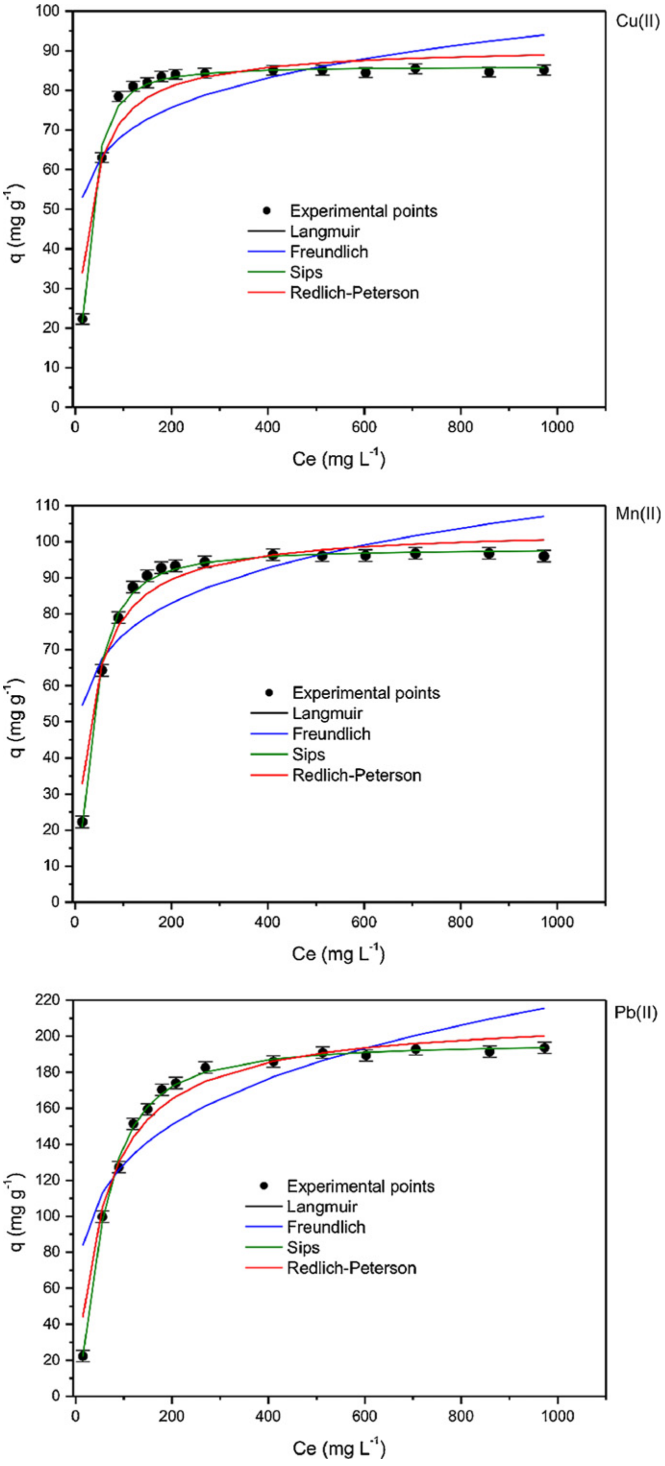


Fig. 6. Adsorption isotherm models for Cu(II), Mn(III) and Pb(II) adsorption from aqueous solutions on PNS biosorbent using batch adsorption procedure at 25 °C, biosorbent dosage of 4.0 g L^{-1} for Pb(II) and 5.0 g L^{-1} for Cu(II) and Mn(II), pH fixed at 5.5 and using a contact time of 120 min.

Table 5
Comparison of maxima adsorption capacities of Cu(II), Mn(II) and Pb(II) on different adsorbents

Adsorbent	Adsorption capacity (mg g^{-1})			
	Cu(II)	Mn(II)	Pb(II)	Reference
4-Azaphenyl-propylsilica (grafted silica)	11.18 (0.1759)[a]	–	–	[3]
4-Phenylenediaminepropylsilica xerogel	33.0 (0.519)[a]	–	–	[8]
7-Amine-4-azahepthylsilica (grafted silica)	29.93 (0.4710)[a]	–	36.53 (0.1763)[a]	[11]
7-Amine-4-azahepthylsilica (grafted silica)	34.53 (0.5434)[a]	–	52.71 (0.2544)[a]	[11]
Brazilian pine-fruit shell	32.2 (0.507)[a]	–	–	[16]
Ponkan peel	83.25 (1.310)[a]	–	–	[17]
Yellow passion-fruit shell	–	–	151.6 (0.7317)[a]	[18]
Lignite	–	25.84 (0.4703)[a]	–	[39]
Clinoptilolite–Fe oxide	–	27.12 (0.4936)[a]	–	[40]
Bacteria *Arthrobacter* sp.	148 (2.33)[a]	406 (7.39)[a]	130 (0.627)[a]	[41]
Sepabeads SP70 resin	–	4.2 (0.076)[a]	2.3 (0.011)[a]	[42]
Diaion SP-850 resin	5.72 (0.0900)[a]	6.04 (0.110)[a]	4.14 (0.0200)[a]	[43]
Vermiculite	–	31.53 (0.5739)[a]	–	[44]
Leached residue of manganese nodules	25.40 (0.3997)[a]	–	97.10 (0.4686)[a]	[45]
Granular activated carbon	–	2.54 (0.0462)[a]	–	[46]
Charcoal	–	–	19.89 (0.09599)[a]	[47]
Activated carbon	–	–	31.08 (0.1500)[a]	[47]
Activated carbon	38.13 (0.6000)[a]	–	121.0 (0.5840)[a]	[48]
Pecan nutshell	85.9 (1.35)[a]	98.0 (1.78)[a]	195.9 (0.946)[a]	This work

[a] mmol g^{-1}.

compared with several different adsorbents. For Cu(II), from 10 different adsorbents, PNS presented higher sorption capacity than 9; for Mn(II) from 7 different adsorbents, PNS was better than 6; and for Pb(II) from 10 different adsorbents the PNS was better than all of then. These outstanding sorption capacities for Cu(II), Mn(II) and Pb(II) places pecan nutshell as one of the best adsorbents for these metallic ion removal from aqueous solutions.

4. Conclusion

Pecan nutshell is a very good alternative biosorbent for removal of Cu(II), Mn(II) and Pb(II) from aqueous solutions. The biosorbent was used without any chemical treatment presenting biosorption capacities of 1.35, 1.78 and 0.946 mmol g^{-1} for Cu(II), Mn(II) and Pb(II), respectively. In this way, the use of pecan nutshell as a biosorbent can be interesting at the commercial point of view because of its low preparation cost and large availability in South of Brazil.

The PNS biosorbent was characterized by FTIR spectroscopy indicating the presence of phenolic, O—H groups, and carboxylic groups (COOH). These data were also confirmed by conventional titrations where the amounts of phenolic and carboxylic groups measured were 1.11 and 1.04 mmol g^{-1}, respectively, in PNS biosorbent.

The adsorption of the metallic ions depended on pH and shaking contact time. The optimum pH for the adsorption of the metallic ion ranged from 5.0 to 6.0 for all the metallic ions and the minimum shaking contact time necessary for reaching the equilibrium was about 120, 240 and 180 min, for Cu(II), Mn(II) and Pb(II), respectively.

There are several indicatives (fractionary kinetic model, intraparticle diffusion model, and desorption experiments) that the mechanism of biosorption of all metallic ions by PNS should be an interaction of the carboxylic and phenolic groups of PNS with the metallic ion at pH ranging from 5.0 to 6.0 (see Scheme 1).

About 95–99% of the metallic ions loaded biosorbent were regenerated, using 1.00 mol L^{-1} of HCl or HNO_3. The regenerated biosorbent could be employed again for metal uptake, keeping at least 75% of the initial sorption capacity. These results reinforce that the use of pecan nutshell could be a good alternative for Cu(II), Mn(II) and Pb(II) removal from aqueous solution.

Acknowledgements

The authors are grateful to Ministério de Ciência e Tecnologia (MCT), and to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support and fellowships. We also thank to PerkinElmer for donating impact beads utilized in the nebulizer of Analyst 200 spectrometer.

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