Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.759156

51 (2013) 5537–5546
August

Taylor & Francis
Taylor & Francis Group

Mexerica mandarin (*Citrus nobilis*) peel as a new biosorbent to remove Cu(II), Cd(II), and Pb(II) from industrial effluent

Camila Suemi Inagaki, Talita de Oliveira Caretta, 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

Received 9 September 2012; Accepted 28 November 2012

ABSTRACT

Adsorption experiments were carried out using waste Mexerica mandarin "*Citrus nobilis*" peel as a new biosorbent to adsorb Cu(II), Cd(II), and Pb(II) ions from aqueous solutions at room temperature. To achieve the best adsorption conditions, the influences of pH and contact time were investigated. The isotherms of adsorption were fitted to the Langmuir and Freundlich equations. Based on the experimental data the adsorption order was Pb(II)>Cd(II)>Cu(II) (in $\mathrm{mg\,g^{-1}}$) on the new biosorbent. This quick adsorption process reached the equilibrium before 20 min, with maximum adsorptions at pH 5.0. Kinetic studies were carried out using the pseudo-first-order and pseudo-second-order models. Thermodynamic aspects of the adsorption process were investigated. The new biosorbent was used in columns for the removal of Cu, Cd, and Pb ions of the samples of industrial effluent and its efficiency and regeneration potential were studied.

Keywords: Biosorption; Heavy metal; Kinetics; Wastewater treatment

1. Introduction

Heavy metal wastewater exists in many industries, such as mineral processing, metal plating, tanneries, electronic, and chemical plants. The disposal of hazardous wastewater is a significant industrial problem. Heavy metals like Cu, Cd, and Pb are toxic and nonbiodegradable, hence, posing a serious threat to environment and public health [1]. Many methods, such as chemical precipitation [2], membrane process [3], ion exchange [4], and adsorption onto activated carbon [5], have been used to remove heavy metal ions from various aqueous solutions. However, these techniques generally need a long detention time, making their implementation difficult, particularly when the metals are dissolved in large volumes of water. Another relevant factor in these treatments is the generation of solid residues that need to be stored and disposed of, causing another serious problem [6]. Furthermore, there is the issue about the high cost of these processes to the industry.

Recently, the search for low-cost adsorbents that possess metal-binding capacities has intensified. Materials locally available in large quantities such as natural materials, agricultural wastes or industry byproducts can be utilized as low-cost adsorbents. Some of the reported biosorbents include crab shell,

---

*Corresponding author.

wheat straw, rice straw, grape bagasse, mango peel, orange waste, and so on [1]. In Brazil, due to the large agricultural production, several agroindustrial by-products and residues are generated, such as Mexerica mandarin *"Citrus nobilis"* peel, lemon peel, orange peel, cashew, green coconut, sawdust, algae, and compost. However, the disposal of these residues has become an environmental problem.

Biosorption is known to occur through the interaction of metal ions with the functional groups present in biopolymers. Groups such as amide, hydroxyl, carboxylate, sulfonate, phosphate, and amino, present on biosorbents, have been reported to be responsible for adsorption. Carboxyl groups are generally the most abundant functional groups present in biomass. The accessibility of biosorbents as well as chemical/physical modifications performed on them also play important roles in enhancing the metal-ion sorption capacity. A variety of mechanisms such as complexation, coordination, chelation, ion adsorption or exchange, and microprecipitation have been proposed [7–13].

The utilization of Mexerica mandarin *"Citrus nobilis"* peel as a biosorbent is considered economically viable to industries that need to treat effluents containing heavy metals because large amounts of this material are discharged from juice, jellies, jams, sweets, and candies industries in Brazil.

In this paper, the Mexerica mandarin *"Citrus nobilis"* peel was studied for the first time as a new biosorbent for Cu, Cd, and Pb ions removal from aqueous solutions. This biomass is produced on a large scale in Brazil and has no previous adsorption studies in the literature. Its feasibility for heavy metals removal was assessed by studying the effect of pH, contact time, initial concentration and temperature on the adsorption process. In addition, in order to evaluate its practicability for heavy metals removal by *"Citrus nobilis"* peel, column study was also carried out using various real samples of battery industry effluents.

2. Material and methods

2.1. Materials

Analytical grade chemical reagents were used throughout the experiment. The stock solution of metal ions was prepared in 20 g L^{-1} concentration using $Cu(NO_3)_2.3H_2O$, $Cd(NO_3)_2.4H_2O$, and $Pb(NO_3)_2$, which were purchased from VETEC (Brazil) then diluted to appropriate concentrations. HCl and NaOH were purchased from SYNTH (Brazil). The water used was Milli-Q_{plus} quality with resistivity of 18 M/cm. Mexerica mandarin *"Citrus nobilis"* peels used in this study were collected from a candies factory and a fruit juice store in Londrina city, Brazil.

2.2. Biosorbent

The Mexerica mandarin *"Citrus nobilis"* peels were washed with water to remove dirt, then oven dried at about 60°C for 24 h. Mexerica mandarin peels were then milled and sieved to obtain smaller particles of diameter between 0.25 and 0.15 mm. This material was denominated as Mexerica mandarin flour (MMF).

About 100 g of MMF was taken in a beaker together with 250 mL 0.1 mol L^{-1} HCl and stirred for 10 min at room temperature. After being filtered, this material was washed with water until its pH was neutral. The filter residue was dried in an oven at 60°C for 24 h. This material was denominated as Mexerica mandarin flour treated (MMFT).

2.3. Scanning electron microscopy (SEM)

The Scanning electron microscopy (SEM) images were obtained by the dispersion of the sample on double-faced conducting tape fixed on a graphite support. The sample was covered with a conductive film of gold. The electronic microscope used was a JEOL JSM T-300.

2.4. FTIR spectroscopy

Spectra of the MMF and MMFT were recorded with a Shimadzu FTIR 8300 spectrophotometer using KBr disks.

2.5. Biosorption experiments

Biosorption experiments were conducted at 25°C by agitating 50 mg of biosorbent with 250 mL of metal ion solution of desired concentration in a stoppered flask using a shaking thermostat machine at a speed of 120 rpm for 1 h except for the contact time experiments. The effect of the solution pH on the equilibrium biosorption of metal ions was investigated under similar experimental conditions between pH 1.0 and 5.5. In the kinetic experiments, 1.0×10^{-3} mol L^{-1}Cu(II), Cd(II), and Pb(II) ion solutions were used. The sorption time varied between 0 and 180 min. In the isotherm experiments, 50 mg of biosorbent was added in 250 mL of Cu(II), Cd(II), and Pb(II) ions solutions at various concentrations ($5.0 \times 10^{-5-1}.0 \times 10^{-1}$mol L^{-1}). Once the preset contact time (1 h) was reached, the supernatant solutions were withdrawn and analyzed for the residual metal ion concentration by using an E-Thermo Jarrell Ash ICAP 61 inductively coupled plasma (ICP-AES) spectrometer. The amount biosorbed (q_e) was calculated using the following equation:

$$q_e = (q_i - q_s)/m \quad (1)$$

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. All the biosorption experiments were conducted in triplicate, and the mean values were reported.

2.6. Determination of the point of zero charge

The point of zero charge (PZC) for the MMFT was determined by the processes described previously in the literature for organic materials [14–16].

3. Results and discussion

3.1. Biosorbent

In preliminary tests of metal ion adsorption, it was observed that MMF has low adsorption capacity. This can be explained by the chemical composition of Mexerica mandarin peel [17] shown in Table 1. There is a large amount of inorganic ions in the peel that are probably blocking the active sites of the biomass. In order to increase the adsorption capacity, the material was treated with HCl solution to removal a portion of the metal ions present and to promote the protonation of the active sites of the MMF.

3.2. Surface morphology

The SEM images of MMF and MMFT are shown in Fig. 1. The image of MMF (Fig. 1(A)) shows a smooth surface with several layers adhered. The image of MMFT (Fig. 1(B)) shows a surface with numerous cavities formed by the removal of metal ions from the active sites (carboxylic groups mostly) of the biomass. The cavities can also be formed by the removal of soluble organic species (small ester or organic acid, lignin, carbohydrates, and amino acids mostly), since it is observed a decrease of 45% of the initial mass of MMF after the acid treatment.

Table 1
Chemical composition of the Mexerica mandarin "*Citrus nobilis*" peels

Parameter	Amount in peel (in 100 g)
Moisture (g)	49.10
Ash (g)	1.75
Fat (g)	0.64
Protein (g)	2.49
Fibers (g)	10.38
Carbohydrates (g)	35.64
Ca (mg)	478.98
Fe (mg)	4.77
Na (mg)	77.76
Mg (mg)	159.59
Zn (mg)	2.83
Cu (mg)	0.58
K (mg)	598.36

3.3. FTIR analysis

Fig. 2 shows the infrared spectra of MMF (curve A) and MMFT (curve B). FTIR analysis is used to identify some characteristic functional groups. Fig. 2 (curve A—MMF) shows the broad and intense absorption band at 3,420 cm^{-1} corresponding to O–H stretching vibrations of cellulose, pectin, adsorbed water,

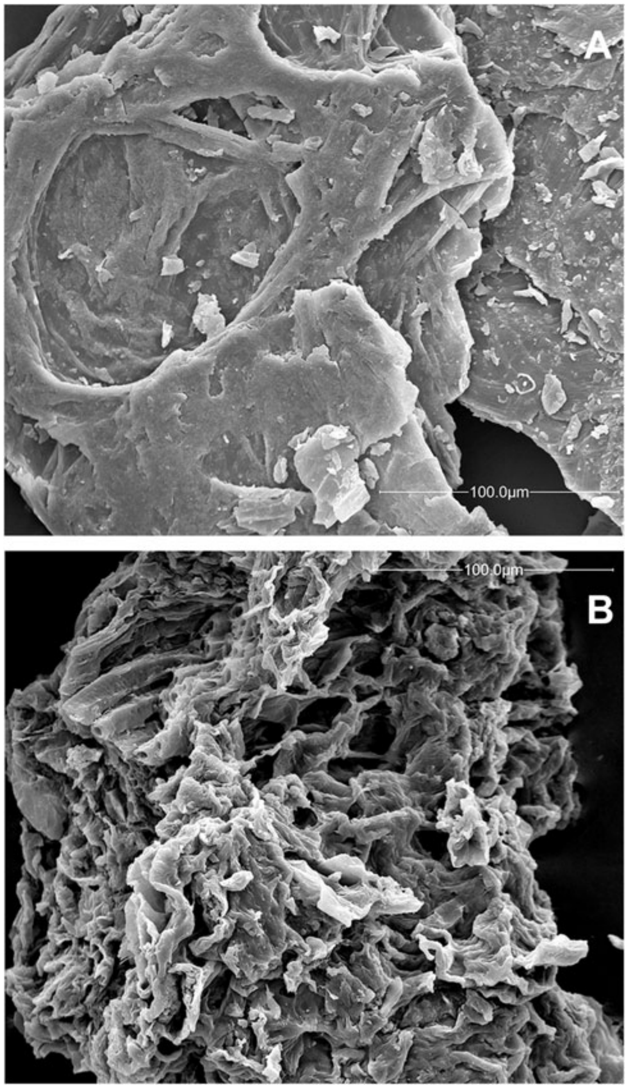

Fig. 1. SEM images of MMF (A) and MMFT (B).

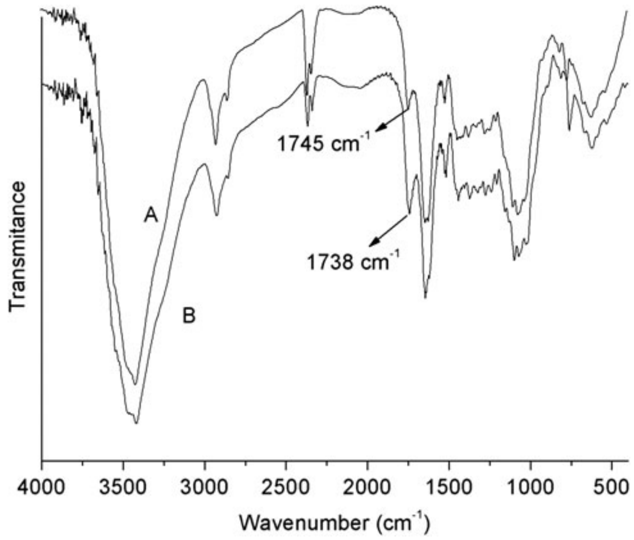

Fig. 2. FTIR spectra of MMF (A) and MMFT (B).

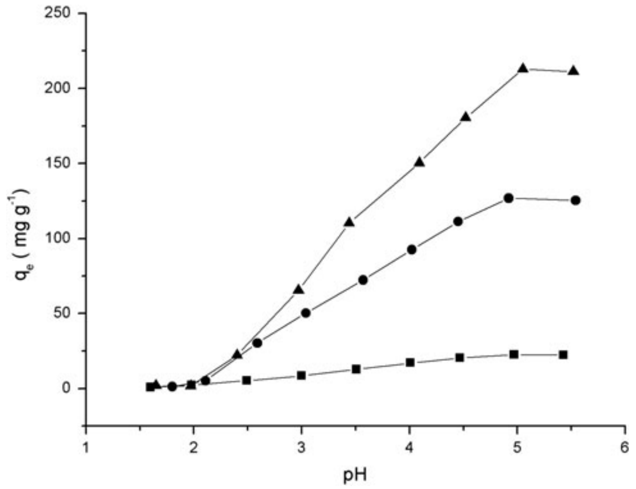

Fig. 3. The effect of pH on biosorption of Cu(II)(■), Cd(II) (●), and Pb(II)(▲) ions on MMFT.

and lignin. The bands observed at 2,920 and 2,865 cm^{-1} can be attributed to the C–H stretching vibrations of methyl, methylene, and methoxy groups. The band observed at 1,745 cm^{-1} is the stretching vibration of the C=O bond due to ionic carboxyl groups (COO^-). After acid treatment in MMF (curve B), the band in 1,745 cm^{-1} observed was shifted to 1,738 cm^{-1} in MMFT. This confirms that ionic carboxyl groups were converted into nonionic carboxyl groups (COOH). The bands in the range 1,300–1,000 cm^{-1} (present in MMF and MMFT) can be assigned to the C–O stretching vibration of carboxylic acids and alcohols.

3.4. *Effects of pH on metal biosorption*

It is well known that pH could affect the protonation of the functional groups on the biomass as well as the metal chemistry. Fig. 3 shows the behavior of Cu(II), Cd(II), and Pb(II) on MMFT as function of pH of the solution. The minimum values of biosorption are at pH 2.0 and increase as the pH increases from 2 to 5.0. The minimum biosorption at low pH 2.0 may be due to the high concentration and high mobility of H^+ ions, so the hydrogen ions are preferentially adsorbed in relation to the metal ions. At higher pH values, the lower number of H^+ results in greater metal ions biosorption. The weakly acidic carboxyl groups (R–COOH) are regarded as the main ligands involved in the metal uptake by MMFT. Because the pK_a value of R–COOH is in the range of 3.5–5.5 [18], more carboxyl groups will be deprotonated at pH over this range, and thus resulting in more negative binding sites. Consequently, the attraction of positively charged metal ions would be enhanced. In this case, the measured PZC to MMFT biosorbent was 4.9. This fact confirms the behavior shown in Fig. 3, where the maximum biosorption occurs at pH 5.0. At higher pH values (greater than 5.5), the metallic ions (Cu, Cd, and Pb) could be suffering hydrolysis, forming $\mathrm{Cu(OH)}^+$, $\mathrm{Cd(OH)}^+$, and $\mathrm{Pb(OH)}^+$ species, which promotes a reduction of the biosorption capacity, due to the diminution of the formal charge of the metallic ion [19].

3.5. *Biosorption kinetics*

Fig. 4 shows the kinetics of the biosorption of $1.0 \times 10^{-3}\,\mathrm{mol\ L}^{-1}$ Cu(II), Cd(II), and Pb(II) ions at 25°C by MMFT. The kinetic curve for heavy metal ions shows that the amount of biosorption sharply increases with increasing contact time in the initial stage (0–10 min), and reaches the equilibrium value quickly at 20 min. A further increase in contact time had a negligible effect on the amount of biosorption. According to these results, the contact time was fixed at 1 h for the rest of the batch experiments to make sure that the equilibrium was reached.

In order to evaluate the kinetic mechanism that controls the biosorption process, the pseudo-first-order and pseudo-second-order models were applied for the biosorption of metal ions on the biosorbent.

Biosorption kinetics data of metal ions were analyzed using the Lagergren pseudo-first-order rate equation [20]:

$$\log(q_\mathrm{e} - q_t) = \log q_\mathrm{e} - (k_1/2.303)t \tag{2}$$

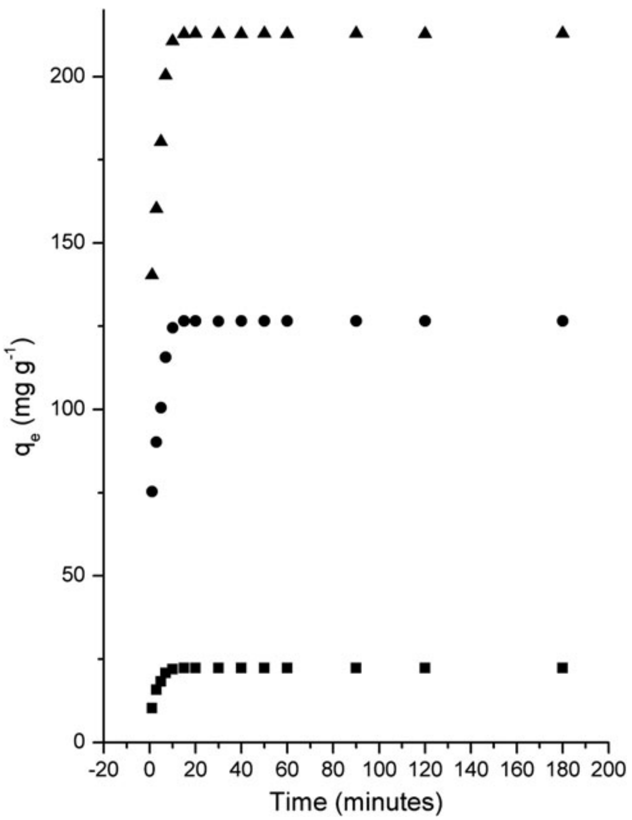

Fig. 4. Biosorption kinetics of Cu(II)(■), Cd(II)(●), and Pb(II)(▲) ions on MMFT.

where q_e and q_t are the amounts of metal ions adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo-first-order biosorption (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). In fact, it is required that calculated equilibrium adsorption capacity values, $q_{e(cal.)}$, should be in accordance with the experimental $q_{e(exp.)}$ values [21]. Although the correlation coefficient values (R^2) are very high, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots (Table 2). This suggests that the biosorption of Cu(II), Cd(II), and Pb(II) ions does not follow pseudo-first-order kinetics.

The biosorption kinetic data can also be described by pseudo-second-order equation [22]:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{3}$$

where 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 (Figure not shown). This model is more likely to predict the kinetic behavior of adsorption of metal ions on MMFT. It was found that the calculated q_e values agree well with experimental q_e values (Table 2). This suggests that the pseudo-second-order kinetic model, based on the assumption that the rate-limiting step may be the chemical sorption involving valance forces through sharing or exchange of electrons between heavy metal ions and the adsorbent, provides the best correlation data for the heavy metal ions. Similar phenomena have been observed in the adsorption of phosphate and thiocyanate on $ZnCl_2$-activated coir pith carbon [23,24].

3.6. Biosorption isotherms

Biosorption isotherms describe how the adsorbate interacts with biosorbents and how equilibrium is established between adsorbed metal ions on the biosorbent and the residual metal ions in the solution during the surface biosorption. The most common types of models describing this type of system are the Langmuir and Freundlich isotherms.

The Langmuir isotherm is based on the assumption that the maximum sorption corresponds to the saturated monolayer of adsorbate molecule on the biosorbent surface, that the energy of sorption is constant and that there is no transmigration of adsorbate in the plane of the surface. While the Freundlich isotherm supposes a heterogeneous surface with a nonuniform distribution of heat of biosorption over the surface and a multilayer biosorption can be expressed. The Langmuir isotherms can be expressed as [25]:

$$C_e/q_e = 1/(bQ_m) + C_e/Q_m \tag{4}$$

Table 2
Kinetic parameters for biosorption of Cu(II), Cd(II), and Pb(II) ions on MMFT

Metal ions	$q_{e(exp.)}$(mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
		$q_{e(calc.)}$(mg g^{-1})	k_1(min^{-1})	R^2	$q_{e(cal.)}$(mg g^{-1})	k_2(g mg^{-1} min^{-1})	R^2
Cu(II)	22.35 ± 0.35	20.90 ± 0.18	0.3835 ± 0.0004	0.9909	22.50 ± 0.22	0.0758 ± 0.0003	0.9997
Cd(II)	126.58 ± 1.25	102.74 ± 0,85	0.3569 ± 0.0006	0.9634	126.55 ± 1.07	0.0124 ± 0.0002	0.9998
Pb(II)	212.85 ± 1.85	111.55 ± 1.04	0.2879 ± 0.0004	0.9695	212.67 ± 1.32	0.0116 ± 0.0001	0.9996

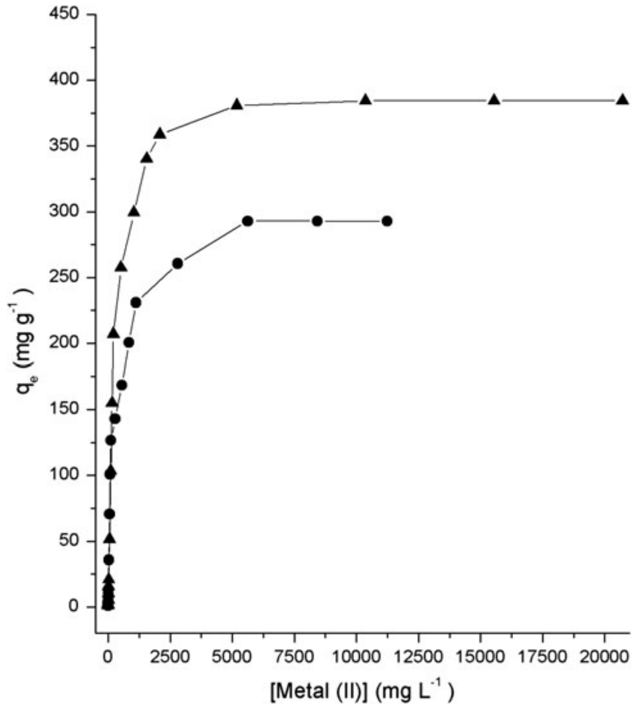

Fig. 5. Biosorption isotherms of Cu(II)(■), Cd(II)(●), and Pb (II)(▲) ions on MMFT.

where C_e (mg L^{-1}) is the concentration of the metal ions solution at equilibrium, Q_m is the maximum adsorbed capacity and represents a practical limiting adsorption capacity when the sorbent 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 Langmuir equation is also used to obtain R_L, the dimensionless equilibrium parameter or the separation factor [26,27] from the expression:

$$R_L = 1/(1 + bC_o) \tag{5}$$

where C_o is the initial concentration of the adsorptive. For favorable adsorption, $0 < R_L < 1$; while $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively, describe unfavorable, linear, and irreversible adsorption [28–30].

The Freundlich equation can be expressed as [31]:

$$\log q_e = \log K_F + (1/n) \log C_e \tag{6}$$

where K_F and $1/n$ are Freundlich isotherm constants related to biosorption capacity and intensity of biosorption, respectively. If Eq. (6) applies a plot of log q_e vs. log C_e will give a straight line of slope $1/n$ and intercept K_F.

Fig. 5 presents the experimental biosorption isotherms of Cu(II), Cd(II), and Pb(II) ions on MMFT at 25ºC. It could be seen that q_e increased initially with an increase in C_e until equilibrium was reached, after which q_e remained constant with further increase in C_e. The Langmuir and Freundlich biosorption constants are listed in Table 3.

As can be seen in Table 3, the Langmuir isotherm gave better fits than the Freundlich isotherm, which illustrated that the biosorption on the surface MMFT was a monolayer biosorption. According to the Langmuir equation, the maximum uptake capacities for Cu(II), Cd(II), and Pb(II) ions were 131.5, 322.6, and 398.4 mg g^{-1}, respectively, much higher than some other biosorbents reported in the literature (Table 4).

3.7. Effects of temperature

The variation of sorption with temperature was studied from 15 to 45ºC for each toxic metal ion under the optimized conditions selected and the data is shown in Fig. 6. The thermodynamic parameters for the adsorption process, ΔH, ΔS, and ΔG, were evaluated using the equation [19]:

$$\ln K_d = \Delta S/R - \Delta H/RT \tag{7}$$

where K_d, known as the distribution coefficient of the adsorbate, is equal to (q_e/C_e), R is the gas constant, and T is the temperature in Kelvin (K). The plot ln K_d vs. $1/T$ is linear with the slope and the intercept giving values of ΔH and ΔS, respectively. These values could be used to compute ΔG from the Gibbs relation,

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

Table 3
Parameters of the Langmuir and Freundlich equations for biosorption of Cu(II), Cd(II), and Pb(II) ions on MMFT

Ions	Langmuir model				Freundlich model		
	Q_m (mg g^{-1})	$b \times 10^3$(L mg^{-1})	R_L	R^2	K_F	n	R^2
Cu^{2+}	131.5 ± 1.2	2.1 ± 0.1	0.076 ± 0.003	0.9999	0.308 ± 0.005	1.704 ± 0.012	0.9811
Cd^{2+}	322.6 ± 3.5	4.2 ± 0.2	0.002 ± 0.0001	0.9997	0.180 ± 0.002	1.236 ± 0.006	0.9766
Pb^{2+}	398.4 ± 3.1	30.3 ± 0.4	0.002 ± 0.0001	0.9993	0.075 ± 0.001	1.113 ± 0.005	0.9894

Table 4
Biosorption capacities of various biosorbents

Biosorbents	Q_m (mg g^{-1})			References
	Cu(II)	Cd(II)	Pb(II)	
Rice husk	10.9	16.7	58.1	[29]
Lemon peel	70.92	54.64	37.87	[30]
Active carbon	138.80	–	109.30	[30]
Orange peel	63.29	41.84	27.10	[31]
Banana peel	52.36	34.13	25.91	[31]
Acacia leucocephala				
Bark powder	147.1	166.7	185.2	[32]
Gymmogongrus torulosus	51.4	74.2	140.9	[33]
Fucus vesiculosus	41.0	52.0	90.0	[34]
Modified sugarcane bagasse	69.4	106.4	222.2	[35]
Modified pine bark	11.3	5.7	6.7	[36]
Mexerica mandarin *Citrus nobilis*	131.5	322.6	398.4	This study

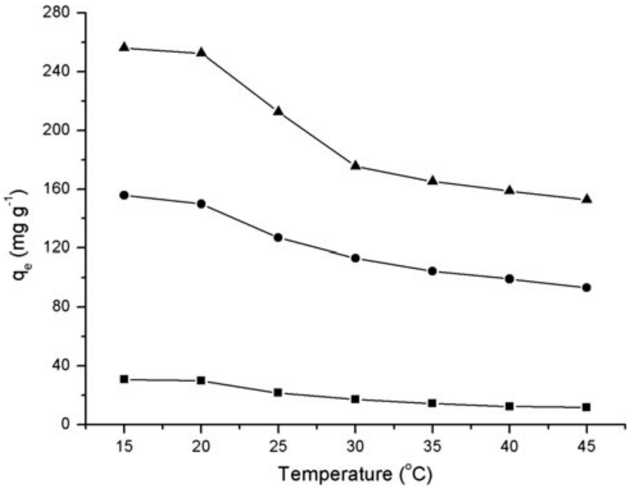

Fig. 6. The effect of temperature on biosorption of Cu(II) (■), Cd(II)(●), and Pb(II)(▲) ions on MMFT.

Table 5
Thermodynamic adsorption

Ion	ΔG(kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS(J mol^{-1} K^{-1})	R^2
Cu(II)	−8.9 ± 0.1	−27.9 ± 0.2	29.8	0.9799
Cd(II)	−11.9 ± 0.2	−15.7 ± 0.3	40.2	0.9684
Pb(II)	−11.7 ± 0.2	−17.1 ± 0.3	39.3	0.9762

at constant temperature. All these relations are valid when the entropy change remains constant in the temperature range.

From the thermodynamic point of view, the data in Table 5 and of Fig. 6 show that the adsorption process of the metals ions on MMFT was exothermic and that the positive entropy indicates an increase in disorganization in solid–liquid interface, suggesting that the process is not driven by the enthalpy but by entropy [37–42].

3.8. Application of the biosorbent studied for wastewater treatment

The 10 real samples of wastewater of seven battery industries in Londrina city—Brazil were analyzed with an E-Thermo Jarrell Ash ICAP 61 inductively coupled plasma (ICP-AES) spectrometer. Before treatment in columns, the samples were filtered and pH of solutions was adjusted to 5.0. The results before and after treatment are given in Table 6. The C_{initial} value represents the concentration of the metals in the wastewater and C_{final} the concentration of metals in the wastewater after treatment in column. It is seen that the biosorbent displays high removal efficiency towards Cu, Cd, and Pb.

3.9. Elution and regeneration

A column with a bed depth of 20 and 0.8 cm was selected for this study. The real sample inside the column (0.5 g) was pumped at a flow rate of 8.5 mL min^{-1}. Desorption was carried out by 0.1 mol L^{-1} HCl solution through the bed in the downward direction at a flow rate of 6.5 mL min^{-1}. The regenerations were carried out 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 [43]. Elution efficiency (%) was calculated by dividing the total adsorption capacity in the second run by the total

Table 6
ICP-AES results of wastewater real samples before and after treatment with the biosorbent

Sample	Ion	$C_{initial}$(mg L^{-1})	C_{final}(mg L^{-1})	Adsorption amount (mg g^{-1})	Removal ratio (%)
1	Cu(II)	2.36 ± 0.02	nd*	2.36	100.0
	Cd(II)	10.21 ± 0.02	nd	10.21	100.0
	Pb(II)	17.27 ± 0.03	nd	17.27	100.0
2	Cu(II)	22.72 ± 0.04	0.01 ± 0.01	22.71	99.9
	Cd(II)	55.38 ± 0.05	nd	55.38	100.0
	Pb(II)	45.23 ± 0.05	nd	45.23	100.0
3	Cu(II)	25.85 ± 0.02	nd	25.85	100.0
	Cd(II)	32.84 ± 0.03	nd	32.84	100.0
	Pb(II)	77.63 ± 0.07	0.01 ± 0.01	77.62	99.9
4	Cu(II)	41.76 ± 0.06	nd	41.76	100.0
	Cd(II)	56.94 ± 0.05	0.02 ± 0.01	56.92	99.9
	Pb(II)	63.21 ± 0.05	0.03 ± 0.01	63.18	99.9
5	Cu(II)	5.78 ± 0.02	nd	5.78	100.0
	Cd(II)	9.23 ± 0.02	nd	9.23	100.0
	Pb(II)	6.13 ± 0.02	nd	6.13	100.0
6	Cu(II)	27.21 ± 0.02	nd	27.21	100.0
	Cd(II)	6.32 ± 0.01	nd	6.32	100.0
	Pb(II)	4.52 ± 0.01	nd	4.52	100.0
7	Cu(II)	3.21 ± 0.01	nd	3.21	100.0
	Cd(II)	5.63 ± 0.02	nd	5.63	100.0
	Pb(II)	3.54 ± 0.02	nd	3.54	100.0
8	Cu(II)	57.95 ± 0.06	0.07 ± 0.01	57.88	99.9
	Cd(II)	32.27 ± 0.05	0.02 ± 0.01	32.25	99.9
	Pb(II)	12.36 ± 0.03	nd	12.36	100.0
9	Cu(II)	4.22 ± 0.01	nd	4.22	100.0
	Cd(II)	3.12 ± 0.01	nd	3.12	100.0
	Pb(II)	2.75 ± 0.01	nd	2.75	100.0
10	Cu(II)	36.55 ± 0.02	0.04 ± 0.01	36.51	99.9
	Cd(II)	48.16 ± 0.02	0.01 ± 0.01	48.15	99.9
	Pb(II)	27.36 ± 0.03	nd	27.36	100.0

*nd = not detected after three repetitions.

adsorption capacity in the first run. The regenerated biosorbent showed uptake capacity comparable to the fresh one over 120 cycles with standard deviation of ± 2.5%.

4. Conclusions

The Mexerica mandarin *"Citrus nobilis"* peel (MMFT) is an attractive biosorbent for Cu(II), Cd(II), and Pb(II) removal from aqueous solutions in a very rapid adsorption process. The maximum adsorption capacities vary with pH values, being higher at pH 5.0, which was experimentally fixed at 25 ± 1°C for all adsorptions, and the values obtained were 131.5, 322.6, and 398.4 mg g^{-1} for Cu(II), Cd(II), and Pb(II), respectively, using batch adsorption system.

The Mexerica mandarin (MMFT) demonstrates a great ability for extracting metal ions from industrial effluent contaminated with Cu(II), Cd(II), and Pb(II) solutions. Use of biosorbent in columns for the removal of heavy metals demonstrated high efficiency for industrial effluents contaminated with Cu, Cd, and Pb. The adsorbed Cu(II), Cd(II), and Pb(II) ions can be recovered using 0.1 mol L^{-1} solutions and the biosorbent MMFT can be regenerated and reused making the biosorption process more economical.

From the thermodynamic point of view, the adsorption process of poisonous metals ions on Mexerica mandarin (MMFT) was exothermic and the positive entropy indicates an increase in disorganization in solid–liquid interface, suggesting that the process is not driven by the enthalpy but by entropy.

Acknowledgments

The authors are grateful to Universidade Estadual de Londrina—UEL, to Conselho Nacional de Desenvolvimento Científico e Tecnológico—CNPq for financial support and fellowship.

List of symbols

b	— Langmuir constant
C_e	— equilibrium metal ions concentration ppm (mg L^{-1})
C_o	— initial metal ions concentration ppm (mg L^{-1})
ΔG	— Gibbs free energy change (kJ mol^{-1})
ΔH	— enthalpy change (kJ mol^{-1})
ΔS	— entropy change (J k^{-1} mol^{-1})
k_1	— pseudo-first-order rate constant (min^{-1})
k_2	— pseudo-second-order rate constant (mg g^{-1} min^{-1})
K_F	— Freundlich adsorption constant (mg g^{-1})
K_d	— distribution coefficient of the adsorbate
MMF	— Mexerica mandarin flour
MMFT	— Mexerica mandarin flour treated
m	— amount of adsorbent added in g
n	— Freundlich constant
PZC	— point of zero charge
Q_m	— equilibrium adsorption capacity using model
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
R^2	— linear regression coefficient
t	— time (min)
T	— temperature (K)

References

[1] S. Liang, X. Guo, Q. Tian, Adsorption of Pb^{2+} and Zn^{2+} from aqueous solutions by sulfured orange peel, Desalination 275 (2011) 212–216.

[2] M.M. Matlock, B.S. Howerton, D.A. Atwood, Chemical precipitation of lead from lead battery recycling plant wastewater, Ind. Eng. Chem. Res. 41 (2002) 1579–1582.

[3] M.E. Páez-Hernández, K. Aguilar-Arteaga, C.A. Galán-Vidal, M. Palomar-Pardavé, M. Romero-Romo, M.T. Ramírez-Silva, Mercury ions removal from aqueous solution using an activated composite membrane, Environ. Sci. Technol. 39 (2005) 7667–7670.

[4] A. Dabrowski, Z. Hubicki, P. Podkošcielny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere 56 (2004) 91–106.

[5] C.J. Moon, J.H. Lee, Use of curdlan and activated carbon composed adsorbents for heavy metal removal, Process Biochem. 40 (2005) 1279–1283.

[6] V.C.G. dos Santos, J.V.T.M. de Souza, C.R.T. Tarley, J. Caetano, D.C. Dragunski, Copper ions adsorption from aqueous medium using the biosorbent sugarcane bagasse in natura and chemically modified, Water Air Soil Pollut. 216 (2011) 351–359.

[7] K. Palomar-Pardavé, Y.S. Yun, Bacterial biosorbents and biosorption, Biotechnol. Adv. 26 (2008) 266–291.

[8] J.L. Wang, C. Chen, Biosorption of heavy metals by Saccharomyces cerevisiae: A review, Biotechnol. Adv. 24 (2006) 427–451.

[9] A.H. Mahvi, Application of agricultural fibers in pollution removal from aqueous solution, Int. J. Environ. Sci. Technol. 5 (2008) 275–285.

[10] U. Suryavanshi, S.R. Shukla, Adsorption of Pb^{2+} by alkali-treated Citrus limetta peels, Ind. Eng. Chem. Res. 49 (2010) 11682–11688.

[11] Y. Chen, L. Ding, J. Nie, Isotherm and thermodynamic studies of the biosorption of lead, cadmium and copper from aqueous solutions by rice bran, Desal. Wat. Treat. 44 (2012) 168–173.

[12] D. Zhang, X. Zeng, P. Ma, H. He, J. Falandysz, The sorption of Cd(II) from aqueous solutions by fixed *Lentimus edodes* mushroom flesh particles, Desal. Wat. Treat. 46 (2012) 21–31.

[13] V. Mishra, C.B. Majumder, V.K. Agarwal, Sorption of Zn(II) ion onto the surface of activated carbon derived from eucalyptus bark saw dust from industrial wastewater: isotherm, kinetics, mechanistic modeling, and thermodynamics, Desal. Wat. Treat. 46 (2012) 332–351.

[14] C. Moreno-Castilla, A.F. Pérez-Cadenas, F.J. Maldonado-Hódar, F. Carrasco-Marín, J.L.G. Fierro, Influence of carbon-oxygen surface complexes on the surface acidity of tungsten oxide catalysts supported on activated carbons, Carbon 41 (2003) 1157–1167.

[15] R. Leyva-Ramos, L.A. Bernal-Jacome, I. Acosta-Rodriguez, Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob, Sep. Purif. Technol. 45 (2005) 41–49.

[16] D. Lu, Q. Cao, X. Cao, F. Luo, Removal of Pb(II) using the modified lawny grass: Mechanism, kinetics, equilibrium and thermodynamic studies, J. Hazard. Mater. 166 (2009) 239–247.

[17] J.A.M. Gondim, M.F.V. Moura, A.S. Dantas, R.L.S. Medeiros, K.L. Santos, Composição centesimal e de minerais em cascas de frutas [Percentile and mineral composition in fruit peel], Ciênc. Tecnol. Aliment. 25 (2005) 825–827.

[18] N. Feng, X. Guo, S. Liang, Y. Zhu, J. Liu, Biosorption of heavy metals from aqueous solutions by chemically modified orange peel, J. Hazard. Mater. 185 (2011) 49–54.

[19] C.G. Rocha, D.A.M. Zaia, R.V.S. Alfaya, A.A.S. Alfaya, Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents, J. Hazard. Mater. 166 (2009) 383–388.

[20] S. Lagergren, Zur theorie der sogenannten adsorption geloester stoffe [The theory of the adsorption of dissolved matter], K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.

[21] J. Febrianto, A.N. Kosasih, J. Sunarso, Y. Ju, N. Indraswati, S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, J. Hazard. Mater. 162 (2009) 616–645.

[22] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–742.

[23] C. Namasivayam, D. Sangeetha, Equilibrium and kinetic studies of adsorption of phosphate onto $ZnCl_2$ activated coir pith carbon, J. Colloid Interf. Sci. 280 (2004) 359–365.

[24] C. Namasivayam, D. Sangeetha, Kinetic studies of adsorption of thiocyanate onto $ZnCl_2$ activated carbon from coir pith, an agricultural solid waste, Chemosphere 60 (2005) 1616–1623.

[25] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[26] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–213.

[27] R.S. Juang, F.C. Wu, R.I. Tseng, The ability of activated clay for the adsorption of dyes from aqueous solutions, Environ. Technol. 18 (1997) 525–531.

[28] G. McKay, Use of adsorbents for the removal of pollutants from wastewaters, CRC Press, Boca Raton, 1995.

[29] G. McKay, H.S. Blair, J.R. Gardener, Adsorption of dyes on chitin. 1. Equilibrium studies, J. Appl. Polym. Sci. 27 (1982) 3043–3057.

[30] K. Kadirvelu, C. Namasivayam, Activated carbon from coconut coir pith as metal adsorbent: Adsorption of Cd(II) from aqueous solution, Adv. Environ. Res. 7 (2003) 471–478.

[31] H. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–470.

[32] K.K. Krishnani, X. Meng, C. Christodoulatos, V.M. Boddu, Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk, J. Hazard. Mater. 153 (2008) 1222–1234.

[33] M. Thirumavalavan, Y. Lai, L. Lin, J. Lee, Cellulose-based native and surface modified fruit peels for the adsorption of heavy metal ions from aqueous solution: Langmuir adsorption isotherms, J. Chem. Eng. Data 55 (2010) 1186–1192.

[34] M. Thirumavalavan, Y. Lai, L. Lin, J. Lee, Fourier transform infrared spectroscopic analysis of fruit peels before and after the adsorption of heavy metal ions from aqueous solution, J. Chem. Eng. Data 56 (2011) 2249–2255.

[35] V.S. Munagapati, V. Yarramuthi, S.K. Nadavala, Biosorption of Cu(II), Cd(II) and Pb(II) by Acacia leucocephala bark powder: Kinetics, equilibrium and thermodynamics, Chem. Eng. J. 157 (2010) 357–365.

[36] M.M. Areco, M.S. Afonso, Copper, zinc, cadmium and lead biosorption by Gymmogongrus torulosus. Thermodynamics and kinetics studies, Coll. Surf. B: Biointerf. 81 (2010) 620–628.

[37] Y.N. Mata, M.L. Blázquez, A. Ballester, F. González, J.A. Muñoz, Characterization of the biosorption of cadmium, lead and copper with the brown alga *Fucus vesiculosus*, J. Hazard. Mater. 158 (2008) 316–323.

[38] L.V.A. Gurgel, F. Gil, Adsorption of Cu(II), Cd(II) and Pb(II) from aqueous single metal solutions by succinylated twice-mercerized sugarcane bagasse functionalized with triethylenetetramine, Water Res. 43 (2009) 4479–4488.

[39] M.E. Argun, S. Dursun, M. Karatas, Removal of Cd(II), Pb(II), Cu(II) and Ni(II) from water using modified pine bark, Desalination 249 (2009) 519–527.

[40] T.K. Naiya, A.K. Bhattacharya, S.K. Das, Adsorptive removal of Cd(II) ions from aqueous solutions by rice husk ash, Environm. Progr. Sustain. Energy 28 (2009) 535–546.

[41] T.K. Naiya, A.K. Bhattacharya, M. Sailendranath, S.K. Das, The sorption of lead(II) ions on rice husk ash, J. Hazard. Mater. 163 (2009) 1254–1264.

[42] M. Mandado, N. Cordeiro, D.S. Natalia, On the stability of metal-aminoacid complexes in water based on water-ligand exchange reactions and electronic properties: Detailed study on iron-glycine hexacoordinated complexes, J. Comput. Chem. 31 (2010) 2735–2745.

[43] C.R. Fox, D.C. Kennedy, Conceptual design of adsorption systems, adsorption technology: A step-by-step approach to process evaluation and application, Marcel Dekker Inc., 1985.