REMOVAL OF Pb (II) FROM AQUEOUS SOLUTION WITH ORANGE SUB-PRODUCTS CHEMICALLY MODIFIED AS BIOSORBENT

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The effects of chemical modification of orange peel, bagasse, and a mixture of peel and bagasse for lead ion removal from aqueous medium were evaluated. The chemical modification of biomass was carried out with sodium hydroxide and citric acid to introduce carboxylate groups on the surface of the biomass. Infrared spectra confirmed the presence of carboxylate groups at 1735 cm^{-1}. Adsorption isotherms performed by static adsorption experiments fitted very well to the linear Langmuir and Freundlich models. The experiments were carried out at pH 5 during 500 min of shaking time. Orange modified peel (O-MP) presented the highest adsorption capacity (84.5 mg g^{-1}), notably higher than other biosorbents described in the literature. The kinetic studies showed that the process obeyed a pseudo-second-order rate expression, thus indicating a strong interaction between the biosorbent and adsorbate. It was found that the chemical modifications of sorbents promoted an adsorption energetically more spontaneous, as indicated by negative values of Gibbs free energy. On the other hand, desorption studies showed low leaching of lead ions from the biosorbent, thus confirming the strong interaction of lead ions and the biosorbent. The satisfactory maximum adsorption capacity obtained and negligible cost of biosorbent makes the sub-products of orange a reliable natural material for the removal of lead ions from aqueous effluents.

Keywords: Isotherms; Kinetics; Lead; Peel; Bagasse; Orange

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INTRODUCTION

Agricultural and industrial activities produce a great quantity of residues, which often contain heavy metals that can harm fauna, flora, and human health. The problem of effluents that contain heavy metals is of great concern because these elements are a source of environmental pollution and present harmful effects to ecosystems, such as physical and chemical changes reflecting the quality of water (Albertini *et al*. 2007). Impacts on human health as a result of heavy metals commonly involve either drinking water or the food chain. Severe toxicological effects on living organisms occur through the blocking of biological activities, specifically by enzymatic inactivation due to the binding between the metal and some functional protein groups, causing irreversible damage. Therefore, the removal of heavy metals using alternative methods before discharging them into the environment has become an important worldwide research field because of the increasing necessity to preserve these natural resources.

Conventional methods for effluent treatment containing heavy metals include precipitation, oxidation or reduction, filtration, and electrochemical treatment, among others. However, these methods have some disadvantages, including high implementation costs, especially when the metals are present at low concentration and dissolved in a large amount of water (Rodrigues *et al*. 2006, Ferreira *et al*. 2007; Romera *et al*. 2007; Sousa *et al.* 2007; Karnitz Júnior *et al*. 2009, 2010).

Adsorption methods, which are based on physical and chemical phenomena that occur when the adsorbate molecules accumulate on the adsorbent surface, present some advantages over other methods, mainly due to low investment costs, as well as the possibility of using environmentally friendly, natural adsorbents, *i.e*. biosorbents. Biosorption results from electrostatic interactions and also from the formation of complexes between the metallic ions and functional groups present in the cell surface, when they exhibit some chemical affinity for the metallic ion (Rodrigues *et al*. 2006; Sousa *et al*. 2007; Dahiya *et al*. 2008; Yan and Viraraghavan 2008).

Organic matter from vegetal, animal, or microbial sources, including materials from their natural or artificial transformation has been successfully applied for removal of heavy metals from aqueous media. In general, some agricultural sub-products, such as sugarcane bagasse, rice husks, coconut husks, *etc*., have gained great attention as biosorbents, since these materials are economically viable, are produced in large quantities, and come from renewable sources (Annadurai *et al*. 2002; Tarley and Arruda, 2003, 2004; Feng *et al*. 2009; Pérez-Marín *et al.* 2007; Karnitz Júnior *et al*. 2009; Karnitz Júnior *et al*. 2010; Dos Santos *et al*. 2011).

Recent studies have demonstrated the utilization of orange residues for the study of metal adsorption due to the great renewable production and low cost for these adsorbents (Kurniawan *et al*. 2006). Besides, the orange waste gel showed high selectivity for some metal ions, such as Pb^{2+}, Fe^{3+}, and Cu^{2+} when separating them from other metals. Taking into account its efficiency, price, and benign behavior toward the environment, this gel can be employed as an alternative adsorbent for metal separation from aquatic media, instead of conventional adsorption gels or resins (Dhakal *et al*. 2005). Moreover, the waste from the orange juice industry has been regarded as a potential biosorbent material for removing Cd^{2+} from aqueous solutions (Pérez-Marín *et al*. 2007). Brazil is considered the world's largest orange producer, having a planted area of over 820,000 hectares. The total orange production is mainly devoted, (*c.a*. 70%) to the production of frozen concentrated orange juice processors (Coltro *et al*. 2009). This biomass exhibits good capacity to retain metallic ions through adsorption process. However, adsorptive properties of biosorbents can be improved significantly by using chemical modification (Marshall *et al*. 1999).

In this paper we propose different procedures for chemical modification of orange residues (peel and bagasse) using sodium hydroxide and citric acid in order to improve the adsorptive behavior of a biosorbent towards lead ions. The maximum adsorption capacity, adsorption kinetics, and adsorption thermodynamic studies were evaluated.

EXPERIMENTAL

Reagents

Analytical grade chemical reagents were used throughout the experiment. Lead stock solution of 1.000 mg L^{-1} was prepared from lead nitrate ($Pb(NO_3)_2$ Vetec, 99%), and necessary dilutions were carried out by using deionized water. The following solutions 0.1 mol L^{-1} NaOH (F. Maia, 97%), 0.1 mol L^{-1} HCl (F. Maia, 37%), and 1.2 mol L^{-1} (F. Maia, 98%) citric acid were also used.

Equipment

A BOMEM (model MB-102) FT-IR infrared spectrometer was used to elucidate the functional groups present in the adsorbents. Peel and bagasse samples were proportionally macerated with KBr crystals (1 mg sample/100 mg KBr) and put in a pastillator, and then the 4000 to 400 cm^{-1} spectral range was analyzed. Images of the biomass surfaces were obtained using a FEI Quanta 200 scanning electron microscope (SEM, Japan) at 30 kV to verify superficial changes in the residues. A flame atomic absorption spectrometer (FAAS; GBC 932plus), equipped with deuterium lamp for background correction and a hollow cathode lamp as radiation source for lead, was used for metal quantification.

Adsorbent Preparation

Orange peel (O-P), bagasse (O-B), and peel with bagasse (O-PB) were obtained from a supermarket from Umuarama—PR, Brazil. Prior to use, the peel, bagasse, and peel with bagasse were dried at 60^{o}C, ground, and sieved (Bertel sieve, 100 mesh) in order to obtain a more homogenous particle size. Next, the chemical modifications were performed.

Modification with NaOH and Citric Acid

The modification of orange peel, bagasse, and peel with bagasse with NaOH was carried out as follows: for each gram of the material, 20 mL of 0.1 mol L^{-1} NaOH solution was added; then the mixture was agitated during 2 h, and the supernatant was discharged. Next, the material was repeatedly washed with deionized water and dried at 55°C for 24 h. After this step, the materials (peel, bagasse, and peel with bagasse) previously treated with NaOH were chemically modified with citric acid, and they were named O-MP, O-MB, and O-MPB, respectively. For this task, a solution of 1.2 mol L^{-1} citric acid was added to the bagasse at 8.3 mL solution/gram of residue ratio. After that, the mixture was agitated for 30 min and the supernatant discharged. The residue was dried at 55°C, and after 24 h the temperature was increased to 120°C and kept for 90 min. Finally, the residues were repeatedly washed with deionized water and dried at 55°C for 24 h (Rodrigues *et al*. 2006).

Points of Zero Charge – PZC

PZC is defined as the pH at which the biomass surface has a neutral charge. In this study, the methodology chosen for determining the PZC was described by Guilarduci *et al*. (2006). This procedure consisted of mixing 0.5 g of the biomass with 50 mL of an aqueous solution at different initial pH values (1, 2, 3, 4, 5, 6, 8, 9, 10, 11, and 12) adjusted at 30°C using HCl and NaOH solutions. The ionic strength of the solution was varied by adding 0.01, 0.1, and 0.5 mol L^{-1} KCl , which resulted in three PZC values for each biomass sample. After reaching equilibrium (24 h), the final pH was measured, making it possible to construct a final pH *vs.* initial pH plot based on these data, and the PZC pH referred to the final pH constant value was determined. All the analyses were carried out in duplicate.

Metal Adsorption Experiment

Effect of pH on adsorption behavior

Batch adsorption experiments were used to measure the amount of lead adsorbed on modified peel (O-MP), bagasse (O-MB), and peel with bagasse (O-MPB) as a function of pH. The experiments were performed in an orbital shaker by using 0.5 g of each material and shaking with 50 mL of lead solution at 700 mg L^{-1}. The pH range investigated was from 2 to 6 at 30°C.

After the selected period of shaking, the amount of lead adsorbed per metal per gram of material (q_{eq}) was calculated as follows,

$$q_{eq} = \left(C_0 - C_{eq}\right) * \frac{V}{M} \tag{1}$$

where C_0 and C_{eq} are the initial and equilibrium metal concentrations of the solution (mg L^{-1}), respectively, V is the solution volume (mL), and M the material mass (g).

Effect of Shaking Time

The effect of shaking time on lead adsorption on materials was evaluated by using 0.5 g of each material and shaking with 50 mL of lead solution at 700 mg L^{-1} concentration. The shaking time range evaluated was from 10 to 1440 min at 30°C. After each shaking time evaluated, an aliquot of 500 μL was taken, followed by addition of the same volume, until the volume reached 50 mL. The concentration of lead ions was determined by FAAS. The necessary correction regarding the amount of lead ions in the initial solution was performed for each aliquot. The amount of adsorbed metal per gram of residue (q_{eq}) as a function of time was calculated based on Equation 1.

Adsorption Isotherms

Solutions of lead ions at different concentrations were prepared, ranging from 100 to 1000 mg L^{-1} at 30°C. Afterwards, 50 mL of lead solutions at pH 5.0 were individually taken and agitated with 0.5 g of bagasse in an orbital shaker for 24 h. Next, the mixtures were filtrated and the solutions were analyzed by FAAS. Again, Equation 1 was employed to determine the amount of lead adsorbed metal per gram of material. The equilibrium adsorption data were fitted according to the Langmuir and Freundlich models (Özacar and Şengil 2003; Doğan *et al.* 2004; Dahiya *et al.* 2008; Gonçalves *et al.* 2008).

Temperature Effect

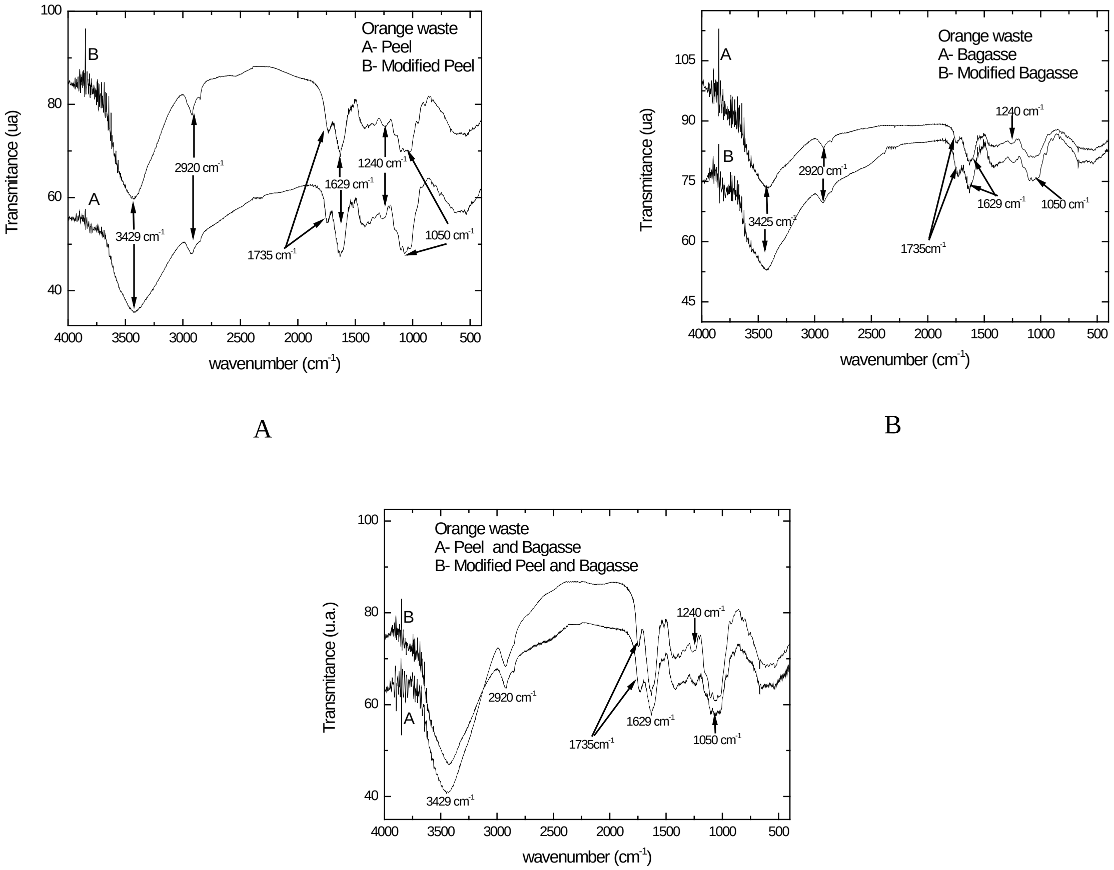
Thermodynamic parameters were obtained from an analysis of the Pb^{2+} adsorption as a function of temperature. To carry out these experiments, 0.5 g of the residue samples

(O-MP, O-MB, O-MPB) and 50 mL of 700 mg L^{-1} Pb^{2+} solution were mixed. The pH was fixed at 5.0, the shaking time was 24 h, and the following temperatures were established: 10, 20, 30, 40, and 60°C. After that, the thermodynamic parameters – enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) – were calculated according to the procedure described by Gök *et al*. (2008) and Chakravarty *et al*. (2008). All the experiments were performed in duplicate. The margin of error was approximately 5% in the experiments.

RESULTS AND DISCUSSION

Infrared Spectra of Materials

The infrared spectra of the materials presented characteristic bands at 3429, 2920, 1735, 1629, 1240, and 1050 cm^{-1} (Fig. 1A,B,C). The broad strong band at 3429 cm^{-1} is attributed to the stretching vibration of the O-H bond. The peak at 2920 cm^{-1} is attributed to the stretching vibration of the C-H bond, while peaks at 1735 and 1629 cm^{-1} are assigned to the stretching vibration of the C-O bond.



A

B

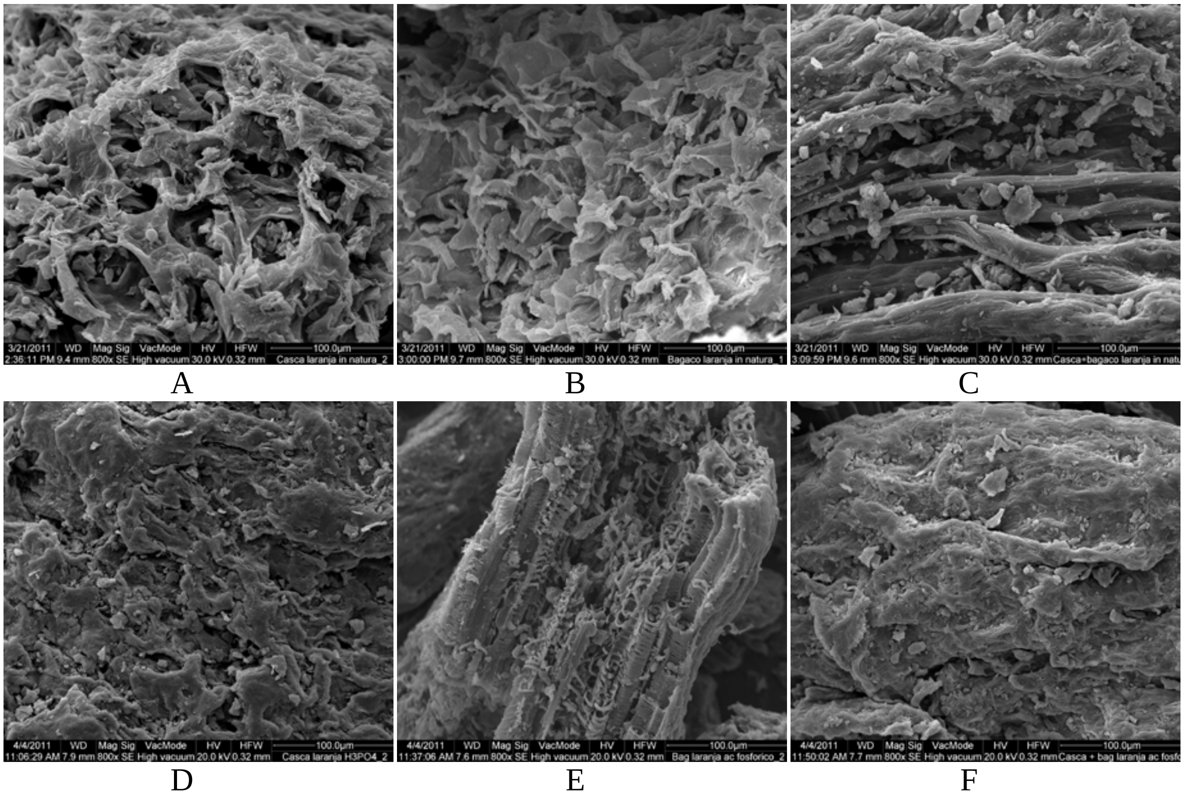
C

Fig. 1. Infrared spectra for samples of *in natura* and modified orange residues: A – orange peel; B – orange bagasse; C – orange peel with bagasse

According to the literature, the presence of a carbonyl group in compounds containing ester and carboxyl groups can be confirmed by absorption at 1735 cm^{-1} (Tana *et al*. 2010). The peak at 1240 cm^{-1} can be attributed to the vibrations of the C-O bond. A strong band at 1050 cm^{-1} confirmed the presence of polysaccharides (Tana *et al*. 2010). As observed from the spectra, the chemical modification of orange residues with citric acid promoted a slight increase in peak intensity at 1735 cm^{-1}, indicating an increase in the quantity of carboxyl groups. These data are in agreement with the results obtained by Rodrigues *et al*. (2006), where paraju sawdust was treated with NaOH and citric acid. The carboxyl groups play an important role on metal adsorption.

Morphological Characterization

The images of the biomass residue surfaces are presented in Fig. 2. They were obtained by scanning electron microscopy (SEM) and magnified 800 times. It can be observed that all the samples had similar morphological characteristics, evidencing an irregular nature, as well as formation of overlapping fiber layers and cracks, which allow for adsorption areas. Comparing the images in Fig. 2, it can be seen that images D, E, and F present a larger surface area. This flat surface favors the adsorption on the walls of the tubes and cracks, as it increases the apparent surface area. Even after the reaction with citric acid, the porosity profile for the material can be seen.



A B C

D E F

Fig. 2. Micrographs of orange residues; Peel (A), Bagasse (B), Peel and Bagasse (C), Modified Peel (D), Modified Bagasse (E), Modified Peel-Bagasse (F)

Point of Zero Charge (PZC)

The PZC describes the condition when the electrical charge density on a surface is zero, and it was determined herein for the biomass in order to check the pH at which the biosorbent surface charge changes from predominantly positive to negative. In the present study, the PZC was evaluated based on the methodology proposed by Guilarduci *et al*. (2006). The adsorption capacity of the orange residue samples is related to ion exchange, chelation, and physical adsorption (Ilhan *et al*. 2004). According to Aksu (2005), these mechanisms generally involve surface groups being able to capture and retain metal species in an aqueous medium, where they can be modified by the pH variation affecting the adsorption process. Therefore, a preliminary study of acid-base behavior of the orange residue was carried out through the PZC determination. The results are demonstrated in Fig. 3 for the 0.1 mol L^{-1} KCl solution only, since the values obtained for the other concentrations were almost the same, indicating that the ionic strength did not change the PZC.

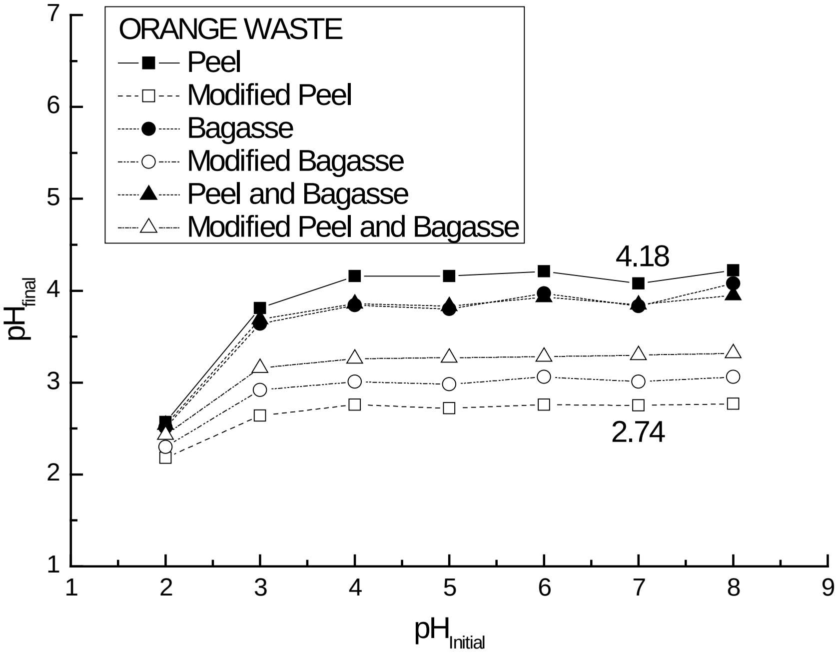


Fig. 3. Point of zero charge (PZC) characterization of *in natura* and modified orange residues. KCl concentration: 0.1 mol L^{-1}

The PZC pH values were found to be between 4.18 (O-P) and 2.75 (O-MP). For the solutions at pH values lower than the PZC, the residue would present predominantly positive surface charges, and at pH values higher than the PZC, the liquid surface charges would be negative. It was observed that the PZC was below pH 5.0 for all the residues, demonstrating the predominantly negative surface charges that attract the positive metal ions.

Influence of pH

The effect of the solution acidity on lead adsorption by biosorbents was studied from pH 2 to 6 (Fig. 4). It was verified that the adsorption process was pH dependent, where the amount of lead adsorbed increased significantly with increasing pH. This might be due to biomass functional groups being positively charged at lower pH values and, as a consequence, electrostatic repulsion occurring between the adsorbate and adsorbent. When the pH was above 4, only a slight increase on lead adsorption was observed. After the chemical treatment, the adsorption performance of the biosorbents was improved. Therefore, solution at pH 5.0 was selected in order to avoid lead precipitation and so that the residue would present predominantly negative surface charges (Tana *et al*. 2010). It is important to emphasize that after chemical treatment, the biosorbents had an improvement on its adsorbent properties.

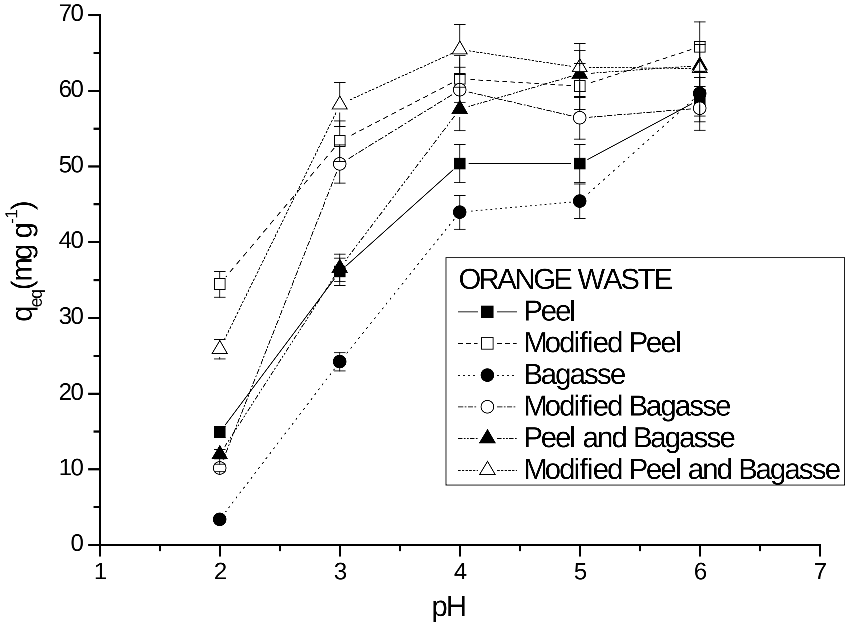


Fig. 4. Adsorbed quantity (q_{eq}) of lead in *in natura* and modified orange residues as a function of pH. Experimental conditions: adsorbent dose: 0.5 g, Pb^{2+} solution (700 mg L^{-1}): 50 mL, shaking time: 24 h

Effect of Shaking Time

The effect of shaking time on lead adsorption on adsorbents is presented in Fig. 5. Higher amounts of lead adsorbed were observed for those materials that had been chemically treated, with predominance to the modified peel. It was found for all experiments that the equilibrium time was achieved at around 500 min. In order to characterize the adsorption kinetics of lead on the materials surfaces, pseudo-first and pseudo-second-order kinetic models were evaluated. Pseudo-first-order kinetics follows Lagergen models expressed by Equation 2 (Doğan *et al*. 2004; Noeline *et al*. 2005; Özcan *et al*. 2005; Pérez-Marín *et al*. 2007; Feng *et al*. 2009),

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{K_1 x\, t}{2.303} \tag{2}$$

where q_t is the adsorbed quantity of lead ion (mg g^{-1}) in t time (min) and K_1 is the pseudo-first-order constant (min^{-1}). Through the linear and angular coefficient of the log graphic ($q_{eq} - q_t$) as a function of time, q_{eq} and K_1 can be calculated, respectively. By comparing the experimentally obtained values of q_{eq} calculated using Equation 2, it was possible to note that the pseudo-first-order kinetic model did not fit well to the experimental data (Table 1). The low coefficient of regression (R^2) also confirms the unsatisfactory nature of the model.

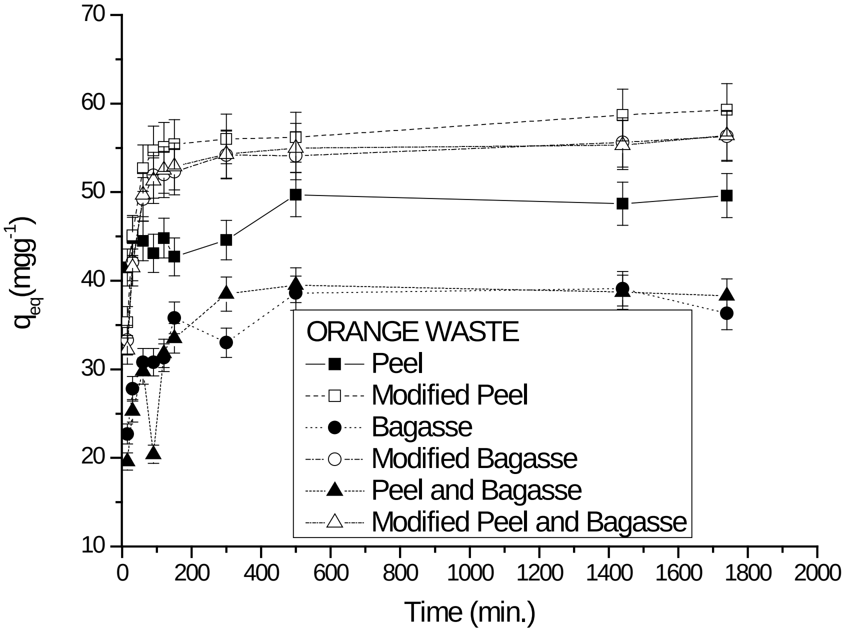


Fig. 5. Kinetics of lead adsorption (700 mg L^{-1}) for *in natura* and modified orange residues. Experimental conditions: adsorbent dose: 0.5 g, Pb^{2+} solution (700 mg L^{-1}): 50 mL

Table 1. Kinetic Parameters of the Pseudo-First and Pseudo-Second-Order Models for Lead Adsorption

Material	q_{eq} (exp.) (mg g^{-1})	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		K_1 (min^{-1})	q_{eq} (cal.)(mg g^{-1})	R^2	K_2 (g mg^{-1}min^{-1})	q_{eq} (cal.)(mg g^{-1})	R^2
O-P	49.60	11.99 x10^{-3}	14.79	0.726	5.87x10^{-4}	54.22	0.989
O-MP	59.30	3.20x10^{-3}	9.91	0.493	1.31x10^{-4}	59.34	0.999
O-B	39.10	5.52x10^{-3}	14.04	0.787	4.69x10^{-3}	37.68	0.995
O-MB	56.30	1.04x10^{-3}	9.92	0.413	2.04x10^{-3}	56.49	0.999
O-PB	39.50	8.24x10^{-3}	19.48	0.501	2.23x10^{-3}	39.14	0.993
O-MPB	56.40	1.90x10^{-3}	9.05	0.350	2.83x10^{-3}	55.74	0.999

The pseudo-second-order model (Equation 3) was applied for the metal adsorption kinetics in different orange residues (Doğan *et al*. 2004; Noeline *et al*. 2005; Özcan *et al*. 2005; Pérez-Marín *et al*. 2007; Feng *et al*. 2009; Yu *et al*. 2011),

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}} \qquad (3)$$

where k_2 is the pseudo-second-order constant (g mg^{-1}min^{-1}) obtained by the slope of the straight line of the graphic of t/q_t as a function of t (Fig. 6), as q_{eq} can be evaluated through the linear coefficient. The experimental and calculated values of q_{eq}, k_2, and R^2 are given in Table 1.

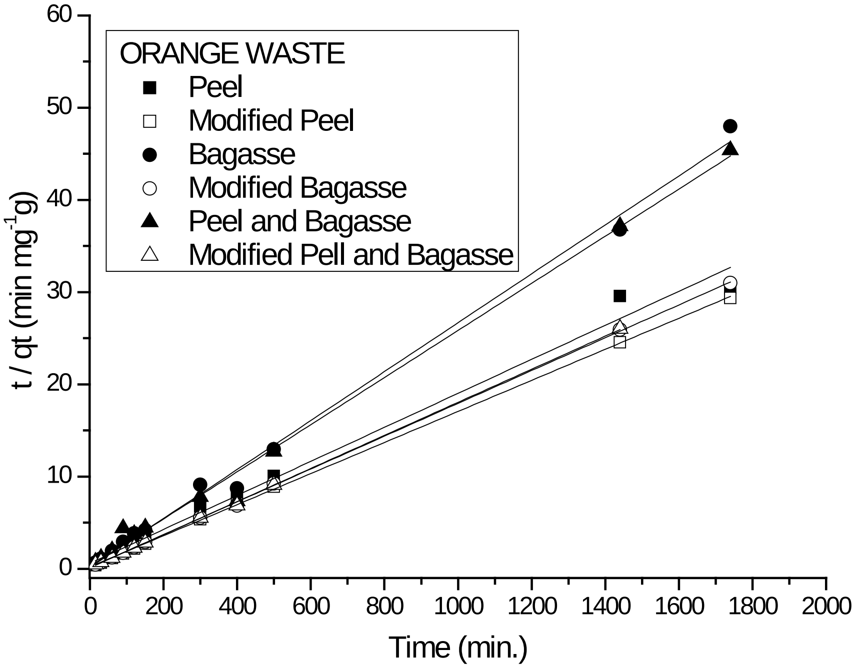


Fig. 6. Pseudo-second-order kinetics for lead adsorption (700 mg L^{-1}) *in natura* and modified orange residues. Experimental conditions: adsorbent dose: 0.5 g, Pb^{2+} solution (700 mg L^{-1}): 50 mL

Experimental data revealed that the kinetic study provided a better adjustment when fitted by the pseudo-second-order equation. Such behavior demonstrates that lead interaction with adsorbent materials is controlled by chemical adsorption (Spinelli *et al*. 2005).

Adsorption Isotherms

Figure 7 shows the effect of increasing concentration of lead on the amount of lead adsorbed by the materials. This isotherm analyses were performed with sufficient time for equilibration, as previously optimized (500 min). As observed for peel, bagasse, and peel mixed with bagasse, with increasing lead concentration in solution, the amount of lead per unit of materials also increased, reaching a saturation condition close to 500 mg L^{-1}. On the other hand, within the range of initial lead concentrations investigated, the adsorption amount of lead on modified peel, bagasse, and modified peel and bagasse increased sharply. The results indicated that citric acid had been immobilized on the surface of biosorbents successfully.

The equilibrium adsorption data were adjusted to the Langmuir (4) and Freundlich (5), Dubinine Radushkevich (DER) (6), and Temkin (7) models, respectively, as shown by the following equations,

Langmuir model: $$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m} \qquad (4)$$

where C_{eq} is the equilibrium of final concentration of lead in solution, b is the Langmuir constant that indicates the adsorption intensity, and q_m is the maximum adsorption capacity.

Freundlich model: $$\log q_{eq} = \log K_f + \left(\frac{1}{n}\right) \log C_{eq} \qquad (5)$$

where K_f is related to the adsorption capacity and the constant n corresponds to the adsorption intensity (Sodré *et al*. 2001). Values of n in the range $1<n<10$ indicate favorable adsorption (Kalavathy *et al*. 2005).

DER model: $$\ln q_{eq} = ln q_d - B_d E^2 \qquad (6)$$

In Eq. 6, B_d is a constant that is related to the average energy per mole free adsorption of adsorbate ($mol^2\ J^{-2}$), q_d is the theoretical saturation capacity, and E is the Polanyi potential which is equal $RTln\left(1 + \left(\frac{1}{C_e}\right)\right)$, where R ($J\ mol^{-1}\ K^{-1}$) is the gas constant and T (K) is the absolute temperature (Ijagbemi *et al*. 2010).

The constant B_d is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution; this energy can be computed using the following relationship (Hasamy and Chaudhary 1996):

$$E = \frac{1}{\sqrt{2B_d}}$$

In this expression E is the energy parameter, which provides information about the adsorption mechanism as chemical ion exchange or physical adsorption.

Temkin model: $$q_{eq} = B_1 \ln K + B_1 ln_c \qquad (7)$$

In Eq. 7, K is the equilibrium binding constant, corresponding to the energy maximum binding, and B_1 relates to the heat of adsorption (Temkin and Pyzhev 1940).

As shown in Table 2, the coefficients of determination for the Langmuir data (R^2) were slightly higher those observed for the Freundlich model. It is reasonable to assume that lead adsorption behavior on biosorbents may take place in one single layer (monolayers), indicating a homogeneous distribution of cavities on the biosorbent surface. However, based on values of the constant *n* from the Freundlich model being higher than 1, as well as from somewhat satisfactory correlation coefficients, the data also are consistent with a model in which the multilayer adsorption takes place on the adsorbent materials. This result is somewhat expected, bearing in mind the complexity of the structure and composition of biosorbents.

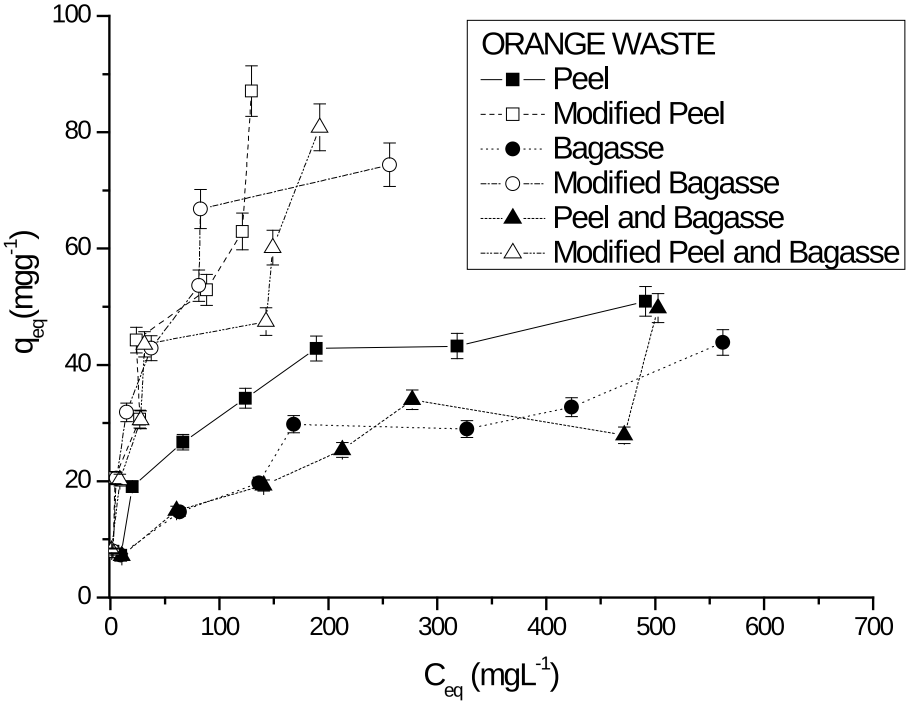


Fig. 7. Adsorption isotherms of Pb (II) for *in natura* and modified orange residues. Experimental conditions: Pb^{2+} solutions: 50 mL, bagasse: 0.5 g, agitation time: 24 h (orbital shaker)

The Dubinin-Radushkevich (D-R) isotherm parameters are given in Table 2. In the present study, the magnitude of the average free energy of the Pb^{2+} adsorption fell in the range of 8.82 to 32.17 kJ mol^{-1}. Since these values exceed 8 kJ mol^{-1}, the Pb^{2+} adsorption to the orange residue was largely governed by chemical ion exchange (Onyango *et al.* 2004).

The Temkin isotherm constants, B_1 and KT, are shown in Table 2. The B_1 value was greater for the modification case, indicating that the heat of the Pb^{2+} adsorption to the orange residue increased, and confirming that the adsorption was stronger for the modified samples, in accordance with the average free energy values of the D-R isotherm.

The highest maximum adsorption capacity was observed for the O-MP material (84.53 mg g^{-1}), which was considerably higher than for orange peel without modification. A comparison of maximum adsorption capacity of O-MP biosorbent for lead with other biosorbents (Table 3) suggests the obvious advantage of the present orange sub-product, when chemically modified.

The peel (P) and bagasse (B) had the highest adsorption capacity values after modification in comparison with the ones obtained for the peel-bagasse (PB). This can be explained by higher porosity of P and B, as demonstrated in Fig. 2.

Table 2. Parameter comparison of Langmuir, Freundlich, D-R and Temkin models for the Adsorption of Lead in *in natura* and Modified Orange Residues

		Material					
		O-P	O-MP	O-B	O-MB	O-PB	O-MPB
Langmuir constants	Q_m (mg g^{-1})	55.52	84.53	46.90	80.19	32.55	73.37
	b (L mg^{-1})	0.018	0.012	0.021	0.012	0.030	0.014
	R^2	0.994	0.938	0.949	0.995	0.974	0.938
Freundlich constants	K_f (L g^{-1})	7.48	7.38	2.77	12.71	2.13	8.49
	n	3.19	2.10	2.37	2.89	2.08	2.50
	R^2	0.970	0.873	0.951	0.948	0.957	0.944
	Q_{exp} (mg g^{-1})	50.87	86.60	43.60	74.27	28.27	80.94
(D-R) constants	q_D (mol^2 kJ^{-2})	0.74	2.10E-3	8.21E-2	1.41E-3	0.23	4.05E-4
	B_d (mol^2 kJ^{-2})	6.42E-9	1.59E-9	5.02E-9	1.33E-9	5.80E-9	4.83E-10
	E (kJ mol^{-1})	8.82	17.74	9.98	19.44	9.29	32.17
	R^2	0.950	0.860	0.703	0.874	0.671	0.670
Temkin constants	K_t (kJ mg^{-1})	0.235	0.650	0.169	0.282	0.236	0.088
	B_1 (dm^3 mg)	10.51	15.39	8.00	22.46	6.47	53.62
	R^2	0.975	0.813	0.817	0.810	0.803	0.880

Table 3. Some Biosorbents Studied for Lead Adsorption

Adsorbents	q_m (mg g^{-1})	pH	Adsorbent Mass(g)	References
Tea leaves	78.87	6	1.8	Tan and Rahman (1988)
Sago	46.60	5	0.5	Quek *et al.* (1998)
Groundnut husks	39.40	6.8	1.0	Okieimen *et al.* (1991)
Hazelnut shell	28.18	6	0.5	Pehlivan *et al.* (2009)
Rice hulls	11.40	6	1.0	Prasad and Freitas (2000)
Rice husk	5.69	5	1.0	Zulkali *et al.* (2006)
Almond shell	8.08	6	0.5	Pehlivan *et al.* (2009)
Modified Sugarcane bagasse	52.63	5	0.5	Dos Santos *et al.* (2010)
Modified Orange Peel (O-MP)	84.53	5	0.5	This study

Thermodynamic Parameters

The thermodynamic parameters for the adsorption ΔH (enthalpy), ΔS (entropy), and ΔG (Gibbs energy) were calculated according to the following equations,

$$\Delta G = -RT \ln K_d \qquad (8)$$

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

where K_d corresponds to the ratio between q_{eq} and Ceq, R is the gas constant (8.314 JK^{-1}mol^{-1}), T is the temperature of the experiment expressed in Kelvin (K). Enthalpy and the other parameters (Table 4) were obtained from the plot of lnK_d versus $1/T$, from Van't Hoff's equation.

Negative values observed for the Gibbs free energy (ΔG) indicates the favorable interaction between adsorbate and adsorbent in a spontaneous process (Gonçalves *et al.* 2008; Guerra *et al.* 2008).

After the chemical modification of the orange peel, bagasse, and peel with bagasse, a decrease in negative value of ΔG was observed in comparison to the residues without modification (Table 4). This result corroborates with higher adsorption capacity (q_m), wherein general higher q_m was accompanied by lower ΔG values (Table 2 and Table 4).

According to the values of enthalpy summarized in Table 4, the adsorption process is endothermic. Positive ΔH values higher than 35 kJmol^{-1} also indicates that retention process of lead ions on the surface of materials takes place by chemical adsorption (Guerra *et al.* 2008), in accordance to pseudo-second-order kinetics and the D-R and Temkin isotherms. Additionally, as observed from Table 4, positive ΔS values indicate that there was an increase of disorder in the solid-solution interface, indicating that the entropy was the most predominant factor for the adsorption spontaneity of these residues.

Table 4. Thermodynamic Parameters Obtained from the Adsorption Results of Lead in *In Natura* and Modified Orange Residues

Material	K_d	ΔG(kJ mol^{-1})	ΔH(kJ mol^{-1})	ΔS(JK^{-1} mol^{-1})
O-P	47.62	-9.73	127.99	458.85
O-MP	351.34	-14.77	36.99	179.58
O-B	49.99	-9.85	104.26	378.62
O-MB	57.53	-10.21	124.93	448.54
O-PB	35.84	-9.02	83.15	313.02
O-MPB	192.95	-13.26	32.80	161.54

Lead Desorption

The regeneration of the materials is likely to be a key factor in improving separation process economics. A great desorption potential means that the material can be re-utilized in new adsorption processes. The assay to evaluate the lead desorption from materials was carried out by loading the materials with known amounts of lead, followed by washing with 150 mL Milli-Q water and drying for 24 h in an oven at 50 °C. After this period, the materials were soaked in a 0.1 mol L^{-1} HCl solution (50 mL) for lead recovery. The obtained values are given in Table 5.

Table 5. Adsorption-Desorption Values of Lead, Initial Concentration of 934 ppm, in *In Natura* and Modified Orange Residues

Material	% Adsorption	% Desorption
C-N	73.5	35.9
C-SCA	74.9	38.0
B-N	66.5	41.3
B-SCA	74.7	6.2
CB-N	65.5	25.0
CB-SCA	74.9	6.5

Low percentage values of lead desorbed were observed even in acid medium. This result indicates the strong adsorption of lead by the materials, thus corroborating the findings from the pseudo second-order kinetics and enthalpy. The desorbed percentage was not considered satisfactory for a possible re-utilization of these materials for new adsorption phases.

CONCLUSIONS

1. In this study, orange peel, bagasse, and peel mixed with bagasse were chemically modified with citric acid in order to improve the adsorption of lead from aqueous medium. The modification was confirmed by infrared spectroscopy, which showed the increase of adsorption sites. The chemical treatment resulted in an improvement of the adsorbent properties of the studied materials. Among the studied orange residues, the modified peel exhibited the highest adsorption capacity with approximately twice the value obtained for the *in natura* samples.
2. The kinetic studies showed that the studied adsorption systems followed pseudo-second-order kinetics.
3. The Langmuir and Freundlich models can be applied to describe the adsorption of lead on biosorbents. The highest maximum adsorption capacity was observed for the O-MP material (84.53 mg g^{-1}).
4. After the chemical modification, a more negative value of ΔG (-14.77 kJ mol^{-1}) was observed, indicating favorable interaction between adsorbate and adsorbent in a spontaneous process. The positive value of ΔH (36.99 kJ mol^{-1}) confirmed the endothermic nature of the adsorption. The positive value of ΔS showed the increase randomness of the solid-solute interface during the adsorption process.
5. From the results obtained in this study, it is concluded that the chemical modification of orange sub-products are promising for heavy metal retention from aqueous medium, in spite of the low desorption rate (38%).

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