Quim. Nova, Vol. 34, No. 6, 928-932, 2011

Fe (II) ADSORPTION ON *Ucides cordatus* CRAB SHELLS

Karina Karla Pacheco Porpino[*]**, Maria da Conceição Silva Barreto, Karina Beltrão Cambuim, José Rodrigues de Carvalho Filho e Ilda Antonieta Salata Toscano**
Departamento de Química, Centro de Ciências Exatas e da Natureza, Universidade Federal da Paraíba, Campus I, 58051-900 João Pessoa - PB, Brasil
Micheline de Azevedo Lima
Departamento de Engenharia e Meio Ambiente, Centro de Ciências Aplicadas e Educação, Universidade Federal da Paraíba, Campus IV, 58297-000 Rio Tinto - PB, Brasil

Recebido em 13/5/10; aceito em 12/1/11; publicado na web em 29/3/11

In this study *Ucides cordatus* crab shells were utilized as Fe (II) sorbent as material of low cost and simple preparation. Values of pH of standard solution, biosorbent mass, particles size, contact time (t_c) and initial concentration of the standard solution were optimized. The best conditions were pH = 2.00, t_c = 840 min and M_c = 0.25 g. The kinetic pseudo first-order model displayed the best description of the adsorption process and the equilibrium study showed that the Langmuir model better describes the adsorption of the Fe (II). There is great affinity between the Fe (II) and the biosorbent.

Keywords: crab shells; iron; adsorption.

INTRODUCTION

Ucides cordatus known as mangrove crab, inhabits burrows in the sediment of the mangrove forest, being appreciated in cooking and the confection *of souvenir*. Due these activities the reminiscent shells are discarded as a pollutant residue. Nowadays some resources are being applied such as biomass used in extraction of chitin and chitosan, in the industry of food and cosmetic, source of calcium in medicaments, soil additive, in promotion of plant growth, raw material in civil construction and as adsorbent of water pollution, as cobalt, copper, nickel, and others.[1-6]

In Brazil, the crab species most abundant is *Ucides cordatus,* commonly known as Uçá crab. The crab shell is a very resistant material in which calcium carbonate is the main constituent and chitin associated to protein and mineral salts.[4] The advantage of the crab shell as sorbent is the low cost and the fact that there is no need of any sophisticated preparation. Commonly the shells are washed in acid solution or water and dried under the sunlight. This process can be easily done by poor communities to clean the water.

The iron is a nutritional element and essential for life, because it is responsible for the oxygen transport. The recommended daily dosage for man and woman is 8-18 mg daily, respectively.[7]

When ingested in high quantity, the iron can cause health problems such as liver cancer, cirrhosis and hereditary hemochromatosis. In the well water may leads to colored waters and changes taste.[8] In Brazil, the Health Ministry recommends certain level up to 0.3 mg L^{-1} of total concentration in drink water.[9]

In this study the *Ucides cordatus* crab shell, was used as iron adsorbent in standard solutions. The biosorbent was characterized physical and chemically as well as tested aiming the adsorption kinetic and equilibrium behavior.

The data of adsorption kinetic curve were treated by the pseudo first-order and pseudo second-order models to establish the order and the rate constant of reaction. The results of the adsorption equilibrium studies were treated by the Langmuir and Freundlich models in order to determine which of them better describes the adsorption of iron by the adsorbent.

EXPERIMENTAL

Biosorbent preparation

The *Ucides cordatus* crab shells used in this study were obtained in a restaurant at João Pessoa – Paraíba, Brazil. The largest carapaces were selected and washed with boiling water to eliminate the residues and then washed at least three times with deionized water and dried at 110 ºC in the oven for 24 h.[10] The dried material was smashed and sieved to obtain different particles size.

Characterization of biosorbent

The crab shells were characterized in regards to moisture, ash, protein, lipids, phosphate and calcium by official methods of analysis.[11] The apparent density and pH of aqueous solutions were determined according to Gratuito and JIS.[12,13]

The superficial area was calculated by BET method (adsorption of N_2 at 77 K) using a Micromeritics Asap 2010 surface analyzer. The infrared spectra of the biosorbent both *in natura* and after acid hydrolysis were recorded with a Bomem-MB spectrometer from 4000 to 400 cm^{-1}.[14]

Adsorption experiments

Before the experiments, the glass laboratorial material was maintained in 10% HNO_3 solution for 24 h. All reagents used in the experiments were analytical grade. The Fe (II) standard solutions were prepared from $Fe(NH_4)_2(SO_4)_2.6H_2O$ (Riedel-de Haën), primary standard grade.[15]

---

*e-mail: kkpporpino@yahoo.com.br

Adsorption experiments were carried out by batch mode. 100 mL of Fe (II) standards solutions were shaken with dried crab shells under 150 rpm at room temperature.[16]

Residual iron was quantified in aliquots of 10 mL of filtered standard solutions by the o-phenanthroline method at 510 nm in a visible spectrophotometer.[15]

The effects of the particle size (0.59, 1.18, and 2.00 mm), pH (2.0, 3.0, 4.0, and 5.0), mass of the biosorbent (0.05, 0.10, 0.25, and 0.50 g), and contact time (several time points within the 0 to 24 h range) on iron adsorption were studied.

Adsorption capacity

Amount of iron ion adsorbed per biosorbent mass unit, Qe, was calculated by the expression: [8,17]

$$Q_e = \frac{(C_i - C_e)V_t}{M_c \cdot 1000} \tag{1}$$

Removal efficiency (%) of Fe (II) was determined by: [8]

$$\%\,Ads = \frac{(C_i - C_e)\cdot 100}{C_i} \tag{2}$$

where: Q_e is the quantity of metal uptake from solution by mass of adsorbent (mg g^{-1}); C_i and C_e are the initial and equilibrium metal concentration (mg L^{-1}), respectively; V_t is the volume of solution in mL and M_c is the dry weight of the adsorbent added (g).

Adsorption equilibrium

The results of adsorption equilibrium experiments were treated by Langmuir and Freundlich models. The Langmuir model assumes that the adsorption occurs on a homogeneous surface to form a monolayer without interaction among the adsorbed ions. The activation energy is distributed over all the surface. It was used the linearised equation of Langmuir.[17-19]

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e \tag{3}$$

Q_m is the Langmuir constant (L g^{-1}) that gives the theoretical adsorption capacity in the monolayer, and K_L (L mg^{-1}) is a constant related with the adsorption energy. The plot of C_e/Q_e against C_e gives a straight line with interception equals to $1/(K_L\ Q_m)$ and slope as $1/Q_m$.

The parameter of equilibrium, R_L, permits to infer the type of adsorption isotherm and can be calculated by the following equation:

$$R_L = \frac{1}{1 + K_L Q_m} \tag{4}$$

If $0 < R_L \leq 1$ the adsorption is favorable, whereas $R_L > 1$ and $R_L < 0$ the adsorption is unfavorable; if $R_L = 0$ the isotherm is irreversible.[17,18,20]

The Freundlich model assumes adsorption in multilayer.[21] Freundlich equation is given by: [22]

$$Q_e = K_F \cdot C_e^{1/n} \tag{5}$$

K_F and 1/n are the Freundlich constants of the system, which are associated with the adsorption capacity and the adsorption intensity, respectively. Values in the range $0.1 < (1/n) < 1$ indicate favorable adsorption. The linearised Freundlich equation is:[22]

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

The plot of ln Q_e against ln C_e gives a straight line with interception equals to ln K_F and slope at 1/n.

Kinetic adsorption

In this study the sorption kinetics of Fe (II) were determined by both a pseudo-first order model and a pseudo-second order model.

The linearised form of the first order model is expressed as follows:

$$\ln (Q_e - Q_t) = \ln \mathrm{Q_e} - \mathrm{k_1} t \tag{7}$$

Q_e (mg g^{-1}) and Q_t (mg g^{-1}) are the amounts of adsorbed metal ions at the equilibrium and at any given time, t, respectively; k_1 is the pseudo first-order equilibrium rate constant.

Linear plots of ln ($Q_e - Q_t$) versus t indicate the applicability of this kinetic model. The straight-line plots of ln ($Q_e - Q_t$) against t has slope equals to $-k_1$ and intercept equals to ln Q_e.[21]

The linearised form of the pseudo-second order kinetic model is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{8}$$

Where k_2 (g mg^{-1} min^{-1}) is the pseudo-second order equilibrium rate constant.

The plot of t/Q_t versus t is linear with slope equals to $1/Q_e$, and intercept equals to $1/(k_2\ Q_e^2)$.

The model that better describes the adsorption was chosen as the one with higher correlation coefficient (R^2).

RESULTS AND DISCUSSION

Crab shell characterization

The results of biosorbent physico-chemical characterization are summarized in Table 1. The precision of the measurements is indicated by the standard deviation.

Table 1. Physical-chemical characterization of the crab shells

Measured parameter	Obtained results
Moisture (%)	3.0 ± 0.6 **
Ashes (%)	75.7 ± 0.8 **
Ca (g/100g)	34 ± 1 **
P(mg/100g)	4.0 ± 0.3 *
Lipids (%)	5.5 ± 0.6 *
Protein (g/100g)	9.3 ± 0.6 *
d (g cm^{-3})	0.57 ± 0.06
pH	9.60
DMP (nm)	5.8
S_{BET} (m^2 g^{-1})	18.2 ± 0.1

** 5 determinations; * 2 determinations

As the biosorbent is rich in minerals salts, high levels of ash content were found (75.71%). Benchimol[2] observed values a little higher of moisture (8,16%), Ca (43.7%), and P (10.6 mg/100 g) for the same species of crabs but from another geographic region of Brazil, while the protein and ash values (6.36 and 71.8%, respectively) were less than those found in the present work.

From the total calcium content measured, it was estimated that 85% corresponds to $CaCO_3$. The alkaline pH (9.60) of the surface agrees with the work by Lee and Davis,[24] where it is proposed that the hydroxide groups are at the surface coordination sites of the biomaterials. It is also likely the adsorption of cations by the biomaterials due to charge difference between the metal ion and the surface.[23,24]

The isotherm of adsorption of $N_2(g)$, at 77K, is a combination of type II and type III according to the classification of Brunauer, with a greater contribution of the last one, which indicates a non-porous biosorbent.[25] Additionally, it was observed that 51.7% of the S_{BET} can be attributed to external surface.

The IR spectra (Figure 1) show characteristic bands of weak and middle intensities, due to axial deformation, within the ranges of 3700-3000, 3000-2880, 1630-1400, and 1100-1000 cm^{-1}. The deformations of the OH and NH_2 axial groups were seen in the 3600-3000 cm^{-1} range. The presence of the NH_2 group is corroborated by the angular deformation in 1632 and 873 cm^{-1}. Several C–O bond stretches from the chitosan structure are confirmed by axial deformations in the 1100-1000 cm^{-1} range. In the CH axial deformation range, corresponding to 3000-2880 cm^{-1}, the chitosan spectra show characteristic bands in 2922 cm^{-1}.[26] The complete deacetylation of the chitin in the crab shells to yield chitosan was confirmed by the absence of characteristic carbonyl amide I and II bands in the range of 1600-1700 cm^{-1}.

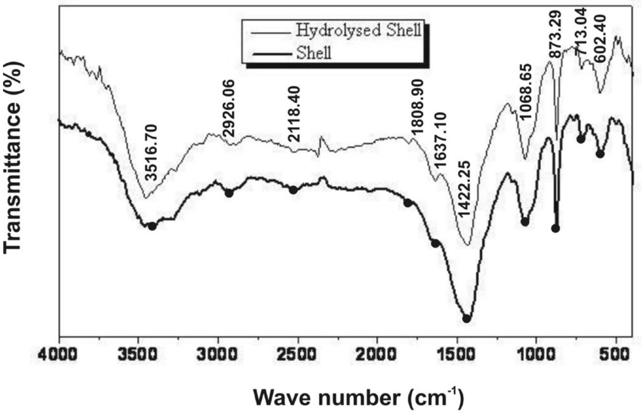

Figure 1. *IR spectra of crab shells*

Particle size effect

Figure 2 shows the results of particle size effect on removal efficiency of Fe(II) by the crab shells.

The removal efficiency is nearly four times higher in the smallest particles (0.59 mm) than the bigger ones (2.00 mm). For this reason, particles of 0.59 mm were chosen to be used in the others experiments.

pH effect

The experiments showed that whenever the value of pH was higher than 2.00, the oxidation of Fe(II) to Fe(III) followed by precipitation of $Fe(OH)_3$ took place. Then, a pH value of 2.00 was chosen for the experiments of adsorption.

Effect of biosorbent mass

Figure 3 reveals that the removal efficiency of Fe(II) increases with the increase of adsorbent mass up to 0.25 g. At adsorbent mass bigger than 0.25 g the removal remained essentially unchanged. A mass of 0.25 g was, thus, chosen for the adsorption experiments.

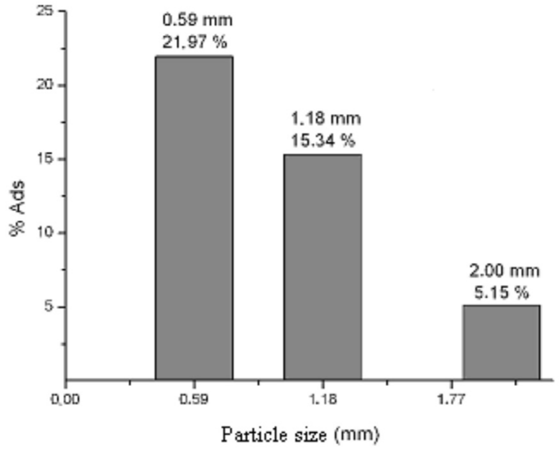

Figure 2. *Effect of the particle size of the biosorbent: Conditions: t = 2 h; pH = 2.00; C_i = 3.00 mg L^{-1}*

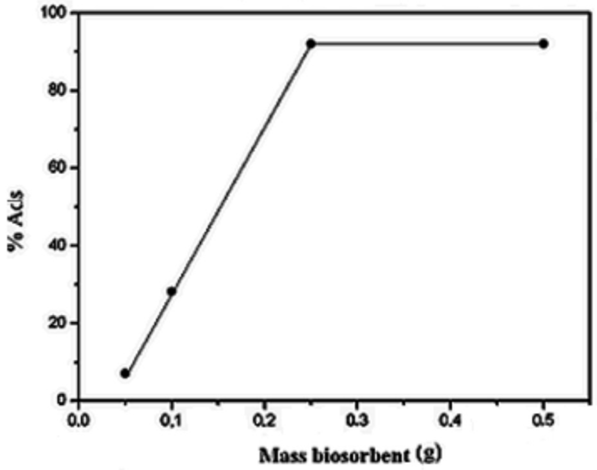

Figure 3. *Effect of the amount of the biosorbent. Conditions: t = 14 h; pH = 2.00; Ci = 3 mg L^{-1}*

Adsorption kinetics

The kinetic profile of Fe(II) adsorption onto the crab shells is shown in Figure 4.

Adsorption equilibrium is reached after 840 min (14 h) of contact between the Fe(II) solution and the biosorbent. Fe(II) removal capacity of the crab shells increases with contact time and reaches 92.0%. The initial concentration of the Fe(II) solution was chosen as 3.00 mg L^{-1} for the kinetic and equilibrium adsorption studies.[27]

The kinetic results were treated by a pseudo-first order model (Figure 5) and by a pseudo-second order one. The kinetic data are in agreement with the pseudo first-order model as correlation coefficient of this model is greater than that of the pseudo second-order one. Additionally, the Qe values (1.08 mg g^{-1}) calculated by the pseudo-first order model is in close agreement with those determined experimentally (1.10 mg g^{-1}). The Q_e values and rate constants calculated for each model are shown in Table 2.

Adsorption equilibrium

Adsorption isotherm of Fe(II) onto *Ucides cordatus* crab shell

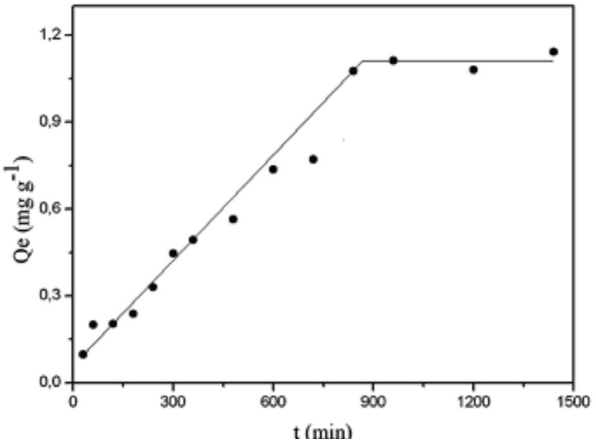

Figure 4. *Fe (II) adsorption kinetic curve*

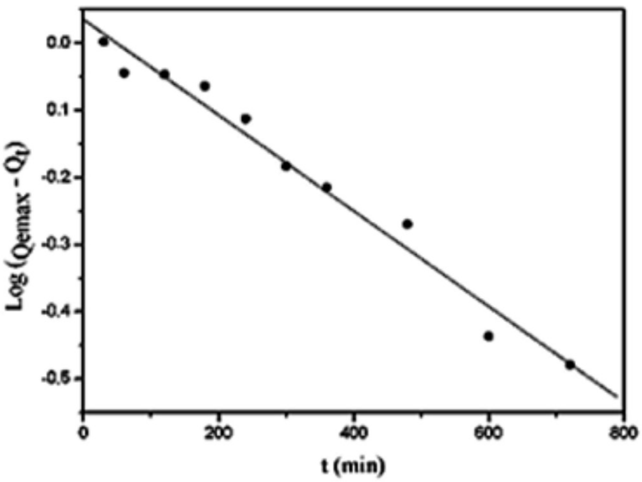

Figure 5. *Pseudo first-order kinetic model*

Table 2. Kinetics parameters and correlation coefficients ($Q_{e\,experimental} = 1.10$ mg g^{-1})

Kinectic model	k x 10^{-3}(min^{-1})	Q_e (mg g^{-1})	R^2
1st order	1.61	1.08	0.975
2nd order	5.68	0.0191	0.786

is showed in the Figure 6. The profile is of a H Type according to Giles classification, which indicates a high affinity between Fe(II) and the crab shell.[28]

The constants and correlation coefficient values for both the Langmuir and Freundlich models are shown in Table 3.

The Langmuir model (Figure 7) was more effective than the Freundlich model in describing the absorption of Fe(II) onto *Ucides cordatus* crab shell because it shows a higher correlation coefficient. This indicates that chemical adsorption between Fe(II) ion takes place on the surface of the crab shells. The calculated R_L value (0.0317) using the parameters given by the Langmuir model indicates a favorable adsorption.

CONCLUSION

The results of this work shows an excellent capacity of *Ucides cordatus* crab shell to adsorb Fe(II) on its surface, which reveals the feasibility of applying this biomaterial in needy communities to purify water of high iron content.

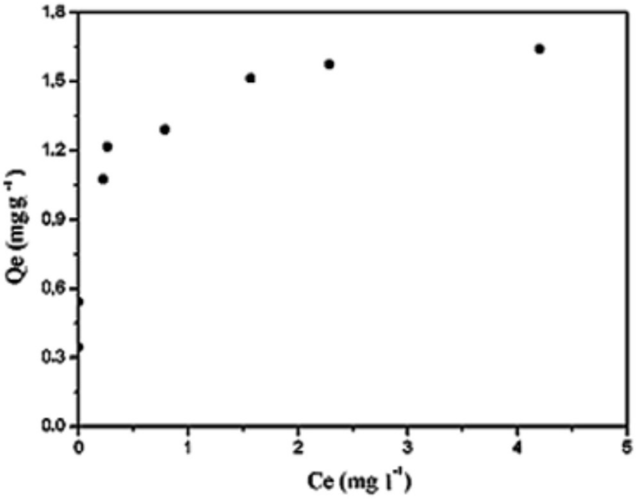

Figure 6. *Fe (II) adsorption isotherm on crab shells. Conditions: t = 14 h; pH = 2.00; M_c = 0.25 g*

Table 3. Langmuir and Freundlich constants

Langmuir constants			***Freundlich constants***		
Q_m (L mg^{-1})	K_L (L g^{-1})	R^2	K_F (mg g^{-1})	1/n	R2
6.11	1.66	0.9978	1.379	0.111	0.9697

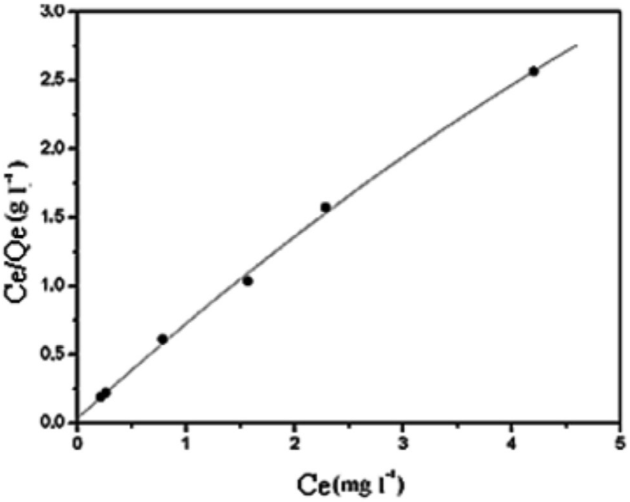

Figure 7. *Langmuir isotherm*

The best adsorption parameters of Fe(II) onto crab shell were found using 0.25 g of biosorbent mass with particle size of 0.59 mm at pH 2.00. Adsorption experiments with pH>2.00, showed that Fe(II) is oxidized to Fe(III) with concomitant formation of Fe $(OH)_3$. The adsorption kinetics follows a pseudo-first-order model with $k_1 = 1.61 \times 10^{-3}$ min^{-1}, and with theoretical and experimental Qe values close to each other. Fe(II) adsorption onto crab shell is better described by the Langmuir model than by the Freundlich model.

ACKNOWLEDGEMENTS

The authors thank CAPES and CNPq for financial support. We thank to A. G. de Souza's research group at UFPB for their collaboration in some laboratory experiments.

REFERENCES

1.. Campana-Filho, S. P.; de Britto, D.; Curti, E.; Abreu, F. R.; Cardoso, M. B.; Battisti, M. V.; Sim, P. C.; Goy, R. C.; Signini, R.; Lavall, R. L.; *Quim. Nova* **2007**, *30*, 644.
2. Benchimol, R. L.; Sutton, J. C.; Dias, F. M. B.; *Fitopatologia Brasileira* **2005**, *31*, 180.
3. Niu, H.; Volesky, B.; *Hydrometallurgy* **2006***, 84*, 28.
4. Vijayaraghavan, K.; Palanivelu, K.; Velan, M.; *Bioresour. Technol*. **2005**, *97*, 1411.
5. Kim, D. S.; *Bioresour. Technol*. **2003**, *94*, 345.
6. Pradhan, S.; Shukla, S. S.; Dorris, K. L.; *J. Hazard. Mater.*.**2005**, *B125*, 201.
7. Yaman, M.; Kaya, G.; *Anal. Chim. Acta* **2005**, *540*, 77.
8. Cambuim, K. B.; *Tese de Doutorado,* Universidade Federal da Paraíba, Brasil, 2009.
9. Ministério da Saúde (MS); *Portaria MS N° 518*, de 25/03/2004, Brasília, 2005.
10. Porpino, K. K. P.; *Dissertação de Mestrado,* Universidade Federal da Paraíba, Brasil, 2009.
11. Association of Official Analytical Chemists; *Official Methods of Analyses of the AOAC*: Washington, 1990.
12. Gratuito, M. K. B.; *Bioresour. Technol*. **2007**, *99*, 4887.
13. Japanese Industrial Standard; (JIS K 1474): *Test methods for activated carbon,* Japanese Standards Association: Tokyo, 1992.
14. Popuri, S. R.; Vijaya, Y.; Boddu, V. M.; Abburi, K.; *Bioresour. Technol*. **2009**, *100*, 194.
15. American Public Health Association (APHA); *Standard Methods for the Examination of Water and Wastewater*, 21th ed.; APHA: Washington, 2005, p. 330.
16. Kim, D. S.; *Bioresour. Technol*. **2003**, *87*, 355.
17. Dahiya, S.; Tripathi, R. M.; Hegde, A. G.; *Bioresour. Technol*. **2008**, *99*, 179.
18. Dogan, M.; Abak, H.; Alkan, M.; *Water, Air, Soil Pollut*. **2008**, *192*, 141.
19. Radhika, M.; Palanivelu, K.; *J. Hazard. Mater*. **2006**, *138*, 116.
20. Arami, M.; Limaee, N. Y.; Mahmoodi, N. M.; *Chem. Eng. J.* **2008**, *139*, 2.
21. Kalavathy, M. H.; Karthikeyan, T.; Rajgopal, S.; Miranda, L. R.; *J. Colloid Interface Sci.* **2005**, *292*, 354.
22. Cochrane, E. L.; Lu, S.; Gibb, S. W.; Villaescusa, I.; *J. Hazard. Mater*. **2006**, *B137*, 198.
23. Moreno-Castilla, C.; *Carbon* **2004**, *42*, 83.
24. Lee, S. M.; Davis, A. P.; *Water Res*. **2001**, *35*, 534.
25. Gregg, S. J.; Sing, K. S. W.; *Adsorption, Surface Area and Porosity*, Academic Press: London, 4th ed., 1982.
26. Silverstein, R. M.; Basler, G. C.; Morrill, T. C.; *Identificação espectrométrica de compostos orgânicos*, 5ª ed., Guanabara Dois S.A.: Rio de Janeiro, 1994.
27. Moreira, S. A.; Sousa, F. W.; Oliveira, S. A. G.; Nascimento, R. F.; Brito, E. S.; *Quim. Nova* **2009**, *32*, 1717.
28. Giles, C. H.; D' Silva, A. P. D.; Trivedi, A. S.; *Surface area determination*, Butterworth: London, 1970, p. 135-47.