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

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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 $M_0 = 0.25$ 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 souvenirs. 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 Ucá 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.7 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 °C 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$_4$)$_3$·6H$_2$O (Riedel-de Haën), primary standard grade.15

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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, \( Q_e \), was calculated by the expression:8,17

\[
Q_e = \frac{(C_i - C_e)V_i}{M_i \cdot 1000}
\]  

(1)

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

\[
\% Ads = \frac{(C_i - C_e) \cdot 100}{C_i}
\]  

(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; \( V_i \) is the volume of solution in mL and \( M_i \) 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

\[
\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e
\]  

(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:

\[
R_L = \frac{1}{1 + K_L Q_m}
\]  

(4)

If \( R_L \geq 1 \) 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

\[
Q_e = K_F C_e^{1/n}
\]  

(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) < 0.7 indicate favorable adsorption. The linearised Freundlich equation is:22

\[
\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e
\]  

(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:

\[
\ln (Q_e - Q_t) = \ln Q_e - k_1 t
\]  

(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:

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t
\]  

(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/(\( k_2 Q_e \)).

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>
<thead>
<tr>
<th>Measured parameter</th>
<th>Obtained results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>3.0 ± 0.6 **</td>
</tr>
<tr>
<td>Ashes (%)</td>
<td>75.7 ± 0.8 **</td>
</tr>
<tr>
<td>Ca (g/100g)</td>
<td>34 ± 1 **</td>
</tr>
<tr>
<td>P (mg/100g)</td>
<td>4.0 ± 0.3 *</td>
</tr>
<tr>
<td>Lipids (%)</td>
<td>5.5 ± 0.6 *</td>
</tr>
<tr>
<td>Protein (g/100g)</td>
<td>9.3 ± 0.6 *</td>
</tr>
<tr>
<td>d (g cm(^{-3}))</td>
<td>0.57 ± 0.06</td>
</tr>
<tr>
<td>pH</td>
<td>9.60</td>
</tr>
<tr>
<td>DMP (nm)</td>
<td>5.8</td>
</tr>
<tr>
<td>S(_{\text{nat}}) (m(^{2}) g(^{-1}))</td>
<td>18.2 ± 0.1</td>
</tr>
</tbody>
</table>

** 5 determinations; * 2 determinations

As the biosorbent is rich in minerals salts, high levels of ash content were found (75.71%), Benchimol1 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 \(\text{CaCO}_3\). 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 \(\text{N}_2\) (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 \(S_{\text{BET}}\) 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\(^{-1}\).

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.

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 \(Q_e\) 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
Fe (II) adsorption on Ucides cordatus crab shells

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

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>$k \times 10^{-3}$ (min$^{-1}$)</th>
<th>$Q_e$ (mg g$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st order</td>
<td>1.61</td>
<td>1.08</td>
<td>0.975</td>
</tr>
<tr>
<td>2nd order</td>
<td>5.68</td>
<td>0.0191</td>
<td>0.786</td>
</tr>
</tbody>
</table>

Table 3. Langmuir and Freundlich constants

<table>
<thead>
<tr>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_m$ (L mg$^{-1}$)</td>
<td>$K_L$ (L g$^{-1}$)</td>
</tr>
<tr>
<td>$R^2$</td>
<td>$K_F$ (mg g$^{-1}$)</td>
</tr>
<tr>
<td>$1/n$</td>
<td>$R_2$</td>
</tr>
<tr>
<td>6.11</td>
<td>1.66</td>
</tr>
<tr>
<td>0.9978</td>
<td>1.379</td>
</tr>
<tr>
<td>0.9978</td>
<td>0.9697</td>
</tr>
</tbody>
</table>

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

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.
REFERENCES