USO DE CASCAS DE JATOBA PARA REMOÇÃO METÁLICA

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RESUMO

Realizou-se testes do poder de adsorção da casca do jatobá (*hymenaca courbanil*) in natura frente a diversos íons. Os resultados mostraram adsorção de: 87% para o Pb^{2+}, 82% para Cu^{2+}, 75% para Fe^{3+}, 9,70% para Ni^{2+} e 9,67% para o íon Mn^{2+}. Estudou-se os efeitos do tempo de contato, pH, concentração, temperatura, quantidade e tamanho de partícula da casca na adsorção do íon de cobre. Através dos estudos das isotermas de Freundlich e de Langmuir, na faixa de temperatura de 30 a 50°C, foi possível estimar os parâmetros termodinâmicos: variação de energia livre, variação de entropia e entalpia para o equilíbrio cobre (II) - casca de jatobá.

Palavras-chave: Casca de jatobá, Adsorventes, Cobre.

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UTILIZATION OF JATOBA SHELLS AS ADSORBENT FOR METALS

ABSTRACT

Adsorption tests were carried out with Jatoba (*Hymenaea courbanil L.*) fruit shells and several ions. The results showed that 87% of Pb^{2+}, 82% of Cu^{2+}, 75% of Fe^{3+}, 9.70% of Ni^{2+} and 9.67% of Mn^{2+} were removed by the shells. The effects of contact time, pH, concentration, temperature, dose, particle size of the adsorbent have been studied through the use of the copper ion. The equilibrium nature of copper (II) adsorption at different temperature (30-50°C) has been described by the Freundlich and Langmuir isotherms. The thermodynamic parameters such as free energy, entropy and enthalpy changes for the adsorption of Cu (II) have also been computed.

Keywords: Jatoba shells; Adsorbent; Copper.

INTRODUCTION

The adsorption phenomenon has still been found economically appealing for the removal of toxic metals from wastewater. Many studies have approached the principle of adsorption as a technique for metals removal from solution. Both Organic and Inorganic adsorbents1-4 have been examined including: iron or aluminum, activated carbon, gravel or crushed brick, hydrated titanium fiber, Portland cement, cellulose xanthate, lignite and peat moss. There have also been many studies examining the metal-adsorption characteristics of products from the food industry. For example, the metal adsorption properties of peanut shells5, coconut shells6, corn residues7, olive residues8, oil-palm fibers9, onion skins10, banana skins11, tea leaves12, coffee powder13, canola meal14, oyster shells, corn cobs, pine wood, red cedar wood15 have been studied.

The biological methods for metal recovery, called biosorption, have been suggested as an effective and economic alternative for wastewater treatment. In this context, the literature reports a great number of data concerning the use of biomass for recovery of several metals including: Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn16. It have been carried out several studies examining metal removal by microbial, vegetal or mineral adsorbents. Jatoba is a huge canopy tree growing up to 40 yards in height with a trunk up to six feet in diameter that grows on ridges or slopes and high riverbanks. It is indigenous to the Amazon Rainforest and parts of tropical Central America. It produces bright green leaves, small red flowers, and an edible brown pod-like fruit of approximately six by three inches. Due to its fruit, the jatoba has limited ornamental use for shade, parks and streets. As the fruit falls and matures, it releases an offensive odor. The objective of this study was to evaluate the performance of the jatoba fruit shells for the metal recovery from solutions containing ions.

MATERIAL AND METHODS

Preparation of jatoba shells for adsorption of metals

Jatoba shells were collected were in Fortaleza, state of Ceará, Brazil. The voucher (sample specimen No. 14359) was deposited in Prisco Bezerra Herbarium of the Universidade Federal do Ceará (UFC), Brazil. The shells were ground using a ball mill and sieved in several particle sizes of 10-200 mesh with ASTM sieves. One hundred grams of ground jatoba shells were placed in a 1 dm^3 beaker and approximately 660 cm^3 of deionized water was added. The shells were mixed using a spatula for 20 min and the liquid was discarded. The wash was repeated twice for a total washing time of 1h using approximately 2 dm^3 of deionized water. Finally, the shells were heated in air oven at 100 – 105°C for 24h. After drying, the adsorbents were used as such and treated with an acid. About 20 g of adsorbent were placed in 100 mL of sulfuric acid (0.75 mol L^{-1}) and the solution was heated at 100°C for 15 min. The treated adsorbent was filtered and then was washed three times with deionized water. Finally, the adsorbent was dried at 40°C during 24 h.

Metal ion solutions

The metal ions chosen for the study were Fe(II), Pb(II), Cu(II), Ni(II) and Mn(II). All single metal ion solutions were prepared at a concentration of 0.01 mol L^{-1}. The synthetic solutions were prepared from standardized solutions of each metal (analytical grade).

Tests with adsorbent

The series of experiments were carried out by using 4.0 g of the adsorbent prepared with and without chemical pre-treatment directly to 30 mL of several metal ion solutions placed in 250 mL Erlenmeyer flasks for 48 hours. The samples were filtered and the filtrates were analyzed spectrophotometrically[17]. All analyses were carried out in triplicate.

Analytical

The metals were analyzed using a GBC 933 plus Atomic absorption spectrometer and a HITACHI U-2001 double beam UV-Visible spectrophotometer equipped with a quartz cell of 1.0 cm path length. An Orion model 420A pH meter was employed for the measurement of pH value of solutions.

Batch adsorption studies

For the detailed study of the batch adsorption of the jatoba shells, the ion copper was selected. The experiments were carried out by using 2.5 g of the Jatoba shells with 11.5 mL aqueous solution of copper(II) of desired concentrations at various pH (1-6) and at 30 – 50°C temperature range in different stopped bottles for different contact times using a temperature-controlled shaker. At the end of the predetermined time interval, the adsorbent was removed by filtration and the equilibrium concentration was estimated by the spectrophotometric method. Also, the experiments were carried out using blanks solution. The effect of pH on the adsorption phenomenon was studied by adding 0.1 mol L^{-1} $KHC_8H_4O_4$ and NaOH in Cu(II) solution. Several quantities of adsorbent were placed in contact with Cu(II) solution.

Effect of temperature on jatoba shells

The Langmuir and Freundlich models were used to quantify the adsorption capacity of jatoba shells for the removal copper (II) ion from aqueous solution. This study employed particles of 70 mesh (0.210 mm) size and Cu(II) concentration range of $5.0\text{x}10^{-3}$ – $3.0\text{x}10^{-2}$ mol L^{-1}.

Langmuir model

Langmuir proposed the following model,

$$Cc/Am = 1/K \cdot 1/b + (1/b) \cdot Cc$$

Where Cc is concentration of residual amount of adsorbate at equilibrium and Am is the amount of adsorbate adsorbed per specified amount of adsorbent (mg/g), K is the equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence, a plot of Cc/Am vs Cc should be a straight line with a slope 1/b and intercept as 1/Kb.

Freundlich model

According to this model

$$Am = K \cdot Cc1 / n$$

or

$$\ln Am = \ln K + 1/n \cdot \ln Cc$$

where K and n are Freundlich constants and are indicators of adsorption capacity and adsorption intensity. Thus a plot of ln(Am) vs ln (Cc) should be a straight line with a slope 1 / n and intercept lnK. This model deals with the multiplayer adsorption of the substance on the adsorbent. The thermodynamic parameters ΔG, ΔS, and ΔH were computed from the equations given below: the free energy change (ΔG) was calculated from the relation,

$$\Delta G = -RT \ln K$$

Similarly, the enthalpy change H between 30 to 50°C was computed based on the Van’t Hoff-Arrhenius equation, or

$$\ln K = -\frac{\Delta H}{RT} + C$$

and the entropy was calculated from the equation,

$$\Delta G = \Delta H - T\Delta S$$

RESULTS AND DISCUSSION

Removal of ions

After 48 hours of exposure, 87% of Pb(II), 82% of Cu(II) and 75% of Fe(II) was removed by the untreated jatoba shells. Removal for the Ni(II) and Mn(II) was weak, 9.70% and 9.67%, respectively. The acid treatment did not improve the capacity of metal removal by jatoba shells. This material removed 64.36% Pb(II), 53.18% Cu(II) and 43.60% of Fe(II). The removal of Ni(II) was not significantly affected by the addition of acid treated adsorbent (12.43%) and for Mn(II) presented a slight decrease in the removal capacity to 4.37%. The removal efficiencies obtained for the different metals examined in the synthetic solution followed this order: $Pb^{2+} > Cu^{2+} > Fe^{2+} > Ni^{2+} > Mn^{2+}$.

The treatment of the material with sulfuric acid should promote an increase in the concentration of the sulfates groups in surface of the jatoba shells, conducting the increase in the adsorption capacity for the positively charged metal ions. However, it was observed that this treatment did not cause significant changes in the adsorption capacity of the resin. This can be considered one advantage because the shell can be used in nature, without previous treatment.

Time of equilibrium

The dependence of adsorption of Cu(II) was studied in the range of 1 at 48 hours. The adsorption increases with increasing contact time and the equilibrium was established after 3 h (Figure 1) with 82 % of adsorption.

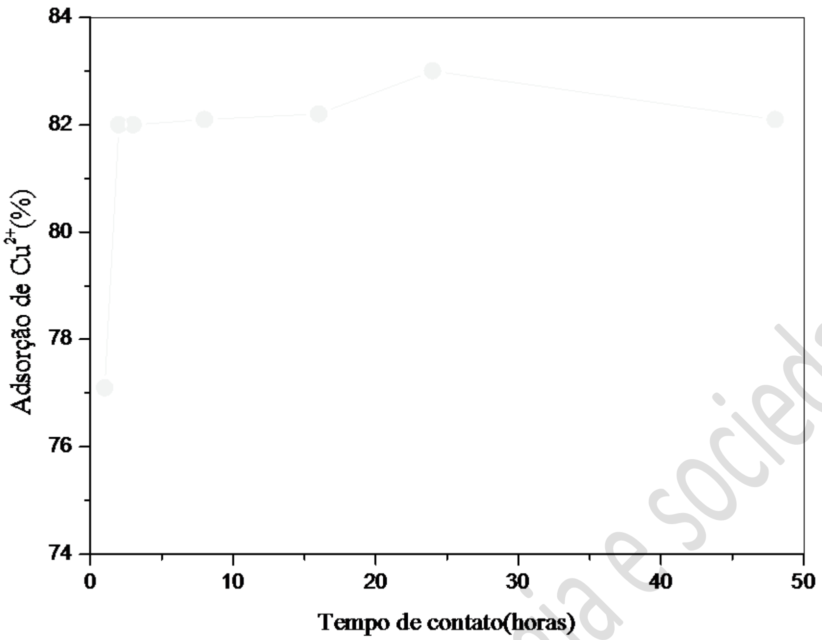

Figure 1: Plots for the adsorption of copper by jatoba *vs* time.

Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. Thus the influence of hydrogen ion concentration was studied at 1.0-6.0 pH range. It was observed the increase in the percentage of the removal capacity from 21.52 to 93.20 with the increase of the pH of the solution. The highest percentage of adsorption of copper (II) was obtained at pH 5.0. At lower pH, the higher concentration of H^+ ions in the reaction mixture compete with Cu(II) ions for the adsorption sites, resulting in the reduced uptake of Cu(II). On the other hand, as pH increases the adsorbent surface becomes more and more negatively charged and, therefore, the adsorption of positively charged Cu(II) and $Cu(OH)^+$ species are more favorable. In the absence of any adsorbent, precipitation of metal hydroxide starts only at pH 5.4.

Effect of amount on the adsorption process

The effect of jatoba shells amount on the adsorption of copper (II) is presented in Table1. The data obtained at pH 5.0 and contact time 3hours, indicates that the adsorption increases with the increase in the amount of shells. The maximum uptake is at 3.0 g of adsorbent for 12 mL of the ion Cu(II) solution.

Table 1: Effect of jatoba shells amount on the Cu(II) ion adsorption process. pH 5.0 *t* = 3h

Amount of the Adsorbent (g/12ml)	% Adsorption
0.50	37.5
1.00	58.1
1.50	70.4
2.00	81.8
2.50	93.2
3.00	100.0

Effect of particle size

The studies were also carried out by using jatoba shells of different particle sizes and they demonstrated that the removal of copper (II) was not significantly affected by the increase in particle size.

Effect of temperature on jatoba shells

The adsorption of copper on jatoba at pH 5.0 follows both Freundlich as well as Langmuir type adsorption isotherms. However, the Langmuir equation (figure 2) is better obeyed by the system than the Freundlich one as suggested by the values of regression coefficients shown in table 2.

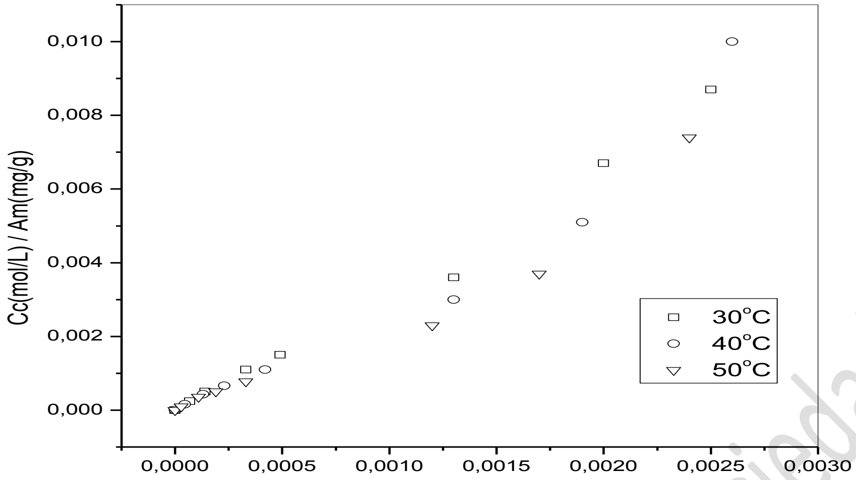

Figure 2: Langmuir plots for the adsorption of copper by jatoba fruit shells.

Table 2: The related parameters for the adsorption of Cu(II) on jatoba shells at different temperatures

Temperature (°C)	Freundlich isotherm			Langmuir isotherm		
	R (±0.02)	*K* (±0.02)	*n* (±0.02)	*R* (±0.02)	*K*	*b* (±0.02)
30	0.95	0.73	9.49	0.99	46.164	0.36
40	0.97	1.02	7.71	0.99	39.493	0.43
50	0.96	1.40	6.52	0.99	29.543	0.53

The Langmuir constants show a linear variation with temperature (figure 3) and hence they were used to calculate the thermodynamic parameters (Table 3). The overall process seems to be exothermic (ΔH = -18.08 kJ/mol), the entropy increases slightly with the temperature. Further the free energy of the process at all temperatures is negative and decreases with the increase in temperature, which indicates that the process is spontaneous in nature and the spontaneity increases with the rise in temperature. Chemical and physical adsorption[18] differs each other by the magnitude of the adsorption heat or free energy, where the chemical adsorption presents the free energy higher than 20 KJ/moL, in some cases reaching a hundred.

Table 3: Thermodynamic parameters for the adsorption of Cu (II) on jatoba shells at different temperatures

Temperature (°C)	Langmuir isotherm			
	lnK (±0.02)	Δ*G*(kJ/mol) (±0.02)	Δ*H* (30-50°C)(kJ/mol) (±0.02)	Δ*S*(kJ/K/mol)
30	10.74	-27.04	-18.08	0.0296
40	10.58	-27.53		0.0300
50	10.29	-27.63		0.0296

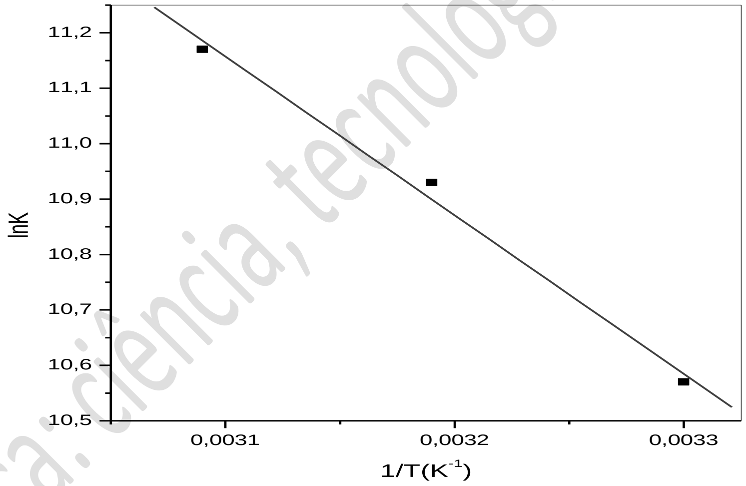

Figure 3: Plot of Langmuir constant (lnK) vs. temperature (1/T).

The values of the Langmuir constant are also very high (K>>1) at each temperature and decrease with the rise in temperature (Table 2). This higher value indicates that copper (II) ions are strongly adsorbed[19] on shells.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL, which is defined by RL

= 1/(1+bCo), where b is the Langmuir constant and Co is the initial concentration of Cu(II). According to Hameed et al[20], RL values between 0 and 1 indicate favorable adsorption. RL values found in this studied were in the 0.989 to 0.998 range.

According to Freundlich model the n value higher than 2 and lower than 10 is characteristic of a favorable process[21]. As can be observed in table 2, the n value is in 6.52-9.49 range suggesting a favorable adsorption process.

As in this work the used conditions was in acid medium, it is difficult to compare the measured adsorption capacities with data presented by others researchers which are reported mainly in neutral or basic medium. It is well-known that the adsorption capacity of metals cations is generally reduced in acidic conditions due to the competition with protons for the adsorption sites.

In comparison the amounts of each metal adsorbed by jatoba shells were significantly higher than other natural adsorbents i.e. corn cobs[15] that present percentage of adsorption of 2.29, 7.14, 8.72 and 5.92% to nickel (II), copper (II), lead (II), Manganese (II) respectively and dissolution of the iron (III) and the peanut shells[5] that present percentage of adsorption of 12.09, 66.77, 4.88% to nickel (II), copper (II) and Manganese (II), respectively. The peanut shells showed higher adsorption of the iron ions (83.15%) and lead ions (92.72%).

CONCLUSIONS

This present study thus reveals the excellent power of Jatoba shells in removal the ions lead, copper and iron from aqueous solutions. The investigations are quite useful in developing an appropriate technology for designing a waste treatment plant. The process is economically feasible and easy to carry out. In a more detailed study for copper was possible to achieve the optimum conditions for absorption of this ion.

The Langmuir isotherm and Freundlich models were used for the adsorption data. According to results for copper, the model that best fit was the Langmuir (R = 0.99) indicating that the process occurs in monolayers. The thermodynamic parameters were calculated based on this model, where was verified the spontaneity of the exothermic process.

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