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Modelagem de Equilíbrio e Cinética de Adsorção: Avaliação do Desempenho do Adsorvente no Abrandamento da Água para Irrigação e o Consumo de Animais

Resumo: O bagaço de coco, um desperdício sólido agrícola foi utilizado como biossorvente para remoção de dureza após tratamento alcalinizado. A adsorção de Ca (II) foi estudada a pH 6,8. A análise das isotermas pelo modelo não-linear mostrou que os dados experimentais foram melhor descritos pelo modelo de Temkin, com menor valor χ^2 obtido. As capacidades máximas de adsorção pelo modelo de Langmuir foi de 30,20 mg.g⁻¹. Os resultados utilizando o método não linear e linear mostraram baixa discrepância entre eles para o estudo de equilíbrio. Os resultados mostram que o adsorvente de CHA pode ser aplicado para a remoção da dureza das águas residuais.

Resumo: Adsorção; mecanismo; cinética; dureza.

Abstract

Coconut bagasse, an agricultural solid waste, was used as a biosorbent for the removal of hardness after alkali treatment. The adsorption of Ca(II) was studied at pH 6.8. The analysis of the isotherms by the nonlinear model showed that the experimental data were best described by the Temkin model, which obtained a lower χ^2 value. The maximum adsorption capacity by the Langmuir model was 30.20 mg.g⁻¹.The results using non-linear and linear methods to study equilibrium showed low discrepancy between them. The results show that the CHA adsorbent can be used for the removal of hardness from wastewater.

Keywords: Adsorption; mechanism; kinetic; hardness.

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Equilibrium and Kinetic Modelling of Adsorption: Evaluating the Performance of Adsorbent in Softening Water for Irrigation and Animal Consumption

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1. Introduction

Water hardness is a traditional measure of the capacity of water to react with soap. Hard water requires considerably more soap to produce a lather. Hard water often produces a noticeable deposit of precipitate (e.g. insoluble metals, soaps or salts) in containers, including "bathtub ring". It is not caused by a single substance but by a variety of dissolved polyvalent metallic ions, predominantly calcium and magnesium cations although other cations (e.g. aluminium, barium, iron, manganese, strontium, and zinc) also contribute. Hardness is most commonly expressed as milligrams of calcium carbonate equivalents per litre.¹ Water containing calcium carbonate at concentrations below 60 mg.L⁻¹ is generally considered as soft; 60-120 mg.L⁻¹, moderately hard; 120–180 mg.L⁻¹, hard; and more than 180 mg.L⁻¹, very hard.² Although hardness is caused by cations, it may also be discussed in terms of carbonate (temporary) non-carbonate and (permanent) hardness. Calcium and magnesium are the fifth and the eighth species in order of abundance in natural waters, respectively, with concentrations ranging from a few to hundreds of mg L⁻¹ depending on the source and the treatment to which the water has been subjected.

Hard water is not a health hazard. In fact, the National Research Council (National Academy of Sciences) states that hard drinking water generally contributes a small amount toward the total calcium and magnesium needed in the human diet. The Council further states that in some instances, where dissolved calcium and magnesium are very high, water could be a major contributor of calcium and magnesium to the diet.³

Much research has been done on the relationship between water hardness and cardiovascular disease mortality. While numerous studies suggest a correlation between hard water and lower cardiovascular disease mortality, no firm conclusions have been drawn. The National Research Council has recommended further studies be conducted. The World Health Organization (WHO) is attempting to coordinate a worldwide study on the effect on cardiovascular disease before and after changes in water supply hardness.

Among the different technologies which need the addition chemicals for water softening are chemical precipitation and ion exchange, and there are those methods which do not need added chemicals; these include reverse osmosis, electrodialysis, nanofiltration, crystallization, distillation, and evaporation.^{1,4-8} These techniques have some problems such as increased sludge, permanent water hardness, water salts like sodium, annual high operation sediment formation costs, and on membranes which requires an effluent post treatment and disposal of residual sludge.9-¹² Recently, growing demand for highquality water has justified the development of modern and low cost technologies for softening hard and very hard water.4,5,11 One of these techniques is the adsorption process, which is being used for the removal of ions, organic matter, dyes, surfactants, oil, and heavy metals from aqueous environments.13-16 Studies have shown that alkali treatment of cellulose leads to a change in structure, facilitating its solubilization. In this context, coconut (Cocos nucifera) shell, а waste lignocellulosic material, contains various polar functional groups such as carboxylic and phenolic acid groups that show affinity for metal complexation.¹⁷

In this study, three adsorption models often reported in the literature were tested to provide the best description of Ca(II) adsorption, namely Langmuir, Freundlinch, and Temkin. It should be noted that for Langmuir, Freundlich, and Temkin models, the set of isotherm parameters was calculated not only by linearization but also in nonlinear forms. For the linear models, the coefficient of determination (R²) is widely used in assessment of isotherm accuracies and is commonly determined by the least squares method. For the nonlinear forms, the various constants of these models were calculated by the error function qui-square (χ^2) using the solver add-in from Microsoft's spreadsheet, Excel (Microsoft, 2007).



2. Materials and Methods

2.1. Adsorbent

Raw coconut husk (RCH) was obtained from EMBRAPA – Agroindústria Tropical (CNPAT) (Fortaleza, CE-BRAZIL). The material was first dried in sunlight and then cut into small pieces. The coconut shells were ground and screened to prepare 59 to 150 mesh size particles. The fractions were further dried in an oven with air circulation at 60 °C for a period of 24 h.

2.2. Alkaline treatment of raw coconut husk (CHA)

The coconut shell powder was treated with NaOH (0.1 M) and heated at 70 $^{\circ}$ C for 1 h under continuous stirring. The solid material was filtered, washed several times with distilled water, and dried at 60 $^{\circ}$ C for 48 h. It was named CHA.

2.3. Ca (II) synthetic solutions

A stock solution of Ca(II) (500 mg.L⁻¹) was prepared by dissolving CaCO₃ (analytical reagent) in deionized water, and it was further diluted to the initial concentrations (40 to 500 mg.L⁻¹).

2.4 Equilibrium study

A series of batch experiments was conducted to study equilibrium. A stock solution of Ca(II) (500 mg.L⁻¹, pH=2.0, adjusted with HCl 10 mol.L⁻¹) was prepared by dissolving CaCO₃ (analytical reagent) in deionized water, and it was further diluted to the initial calcium concentrations (40 to 500 mg.L⁻¹, pH=6.8 adjusted with HCl/NaOH 0.1 mol.L⁻¹).

Batch adsorption studies were carried out by shaking 100 mL conical flasks containing 50 mg of CHA and 25 mL of Ca(II) solution (40 to 500 mg.L⁻¹) on an orbital shaker machine at 150 rpm, at ambient temperature (28 °C), and at an initial pH 6.8 (see item 2.4) for 120 min.

The supernatant solution was separated by filtration, and the metal concentrations were measured using a complexometric EDTA titration method. The effect of contact time was studied at predetermined time intervals, and residual Ca(II) concentrations were analysed. The amount of Ca (II) adsorbed (mg.g⁻¹) was calculated using (1):

$$q_e = \frac{(Co - Ce).V}{m} \tag{1}$$

where Co and Ce are the initial and final calcium ion concentrations $(mg.L^{-1})$ in solution respectively, V is the volume of solution (L), and m the mass of sorbent (g). For batch kinetic study, the same procedure was followed, and aqueous samples (100 and 500 mg.L⁻¹) were taken at pre-set time intervals. The concentration of Ca(II) was similarly measured. The Ca(II) uptake at any time, qt (mg.g⁻¹), was calculated using (2):

$$q_t = \frac{(Co - Ct).V}{m}$$
(2)

where Ct (mg.L⁻¹) is the liquid-phase concentration of Ca(II) at any time, t (min).

2.5. Zero potential charge analysis

A Zetasizer Nano ZS instrument (Malvern, GBR) was used to measure the zeta potentials of all of the samples.

3. Results and Discussion

3.1. Zeta potential

The zeta potential of a surface is the potential that is measured, when one measures the velocity of the particles in an electric field. The point where the plot passes through zero zeta potential is called the isoelectric point, which is very important from a practical consideration. The most important factor that affects zeta potential is the pH. A zeta potential value on its own without a quoted pH is a virtually meaningless number. Therefore a zeta potential versus pH curve will often be positive at low pH and lower or negative at high pH¹⁷. The plot of zeta potential versus pH is shown in Figure (1) with a point of zero zeta potential at a pH around 2.0 and 4.5 to CHA and RCH adsorbents, respectively.





Figure 1. Zeta potential of raw coconut husk (RCH) and coconut husk alkalized (CHA)

3.2. Equilibrium Study

Adsorption equilibrium is established when the quantity of the specie being adsorbed (qe) is equal to the quantity being desorbed. Then, the equilibrium concentration in solution (Ce) remains constant.

3.2.1 Langmuir Isotherm

The most widely used isotherm equation for modelling the biosorption equilibrium data is the Langmuir equation.^{20,21} The Langmuir model suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed species. This model is described by (3):

$$q_e = \frac{q_{\text{max.}K_L.C_e}}{(1+K_L.C_e)}$$
(3)

where qe (mg.g⁻¹) and Ce (mg.L⁻¹) are the amount of adsorbed per unit mass of sorbent and the metal concentration in solution at equilibrium, respectively; qmax is the maximum amount of the metal per unit mass of sorbent to form a complete monolayer bound on the surface at high Ce. The parameter k_{L} (L.mg⁻¹) is a constant related to the affinity of the binding sites. The Langmuir equation can be described in linearized form as shown in (4).

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max K_L}} \quad (4)$$

The Langmuir constants $(q_{max} and K_L)$ were determined from adsorption isotherm Figure (2a) by the linear method, and they are presented in Table 1. The values of maximum adsorption capacity can be obtained from the slope of the plot of Ce/qe versus Ce. The K_L value was found to be 2.77x10⁻² and 2.87x10⁻² L.mg⁻¹ for linear and non-linear methods, respectively. The maximum adsorption capacity to CHA adsorbent (qmax) was 30.30 mg.g⁻¹ and 30.20 mg.g⁻¹ using the linear and non-linear methods, respectively. The Figure (2b) shows that theoretical data from the Langmuir linear model has very good agreement with the experiment data. Table 1 shows adsorption capacity values for Ca (II) uptake by CHA adsorbent.

The essential feature of the Langmuir model can be expressed in terms of a dimensionless constant separation factor (RL) given by (5):

$$R_L = \frac{1}{1 + K_L \cdot C_o} \tag{5}$$

where K_{L} is the Langmuir constant (L.mg⁻¹) and Co is the initial calcium concentration (mg.L⁻¹). It has been established that for favourable adsorption, $0 < R_{L} < 1$; unfavourable adsorption, $R_{L} > 1$; linear adsorption, $R_{L} = 1$; and the adsorption process is irreversible if $R_{L} = 0$. In the Figure (3a), it is shown that the values of R_{L} lie between 0.067 and 0.47 for the initial calcium concentration range from 40 to 400 mg.L⁻¹. This indicates favourable adsorption of



Figure 2. (a) Theoretical data and experimental data for adsorption of Ca(II) onto CHA; (b)Langmuir isotherm linearized; (c) RL values for the adsorption of Ca(II) onto CHA adsorbent

calcium onto CHA adsorbent. On the other hand, it is possible write the Langmuir isotherm in dimensionless form as (6). This way it is possible, through the R_L, to study how the concentration affects the adsorption process.

$$y = \frac{x}{R_L + (1 - R_L)x} \tag{6}$$

where
$$y = \frac{q_e}{q_{max}}$$
 and $x = \frac{C_e}{C_o}$

Figure 3b shows the dimensionless Langmuir isotherm for CHA adsorbent. It shows that it has a good adsorption performance in the concentrations studied. This occurs because in the initial calcium concentration the CHA (R_L = 0.474) shows a good curve no similar to the linear isotherm case (R_L =1) which indicates good performance in low calcium concentrations. At high concentrations, CHA adsorbent (R_L = 0.067) shows a convex shape, indicating a better performance than at low concentrations.

3.2.2. The Freundlich isotherm model

The Freundlich equilibrium isotherm equation is an empirical equation used for the description of multilayer adsorption with interaction between adsorbed molecules. It is expressed as (7):

$$qe = K_F C_e^{1/n}$$
(7)

Applying the property of the logarithms to both sides of the equation, (7) is obtained in linearized form (8):

$$\ln(q_e) = \ln(k_F) + \frac{1}{n}\ln(C_e)$$
(8)

where qe is the equilibrium amount adsorbed (mg.g⁻¹), Ce the equilibrium concentration of the adsorbate (mg.L⁻¹), k_F and n are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. k_T and l/n are related to the sorption intensity which is defined by (9):





Figure 3. (a) RL values for the adsorption of Ca(II) onto CHA adsorbent (b) Adsorption performance curve at 28 °C as a function of the separation factor for adsorption of Ca (II) adsorbent in CHA where Y is according (6) and X = Ce / Co

$$\frac{1}{n} = \frac{RTq_m}{\sigma_0 - \sigma_1} \tag{9}$$

where qm is the monolayer capacity of the sorbent for the solute, σ_{o} - σ_{1} is the free energies of the surface covered with pure solvent and with a monolayer of solute, respectively. Although this model is used to describe the adsorption process, its fit to the experimental data does not necessarily imply that only a "pure" adsorption phenomenon has taken place.^{18,19}

The estimated parameters of the Freundlich model have been evaluated by both linear regression and non-linear analysis. The results are shown in Table 1. Figure (4) shows the Freundlich isotherm obtained for the Ca²⁺ (synthetic batch) adsorption on RCA by the linear method. For the CHA adsorbent, the k_F and n values were found to be 6.52 and 4.11, respectively. The numerical value of n > 1 represents a favourable adsorption. Figure (5) shows the theoretical data and experiment data.

3.2.3. The Tenkim isotherm model

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions,¹⁹ and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy. The Temkin model is given by (10) and in linearized form (11):

$$\theta = \frac{RT}{\Delta Q} ln(K_T C_e)$$
(10)

$$\theta = \frac{RT}{\Delta Q} \ln(K_T) + \frac{RT}{\Delta Q} \ln(C_e)$$
(11)

where θ is the fractional coverage (qe/<u>g</u>_m), R the universal gas constant (J.mol⁻¹ K⁻¹), T the temperature (K), $\Delta Q = (-\Delta H)$ the variation of adsorption energy (J.mol⁻¹), and k_T is the Temkin equilibrium constant (L.mg⁻¹). By the linear method, the ΔH value found was -15.77 kJ.mol⁻¹ and k_T was 0.75L.mg⁻¹. $\Delta H < 0$



indicates that Ca(II) adsorption onto CHA adsorbent is a exothermic process. Figure (6) shows that the theoretical data have a very

good agreement with the experiment data. In Table 1, the Temkin parameters are shown using linear and nonlinear methods.



Figure 4. Freundlich isotherm linearized of Ca(II) adsorbed onto CHA



Figure 5. Linear method: theoretical data and experiment data



Figure 6. Temkin linear model: theoretical data and experiment data



Table 1 shows the maximum Ca ion adsorption capacity of mercerized coconut husk (CHA) and of some adsorbents found in the literature. In Table 1, it is verified that the mercerized coconut husk presented a good capacity of adsorption for calcium ion in relation to other adsorbents found in the literature.

 Table 1. Langmuir, Freundlich, and Temkin Models. Parameters for Adsorption of Ca(II)

 (Synthetic Batch) onto CHA adsorbent

Models	qe experimental	Parameters	Linear	Non Linear
Langmuir	28.00	q _e (mg.g ⁻¹⁾	30.30	30.20
		k₁(mg.L⁻¹)	2.77x10 ⁻²	2.87X10 ⁻²
		R ²	0.995	0.992
		χ ²		2.70
Freundlich	28.00	n	4.11	4.05
		$k_{F}(mg^{1(-1/n)}L^{1/n}g^{-1})$	6.52	6.42
		R ²	0.967	0.999
		χ²		0.32
Temkin	28.00	∆H(kJ.mol¹)	-15.77	-15.82
		k⊤(L.mg⁻¹)	0.75	0.78
		R ²	0.941	0.979
		χ ²		0.021

3.3. Qui-square (χ^2): Analysis of Nonlinear Regression

The difference in the axial settings of linear equations (of individual isotherm models) will alter the result of a linear regression process, thereby influencing the determination of the model parameters. Whereas, in the nonlinear χ^2 -analysis suggested by Ho,²⁰ all isotherms are being compared on the same abscissa and ordinate, thus avoiding such errors of linearization. The equivalent mathematical statement is (11).

$$\chi^2 = \sum \frac{(q_{exp} - q_{cal})^2}{q_{cal}}$$
(11)

So, if data from the model were similar to the experimental data, χ^2 would be a small number and vice versa.

The minimum values of χ^2 found for the Temkin (χ^2 =0.021) and Freundlich (χ^2 =0.32) and Langmuir models (χ^2 =2.70) also suggests the best correlation between the model and experimental data. It is clear that all isotherm models suggest an enhanced uptake of Ca(II)

by CHA adsorbent. However, it is verified in Table 1 that the Temkin model was the one that best described the adsorption process (for the experimental conditions studied), because it presented the lowest error according to the nonlinear regression analysis (χ^2 =0.021).

3.4. Kinetic and mechanism study

The effects of contact time on biosorption of Ca(II) by CHA are shown in Figure (7). The amount of Ca(II) biosorbed increased with an increase in contact time, and equilibrium was reached after 15 min.

Figure (7) shows the effect of contact time on batch adsorption of 85 mg.L⁻¹ at 30 °C. The amount of adsorption sharply increases with time in the initial stage (0–6 min range), and then gradually increases to reach an equilibrium value in approximately 15 min. A further increase in contact time had a negligible effect on the amount of adsorption. According to these results, the agitation time was fixed at 40 min for the rest of the batch experiments to make sure



that the equilibrium was reached. The rapid adsorption of Ca(II) in the first minutes (< 2 min) can be attributed to the availability of a large number of vacant surface sites on fresh CHA. The adsorption rate gradually decreases during the adsorption process until the equilibrium is reached. The decreasing Ca(II) adsorption rate is perhaps due to the slow pore diffusion of Ca(II) ions into the bulk of CHA.



Figure 7. The variation in the amount of adsorption of Ca(II) with time for 85 mg.L⁻¹ concentration at 30 °C. Conditions: adsorbent dose, 2g.L⁻¹; speed,150 rpm; pH=6.8; temperature, 30 °C

3.4.1. Kinetic models

In order to determine the kinetic parameters of Ca(II) adsorption on the CHA, the kinetic models including the pseudo-first-order, pseudo-second-order, and Elovich equations were applied to fit the experimental data by non-linear regression. The calculated results of the fits are listed in Table 2

3.4.2. The Elovich equation

The Elovich equation assumes that the actual solid surfaces are energetically heterogeneous and that neither desorption nor interactions between the adsorbed species could substantially affect the kinetics of adsorption at low surface coverage. The crucial effect of the surface energetic heterogeneity on adsorption equilibrium in the gas/solid systems has been demonstrated,²¹ but the extension of the same to a liquid/solid system is not known.

The Elovich equation^{22,23} is generally expressed as (12):

$$\frac{dq_t}{dt} = \propto \exp(-\beta q_t) \tag{12}$$

On integration, the Elovich rate equation with boundary conditions $q=q_t$ at t=t and q=0 at t=0 becomes (13):

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \tag{13}$$

where q_t is the sorption capacity at time t (mg g⁻¹), α is the initial sorption rate (mg g⁻¹min⁻¹), and β is the desorption constant (g.mg⁻¹) during any one experiment. The initial adsorption rate (Elovich α) had values of 1071 mg (g.min)⁻¹, and the desorption coefficient (Elovich β) was 0.68 mg.L⁻¹. Figure (8) shows that theoretical data from the Elovich model had very good agreement with the experimental data. In Table 2, the Elovich parameters are shown using nonlinear methods.





Figure 8. Kinetic models for adsorption of Ca(II). Comparison of experimental and predicted kinetic models. Experimental conditions: adsorbent dose, 2 g.L⁻¹; speed, 150 rpm; pH=6.8; temperature, 30 °C

3.4.3. Pseudo-second order

The rate of the pseudo-second-order reaction is dependent on the amount of solute adsorbed on the surface of the adsorbent and the amount adsorbed at equilibrium. The pseudo-second-order model can be represented in the following form:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$$
(14)

where k_2 is the rate constant of pseudosecond-order model (g.mg⁻¹.min⁻¹). k_2 often depends on the applied operating conditions, namely, initial metal concentration, pH of solution, temperature and agitation rate. After integrating (19) for boundary conditions, qt = 0 at t = 0 and qt = qt at t = t, the following non-linear form (20) can be obtained:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$
(15)

Adsorption of Ca(II) on CHA reached equilibrium within 15 min (Fig. 6). In Table 3, it is shown that the rate coefficient decreased with increasing initial metal ion concentration. The order rate coefficient, k₂, for Ca(II) was 9.65x10⁻². The constants k₂ and ge determined from the model are shown in Table 2 along with the corresponding correlation coefficients and error function χ^2 . Figure (8) shows that theoretical data from the pseudo second order model had a very good agreement with the experimental data. The pseudo second order parameters using nonlinear methods are shown in Table 2.

The half-adsorption time $t_{1/2}$ is another parameter which can be calculated from the

Table 2. Comparison of the first and second-order equations and the Elovich equation

 rate constants and the calculated and experimental qe values

Kinetics parameters									
Models Pseudo second ordem	qe (mg.g ⁻¹)	qe (experimental)	k₂ g.(mg.min)⁻¹	R ²	χ²				
85(mg.L ⁻¹)	14.37	14.5	9.65X10 ⁻²	0.999	0.37				
Elovich equation 85 (mg.L-1)	lpha mg.(g.min) ⁻¹	β (mg.g ⁻¹)		R ²	χ²				
	1041	0.68		0.999	0.33				



equilibrium concentration and the diffusion coefficient rate values. This was calculated by using the following equation (16).²⁴

$$t_{1/2} = \frac{1}{k_2 q e}$$
(16)

The values of $t_{1/2}$ determined for the tested parameters are given in Table 3. For the calculation of the *r* value, it was assumed that the solid phase consists of particles which are spherical in nature. Calculated values of $t_{1/2}$ and D are given in Table 3.

The experimental data for the adsorption of the calcium ion onto CHA treated with the above kinetic models were used to evaluate the controlling mechanism of adsorption processes. The diffusion coefficient for the intra-particle transport of the Ca(II) was also calculated by using the following relationship (17):

$$D = \frac{0.03r^2}{t_{1/2}} \tag{17}$$

where r is the radius of the adsorbent particle in centimetres and D is the diffusion coefficient value in cm².min⁻¹.

The higher correlation coefficient (R^2) values and low χ^2 values confirmed that the adsorption data were well represented by pseudo second order kinetics for the entire adsorption period (Table 2).

3.4.4 Mechanism study

The adsorption mechanism for the removal of Ca(II) may be assumed to involve the following three steps: (a) diffusion of the Ca(II) through the boundary layer; (b) intraparticle diffusion, and (c) adsorption of the Ca(II) on the sorbent surface.

Most of the adsorption processes may be described by either the external mass transfer (boundary layer diffusion) or intraparticle diffusion model. The Weber–Morris model is given by (18):

$$qt = k_d t^{1/2} + C$$
 (18)

where q_t is the amount of adsorbed metal ions on the biomass at time t (mg.g⁻¹); t is the time (min); and k_d is the diffusion coefficient in the solid (mg.g⁻¹.min^{-1/2}). The values of C provide information about the thickness of the boundary layer. In general, the larger the intercept, the greater is the boundary layer effect²⁵. If intraparticle diffusion is controlling, then qt versus t^{1/2} will be linear, and if the plot passes through the origin, then the rate limiting process is only due to intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion must also be involved. Pore-diffusion plots often show several linear segments. It has been proposed that these linear segments represent porediffusion in pores of progressively smaller sizes²⁶. Eventually, equilibrium is reached and adsorption (ge) stops changing with time, and a final horizontal line is established at ge. When points in a group are identified as belonging to a linear segment, linear regression can then be applied to these points, and the corresponding k_{id} is estimated.

In the equation (18), k_d (mg.g⁻¹.min^{-1/2}) is defined as the intraparticle diffusion rate constant and is related to the intraparticle diffusivity in the following way (19).

$$k_d = \frac{6q_e}{r} \sqrt{\frac{D}{\pi}}$$
(19)

Where r (cm) is the particle radius, D (cm².min⁻¹) is diffusion coefficient, and qe (mg.g⁻¹) is the solid phase concentration at equilibrium²⁵.

Figure (9) is a plot of qt versus t $^{1/2}$ that confirms the validity of the linear relationship. The results (summarized in Table 3) can be represented by such a linear relationship, but they do not pass through the origin. This indicates that intraparticle diffusion is involved in the sorption process, but it is not the only rate-limiting mechanism and that some other mechanisms are involved. Applying Weber's model in the step (I) (shown in the figure 9) the values of $k_{id}(I)$, C(I), D, and R^2 obtained for the plots were 1.75 mg g⁻¹min^{-1/2}, 8.0 mg g⁻¹, 3.7x10⁻⁸ (cm².min⁻¹), and 0.818, respectively. The break point in the Figure (9) is at 15 min.





Figure 9. Intraparticle diffusion (from equation 18) plots for the Ca(II) adsorption on CHA for initial concentration 85 mg.L⁻¹ and adsorbent dose = 2 g.L^{-1})



Figure 10. Webber-Morris model and experimental data for the adsorption of Ca(II) onto CHA. Experimental conditions: Ca(II) = 85 mg L⁻¹ and adsorbent dose = 2 g L⁻¹)

The first step (I) linear can to be attributed to the intraparticle diffusion states that are highly involved in the rate control of this mechanism. The second step (II) is attributed to the equilibrium stage. It is worth noting the fact that the first linear (step I) plots did not pass by the origin which indicates that intraparticle diffusion is involved in the adsorption process, but it is not the only rate controlling step. In step I the large deviation from the origin shows that the boundary layer diffusion affects the adsorption to some extent (Fig. 9).

Webber - Morris model									
C0 (mg,L ⁻¹)	Kd (mg.g.min ^{-1/2})	С	R ²	D (cm ² . min ⁻¹)					
85	1.75	8.0	0.818	4.60x10 ⁻⁶					
Diffusion coefficient and t _{1/2} from Pseudo second order model									
C0 (mg.L ⁻¹	k₂.qe	t _{1/2} (min)	D(cm ² .min ⁻¹)						
85	1.39	0.71	3.42x10 ⁻⁶						

Table 3. Diffussion coefficient values for different Ca(II) concentrations calculated from (17) and (19) considering r= 0.009 cm. $t_{1/2}$ was calculated from (17) considering r= 0.009 cm



4. Conclusion

The adsorption equilibrium, kinetics, and mechanism have been studied for using a CHA adsorbent to remove hardness. Alkaline treatment was used to modify the surface of coconut bagasse. The removal of as hardness as Ca(II) from aqueous solution by modified CHA adsorbent was found to be effective. The adsorption kinetics indicated that the adsorption equilibrium was reached within 15 min under the conditions studied, and that intraparticle diffusion was not the only rate controlling step in the adsorption mechanism. The Elovich equation showed that the adsorption process involved chemisorption. The analysis of the isotherms by the nonlinear model showed that the experimental data were best described by the Temkin model with lower (χ^2 =.021) value was obtained. The maximum adsorption capacity by the Langmuir model was 30.20 mg.g⁻¹. The results using nonlinear and linear methods to study equilibrium showed low discrepancy between them. The results show that the CHA adsorbent can be applied for the removal of hardness from wastewater.

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