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HIGH PERFORMANCE MALEATED LIGNOCELLULOSE EPICARP FIBERS FOR COPPER ION REMOVAL

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Abstract - Natural lignocellulosic fiber epicarp extracted from the babassu coconut (*Orbignya speciosa*) was chemically modified through reaction with molten maleic anhydride without solvent, with incorporation of 189.34 mg g⁻¹ of carboxylic acid groups into the biopolymer structure. The success of this reaction was also confirmed by the presence of carboxylic acid bands at 1741 and 1164 cm⁻¹ in the infrared spectrum. Identically, the same group is observed through ¹³C NMR CP/MAS in the solid state, via high field signals in the 167 pm region. Both the precursor and the immobilized maleated biopolymers presented nearly the same thermal stability and similar crystallinity to cellulose. However, the pendant carboxylic groups have the ability to remove copper with maximum sorption through a batchwise process at pH 6.0, as expected from the point of zero charge, determined to be 6.45. The sorption kinetic data were fitted to pseudo-first order, pseudo-second order, Elovich-chemisorption and intra-particle diffusion models and the equilibrium data were fitted to the Langmuir, the Freundlich and Tenkim isotherm models. Taking into account a statistical error function and determination coefficients, the data were fit to the pseudo-first and pseudo-second order kinetic and Langmuir isotherm models, with a maximum sorption capacity of copper ions of 55.09 mg g⁻¹. This value suggests the application of this biopolymer with incorporated carboxylate groups as a favorable agent for copper removal from appropriate systems.

Keywords: Babassu; Coconut epicarp; Maleic anhydride; Sorption; Copper; Kinetics.

INTRODUCTION

Natural materials derived from agricultural residues consist of a rich source, with the advantage of reuse and recycling, minimizing the environmental problems associated with their build-up, and also reducing the use of other noble starting materials. This trend has contributed to the reconsideration of the use of traditional biomaterials, such as natural fibers, to substitute synthetic polymers (Liu *et al.*, 2007a, 2007b).

Brazil has a high potential for lignocellulosic fiber production. For example, the babassu palm (*Orbignya speciosa*) is a very abundant palm in the north-central region of the country. This tree grows to large size, up to 20 m, with a cylindrical trunk with a crown containing a number of fruits of ellipsoidal form. Each fruit is constituted by epicarp, mesocarp, endocarp and almond with 11, 23, 59 and 7% in mass, respectively (Teixeira, 2008; Vieira *et al.*, 2011). Babassu epicarp is an agricultural lignocellulosic by-product, a fibrous residue left after crushing and

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extracting the fruits. The most common use for epicarp is coal production due to its hardness. Recent research has explored other applications, such as pollutant removal or use as an immobilization support for functional groups in order to improve its potential as a sorbent (Vieira *et al.*, 2011, Santana *et al.*, 2010).

Chemical modification of lignocellulosic fiber is a valuable method to improve derivative products and, is based on reactions of the free hydroxyl groups in the anhydroglucose units (Liu *et al.*, 2007a; Jiang *et al.*, 2009; Šaëiban *et al.*, 2008). Among the many methods of chemical modification of these materials, one of the most effective processes is esterification with dicarboxylic acid anhydrides (Liu *et al.*, 2007a, 2007b, Jiang *et al.*, 2009), with the focus related on agricultural residues (Liu *et al.*, 2007a, 2007b; Santana *et al.*, 2010; Jiang *et al.*, 2009; Šaëiban *et al.*, 2008; Doczekalska *et al.*, 2007; Tchiama *et al.*, 2007; Karnitz Jr. *et al.*, 2007; Gellerstedt *et al.*, 1999). Esterification processes are normally conducted in organic solvents, such as xylene, N,N-dimethylformamide or pyridine (Doczekalska *et al.*, 2007; Tchiama *et al.*, 2007, Karnitz Jr. *et al.*, 2007; Gellerstedt *et al.*, 1999), whose use can cause environmental disturbances. Nevertheless, the major problems associated with solvents are the toxic vapors in the atmosphere and the production of other volatile molecules, as well as other combustion products such as carbon dioxide, which is the main substance responsible for the greenhouse effect, causing enormous impact on the environment (Melo *et al.*, 2009).

Taking into account the facility of having abundant natural fibers and also the undesirable use of solvents, the present investigation deals with chemical modification of the babassu coconut epicarp, without using organic solvents in the synthetic procedure, by successfully exploring the low melting point of maleic anhydride (Melo *et al.*, 2009). Structural chemical modifications of such biopolymers consist of incorporating esters and carboxylic acids as pendant chains covalently bonded to the main polymeric framework. The applicability of these new synthesized materials is related to the ability of the available attached basic centers in the pendant chains to sorb copper from aqueous solution.

EXPERIMENTAL

Materials

The epicarp component was extracted from raw babassu fruit, acquired in the city of São Luís, Maranhão state, Brazil, and was used after crushing

the raw material into particle sizes in the 0.088–0.177 mm range. Hydrated divalent copper nitrate (Carlo Erba, 99.5%) was used to prepare all solutions. Maleic anhydride (MA) (Aldrich, 99%) and N,N-dimethylacetamide (DMA) (Synth, 99%) were used without prior purification.

Synthesis of Babassu Coconut Epicarp Modified with Maleic Anhydride

The general synthetic route for the chemical modification of the natural biopolymer is shown in Figure 1. A sample of babassu coconut epicarp (BE) was added to the molten anhydride, to maintain an epicarp/maleic anhydride ratio of 1:10, in a reaction flask immersed in an oil bath at 388 K, under magnetic stirring for 30 min. Then the mixture was separated by filtration while hot, washed in sequence with DMA, acetone and distilled water to remove unreacted anhydride and dried for 12 h at 353 K. Before the sorption experiments, the new synthesized material (BEM) was proton/sodium exchanged by treatment with saturated sodium bicarbonate solution (Doczekalska *et al.*, 2007).

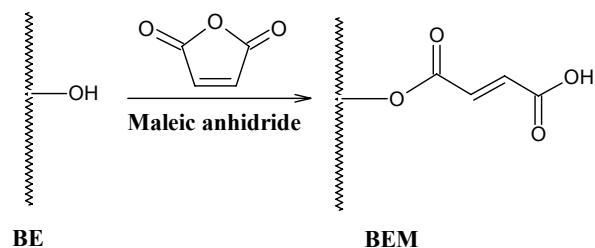


Figure 1: A general scheme for synthesis of the immobilized maleic anhydride on epicarp.

Degree of Substitution

The degrees of substitution of the chemically modified biopolymers were determined by measuring the amount of carboxylic functions attached on the surface through retro-titration. For this purpose, 0.1000 g of each material was mixed with 100.0 cm³ of 400.0 mg dm⁻³ sodium hydroxide solution for 1 h under constant magnetic stirring. The solid was separated by filtration and three aliquots of 20.0 cm³ of each solution were titrated with 365.0 mg dm⁻³ hydrochloric acid solution. The amount of the carboxylic function attached was calculated (Vieira *et al.*, 2011) by Equation (1).

$$Q_{COOH} = \frac{[(C_{NaOH} \times V_{NaOH}) - (5 \times C_{HCl} \times V_{HCl})]}{m} \quad (1)$$

where C_{NaOH} and C_{HCl} are the hydroxide and acid (mg dm^{-3}) concentrations, V_{NaOH} and V_{HCl} are the volumes of hydroxide and hydrochloric acid (cm^3) used in the titration and m is the mass (g) of the final chemically modified material used.

Instrumentation

Infrared spectra were obtained in the 4000 to 400 cm^{-1} range on a MB-Bomen FTIR spectrophotometer using KBr pellets with a resolution of 4 cm^{-1} by accumulating 32 scans. ^{13}C NMR spectra for samples in the solid state were obtained on a Bruker AC 400/P spectrometer at room temperature, at frequencies of 75.47 MHz with a magic angle spinning of 10 kHz. To increase the signal/noise ratio, the CP/MAS technique was used, with pulse repetition of 5 s and a contact time of 1 ms. X-ray diffraction patterns were obtained on a Shimadzu model XRD 7000 diffractometer with 40 kV applied voltage, current of 30 mA and Cu-K α ($\alpha = 154.1$ pm) radiation source scanned from 5 to 45°. Thermogravimetric curves in an argon atmosphere were obtained on a TA instrument, coupled to a model 1090 B thermobalance, using a heating rate of 0.167 K s^{-1} , under a flow of 30 $\text{cm}^3 \text{s}^{-1}$, varying from room temperature to 773 K, with an initial mass of approximately 10 mg of solid sample.

Point of Zero Charge

The points of zero charge for BE and BEM biopolymers were determined by the solid addition method (Srivatava *et al.*, 2005). 20 cm^3 of solutions with pH varying from 1 to 12 were transferred to erlenmeyers and the pH_i values of each solution were adjusted by adding either 0.10 mol dm^{-3} hydrochloric acid or sodium hydroxide. The pH_i of the solutions was then accurately noted and 0.10 g of BE or BEM material was individually added to each flask, which was capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 24 h, after which the pH_f value of the supernatant of each flask was noted. The difference between the initial and final pH values ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) was plotted against the pH_i and the point of intersection of the resulting curve at which $\Delta\text{pH} = 0$ gave the pH_{PZC} value.

Sorption

Effect of pH

The effect of pH on the sorption was performed by an using identical series of flasks containing

100.0 mg of biomaterial with 100.0 cm^3 of the 200.0 mg dm^{-3} solution of copper ions, maintaining stirring for 24 h. The pH in the range from 1.0 to 6.0, was adjusted when necessary with 0.10 mol dm^{-3} hydrochloric acid or sodium hydroxide solutions. The content of free copper ion in the supernatant was determined through complexometric titration with standardized EDTA solutions (Flaschka, 1959). The amount of copper ions sorbed by the BEM in all experiments was given by the Equation (2).

$$q_e = \frac{(C_i - C_e)}{m} \times V \quad (2)$$

where q_e is the amount of copper ion sorbed by BEM (mg g^{-1}), C_i and C_e are the initial and final copper concentrations in the aqueous phase (mg dm^{-3}), respectively, m is the mass of BEM (g) and V is the volume of metal ion solution (dm^3).

Sorption Kinetics

For kinetic experiments, an aliquot of 100.0 cm^3 of 200.0 mg dm^{-3} copper solution was added to a series of flasks containing 0.1000 g of BEM. The flasks were capped and the system was stirred for variable times. For all experiments the aqueous solution pH was adjusted at 6.0, using hydrochloric acid/sodium hydroxide solutions. After filtration, the cation was determined as previously described. To investigate the possible mechanism of sorption, several kinetic models were used: the Lagergren, also known as pseudo-first order (Ho and McKay, 2000), pseudo-second order kinetics (Ho and MacKay, 1999), Elovich-chemisorption (Perez-Marin *et al.*, 2007) and intra-particle diffusion (Weber and Morris, 1962), represented by the non-linear Equations (3) to (6), respectively:

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + q_e k_2 t} \quad (4)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

$$q_t = k_{id} \sqrt{t} \quad (6)$$

where q_e and q_t are the amounts of copper ion sorbed on BEM (mg g^{-1}) at equilibrium and at time t (min), and k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are pseudo-first

order and pseudo-second order rate constants, respectively; α ($\text{mg g}^{-1} \text{min}^{-1}$) and β (g mg^{-1}) are constants of the Elovich model and k_{id} ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the intra-particle diffusion rate constant.

Sorption Isotherms

The isotherms were obtained using a batchwise method, which consisted of suspending 0.1000 g of BEM in 100.0 cm^3 of aqueous copper ion solutions having different concentrations, varying from 100.0 to 500.0 mg dm^{-3} . The suspensions were shaken for 30 min and the experiments were performed at 298 ± 1 K and at pH 6.0. The solid was separated by filtration at the end of this process and the amount of metal sorbed was determined as previously described. The isotherms of the Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906) and Temkin (Temkin and Pyzhev, 1940) models in their non-linear forms, Equations (7) to (9) respectively, were applied to the equilibrium data for sorption of copper ion on BEM.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

$$q_e = K_F C_e^{1/n_F} \quad (8)$$

$$q_e = \ln(K_T C_e)^{n_T} \quad (9)$$

where q_e (mg g^{-1}) is the amount of copper sorbed per unit mass of sorbent, Q_m is the maximum Langmuir sorption capacity (mg g^{-1}), K_L ($\text{dm}^3 \text{mg}^{-1}$), K_F [$\text{mg g}^{-1} (\text{dm}^3 \text{mg}^{-1})^{1/n}$], n_F , K_T ($\text{dm}^3 \text{g}^{-1}$) and n_T (J mol^{-1}) are the Langmuir, Freundlich and Temkin constants, respectively.

The Langmuir isotherm assumes monolayer sorption onto a surface containing a finite number of sorption sites with uniform strategies of sorption and no transmigration of sorbate on the plane of the surface (Langmuir, 1916). The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor or equilibrium parameter, R_L (Weber and Chakkravorti, 1974), as:

$$R_L = \frac{1}{1 + K_L C_i} \quad (10)$$

where C_i is the initial concentration of copper ion (mg dm^{-3}).

The Freundlich model is an empirical equation based on sorption on heterogeneous surfaces or

surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation (Freundlich, 1906).

The Temkin isotherm (Temkin, 1940) contains a factor that explicitly takes into account sorbent–sorbate interactions. The heat of sorption of all the molecules in the layer is assumed to decrease linearly with coverage due to sorbent–sorbate interactions. The sorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

Statistical Evaluation of the Kinetic and Isotherm Parameters

The experimental values were adjusted to the non linear equations by using the Origin® scientific plotting software in order to determine the kinetic and isotherm parameters. The curves show the superposition of experimental results (points) and the calculated values (lines). Determination coefficients (R^2) indicated the fit between experimental data and the non-linearized forms of the isotherm and kinetic equations, while the chi square test (χ^2), indicated the fit between the experimental and predicted values for sorption capacity after plotting the isotherm curves (Vagheti *et al.*, 2009).

RESULTS AND DISCUSSION

Characterization of the Sorbent

The amount of carboxylic groups incorporated on the epicarp surface by reaction with maleic anhydride was determined to be 189.34 mg g^{-1} , while the amount of carboxylic groups in fresh unreacted epicarp was 52.29 mg g^{-1} . Thus, a considerable increase in carboxylic groups was detected when comparing the modified product to the unmodified precursor, which confirmed the success of the proposed chemical modification.

The FTIR absorption spectra of unmodified epicarp BE and maleated epicarp BEM are shown in Figure 2. A broad band in the 3200 to 3600 cm^{-1} range corresponds to O–H stretching vibrations and the band at 2934 cm^{-1} arises from C–H stretchings. The small absorbances at 1607, 1511, 1427, and 1323 cm^{-1} correspond to aromatic skeletal vibrations, ring breathing with C–O stretching in lignin components (Sun *et al.*, 2003). The bands at 1369 and 1253 cm^{-1} are attributed to C–H and C–O stretching vibrations

of the acetyl group in hemicelluloses, respectively. The strong band at 1047 cm^{-1} is assigned to C–O stretching in cellulose, hemicelluloses and lignin or C–O–C stretching in cellulose and hemicelluloses. The small sharp bands at 860 , 769 and 710 cm^{-1} are related to vibrations of esters and monosubstituted aromatic rings due to the lignin fraction in the material (Vieira *et al.*, 2011). The carbonyl stretching vibrations of ester and carboxyl groups in hemicelluloses are attributed to the small band at 1741 cm^{-1} . The spectrum of maleated epicarp BEM shown in Figure 2b shows the success of the reaction due to the presence of important ester bands at 1741 and 1164 cm^{-1} . The band at 1741 cm^{-1} is indicative of carboxyl and ester carbonyl bond vibrations and the band at 1164 cm^{-1} is characterized by the C–O stretching in the esters. A relative decrease in the intensity of the band at 3427 cm^{-1} , as shown in Figure 2b, is a clear indication of the occurrence of the esterification (Liu *et al.*, 2007b). As expected, the absence of absorption in the 1850 – 1750 cm^{-1} region in the spectrum, as shown in Figure 2b, indicated that the product is free of unreacted maleic anhydride (Talinli *et al.*, 1997).

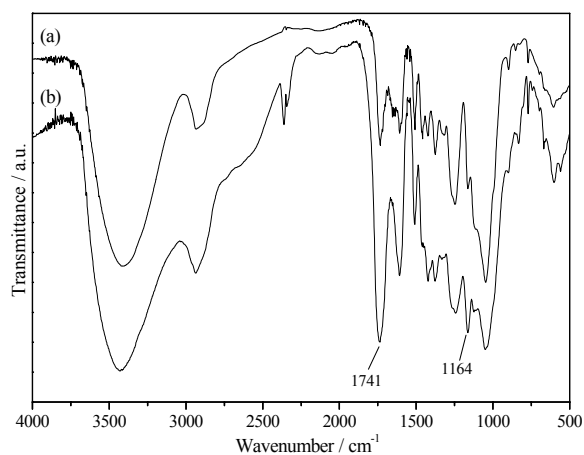


Figure 2: Infrared spectra of the babassu coconut epicarp BE (a) and the chemically modified form BEM (b).

The ^{13}C CPMAS NMR spectra for natural (BE) and chemically modified (BEM) epicarp are shown in Figure 3. The signal for carbon 1 in the polysaccharide at 104 ppm was attributed by considering that it is bonded to two electronegative oxygen atoms. The peak at 83 ppm was attributed to carbon C4 in the cellulose skeleton and carbons C2, C3 and C5 were assigned to the signals in the 71 to 75 ppm interval. The peaks between 64 and 62 ppm were assigned to carbon C6 in crystalline and amorphous regions,

respectively. The spectra also showed a signal at 22 ppm related to methyl groups belonging to lignin, while the signals at 116 to 120 , 133 and 149 to 153 ppm are attributed to aromatic carbons, which are also present in the same component. The broad signals at 160 and 178 ppm corresponded to aldehydes, ketones and esters, originating from the complex structure of the lignin (Vieira *et al.*, 2011; Santana *et al.*, 2010). The carbonyl group at 167 ppm in the spectrum in Figure 3b is assigned to C7 and C10 and reveals the occurrence of epicarp maleation. The intensity of the signals in the lignin region strengthened and the peaks at 136 and 126 ppm , assigned to the C8 and C9 carbons, also confirm the reaction of the lignin with maleic anhydride (Liu *et al.*, 2007b; Melo *et al.*, 2009).

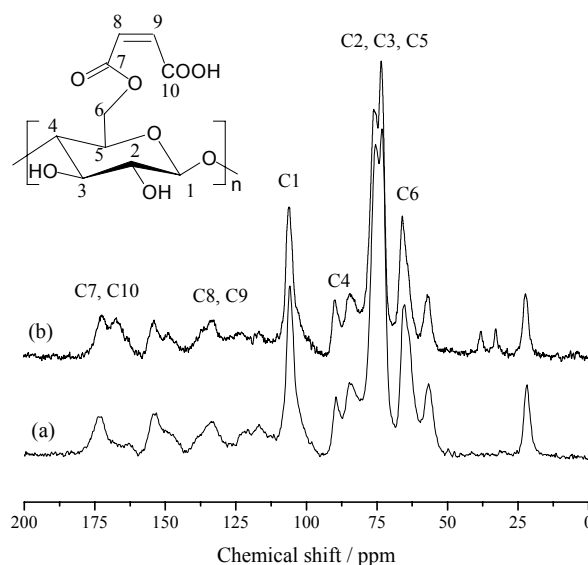


Figure 3: ^{13}C NMR of the babassu coconut epicarp BE (a) and the chemically modified form BEM (b).

X-ray diffraction patterns for the original and chemically modified epicarp are very similar to cellulose (Vieira *et al.*, 2011), as shown in Figure 4. The diffractograms obtained from the new materials containing the cellulosic structure are dominated by the original and not by any novel crystalline changes in the modified biopolymer. Thus, in this synthetic procedure, the chemical modification is expected to occur first on the more available hydroxyl groups in the para-crystalline region, located on the original polymeric surface. Thus, the diffraction patterns do not change in the chemically modified material (Melo *et al.*, 2009), with the maintenance of the same patterns for natural and anhydride-incorporated moieties.

The thermal behavior of the BE and BEM forms are shown in Figure 5 with identical thermal stabilities. BE and BEM components showed mass losses of 11% from 298 to 375 K and 12% from 298 to 500 K, respectively. This first step of decomposition can be attributed to the release of low mass carbon-rich molecules and sorbed water. The second stage of decomposition between 521 and 675 K corresponds to mass losses of 56% due to the decomposition of organic material resulting in the expected breakdown of fibers to give the final residue (Vieira *et al.*, 2011; Santana *et al.*, 2010).

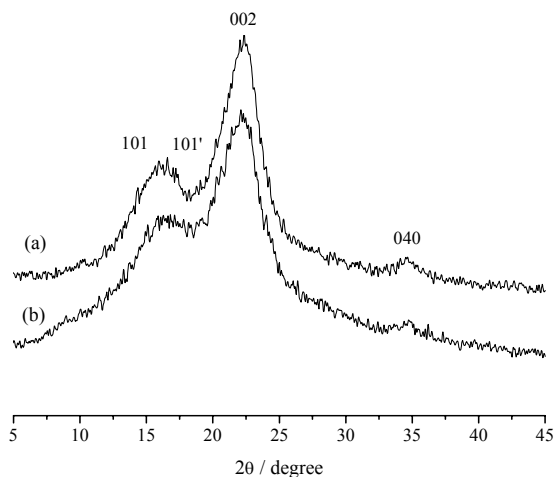


Figure 4: X-ray diffraction patterns for babassu coconut epicarp BE (a) and the chemically modified form BEM (b).

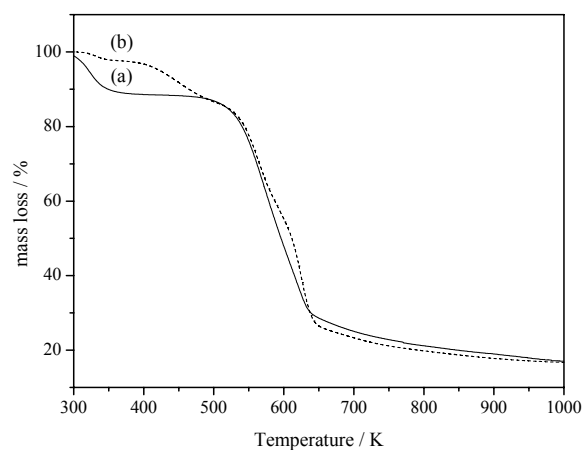


Figure 5: Thermogravimetric curves of the babassu coconut epicarp BE (a) and the chemically modified form BEM (b).

Effects of pH

The effect of pH on the sorption efficiency of copper ion on BEM and the pH_{PZC} of the material is

shown in Figure 6. The increase of carboxylic groups in the chemically modified biopolymer caused a decrease in the pH_{PZC} value from 6.95 to 6.45. This indicates that the attraction of positive charge by BEM must be favorable at $pH > 6.45$ because of the negative charge on the sorbent surface (Vieira *et al.*, 2009). Under acidic conditions, the sorbent can be protonated and the amount of cations sorbed decreases. On the other hand, an increase in pH deprotonates the carboxylate groups, a condition that favors the chelating abilities and, consequently, the amount of sorbed copper ion is increased.

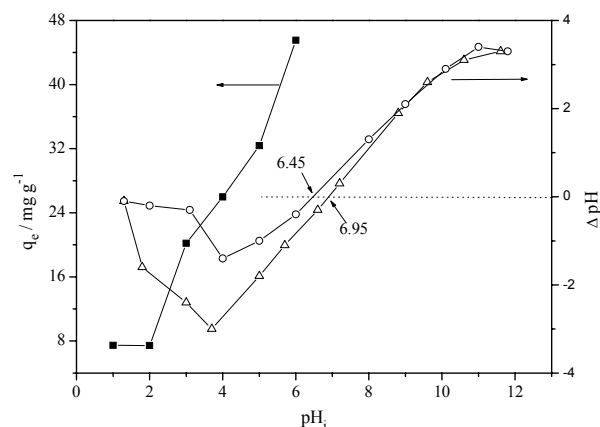


Figure 6: Effect of pH on copper ion sorption in aqueous solution by BEM (■) and the pH_{PZC} of BEM (○) and BE (Δ).

The sorption of cations increases with the increase in pH and reaches a maximum value at pH 6. Experiments were not performed above this value since the formation of copper hydroxide is expected (Vieira *et al.*, 2010). Therefore, pH 6.0 was chosen as the optimum for the subsequent sorption experiments.

Sorption Kinetics

An sorption kinetics study is important in the treatment of aqueous effluents as it provides valuable information on the reaction pathways and sorption mechanism (Lima *et al.*, 2008). The equilibrium behavior of the sorption process and the fit to kinetic models are shown in Figure 7. Equilibrium involving BEM and copper ions is observed after 30 min of contact.

According to the parameters obtained by nonlinear regression presented in Table 1, the kinetic data show good fits to all experimental models. However, the values of the determination coefficients (R^2) for the pseudo-first and second-order model are larger than for the Elovich model and still have low values

of χ^2 . Additionally, it was verified that the q_e values found for the pseudo-second and pseudo-first order were closer to the experimental q_e values, when compared with the other kinetic models. These results indicate that both pseudo-first and second-order models could explain the sorption process of copper ion by the BEM sorbent. These kinetic equations have been successfully employed to explain several kinetic processes of different sorbents (Santana *et al.*, 2010; Vieira *et al.*, 2010; Demirbasa *et al.*, 2009).

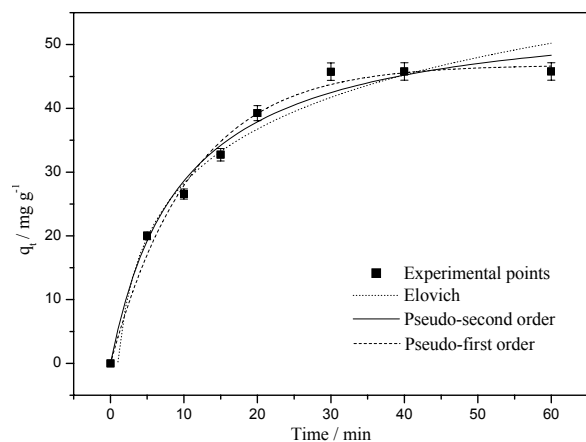


Figure 7: Non-linear kinetic models for copper ion sorption from aqueous solution by BEM.

Table 1: Kinetic data for copper ion sorption, using BEM as sorbent at 298 ± 1 K.

Pseudo-first order	Constant
k_1 / min^{-1}	0.090
$q_e / \text{mg g}^{-1}$	46.820
R^2	0.989
$F_{\text{error}} / \%$	3.250
Pseudo-second order	
$k_2 / \text{g mg}^{-1} \text{min}^{-1}$	0.001
$q_e / \text{mg g}^{-1}$	56.020
$h = k_2 q_e^2 / \text{mg g}^{-1} \text{min}^{-1}$	3.138
R^2	0.985
$F_{\text{error}} / \%$	4.390
Elovich – Chemisorption	
$\alpha / \text{mg g}^{-1} \text{min}^{-1}$	33.010
$\beta / \text{g mg}^{-1}$	0.081
R^2	0.920
$F_{\text{error}} / \%$	9.110
Intra-particle diffusion	
$k_{id1} / \text{mg g}^{-1} \text{min}^{-0.5}$	8.180
R_1^2	0.996
$K_{id2} / \text{mg g}^{-1} \text{min}^{-0.5}$	0.015
R_2^2	0.784

The intra-particle diffusion study demonstrated that the sorption kinetics occur with multi-linearity for copper ion using BEM as sorbent, as shown in Figure 8. For this process two kinetic stages are involved that can be attributed to two linear parts. The first linear part can be attributed to intra-particle diffusion with instantaneous sorption and to external surface sorption, while the second region is the gradual sorption stage, where intra-particle diffusion is rate limiting. It is also observed in Table 1 that the value of k_{id1} is greater than the value of k_{id2} , a difference that is due to the fact that the process of intra-particle diffusion starts to decrease after about 30 min, when kinetic equilibrium is established (Hameed *et al.*, 2008).

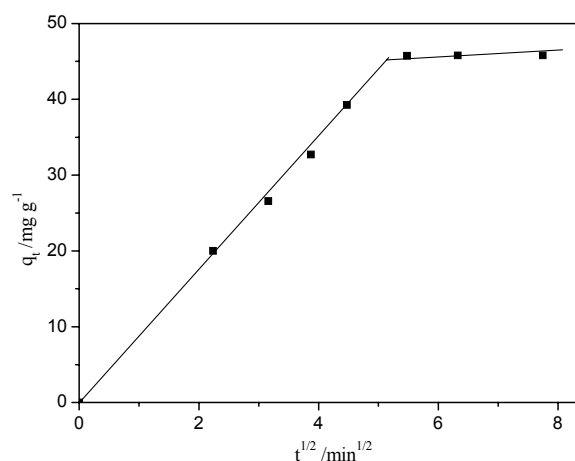


Figure 8: Intra-particle diffusion model for copper ion sorption from aqueous solution by BEM.

Sorption Isotherms

The isotherms of copper ion sorption by BEM predicted from all three models are plotted in Figure 9. All the correlation coefficient R^2 values and the constants obtained for the models are summarized in Table 2. The Langmuir model yielded the best fit with the highest R^2 value of 0.998 and lowest average percentage errors. Thus the Langmuir isotherm was the most suitable equation to describe the adsorption equilibrium for copper. As can be seen from Figure 9, the q_e values predicted from the substitution of the experimental data into the Langmuir isotherm equation indicate the formation of a monolayer coverage of copper ions at the outer surface of BEM. Similar phenomena were observed in the sorption of copper ions by babassu coconut mesocarp modified with maleic, phthalic and succinic anhydrides (Vieira *et al.*, 2010), and by

babassu coconut epicarp and mesocarp modified with ethylenesulfide (Santana *et al.*, 2010).

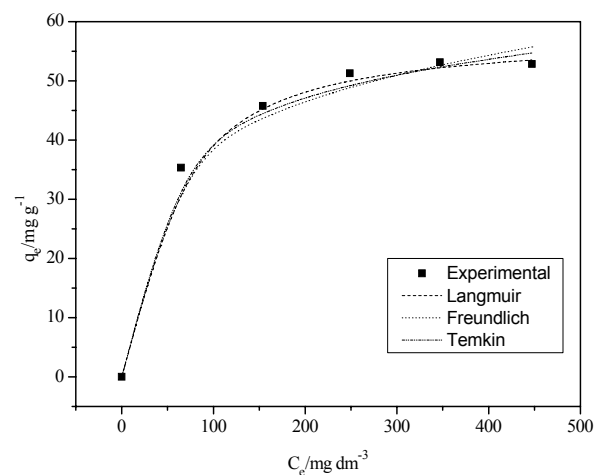


Figure 9: Sorption isotherm models for copper ion sorption from aqueous solutions by BEM.

Table 2: Isotherm data for copper, using BEM as sorbent at 298 ± 1 K.

Freundlich	Constant
$K_F / \text{mg g}^{-1} (\text{dm}^3 \text{mg}^{-1})^{1/n}$	14.7
n_F	4.58
R^2	0.938
$F_{\text{error}} / \%$	4.28
Langmuir	
$K_L / \text{dm}^3 \text{mg}^{-1}$	5.0×10^{-2}
$Q_m / \text{mg g}^{-1}$	55.1
R^2	0.998
$F_{\text{error}} / \%$	1.90
Temkin	
$K_T / \text{dm}^3 \text{g}^{-1}$	0.97
$n_T / \text{J mol}^{-1}$	9.00
R^2	0.990
$F_{\text{error}} / \%$	3.84

The parameter R_L , obtained through the Langmuir equation, indicates favorable sorption for values of $0 < R_L < 1$, unfavorable for $R > 1$ and irreversible for values of $R_L = 0$. Figure 10 represents the calculated R_L values versus the initial concentration of copper. All the R_L values were between 0 and 1, indicating that the sorption of copper by BEM was favorable under the conditions studied. However, as the initial concentration increased from 100 to 500 mg dm^{-3} , the R_L values decreased from 0.166 to 0.038, a

behavior which indicates that the sorption was more favorable at higher concentrations. A comparison of the maximum monolayer sorption capacity of copper ions with different sorbents is listed in Table 3. BEM presents high sorption capacity when compared with the other listed materials. Epicarp and mesocarp from babassu coconut chemically modified with ethylene sulfide (Santana *et al.*, 2010) presented lower sorption capacity than, epicarp is modified with maleic anhydride. This could be associated with the nature of the soft sulfur atom in the SH chelating groups, that differs from oxygen hardness in the carboxylic groups. However, when comparing the mesocarp modified with maleic, phthalic and succinic anhydrides (Vieira *et al.*, 2010), which present the same chelating groups, the epicarp derivative is still higher in sorption. On the other hand, another contribution to this phenomenon could be associated with phenol moieties present in lignin that are able to interact with copper ion. The biopolymer chitosan, which has the ability to bond cations due to its basic nitrogen atom (Lima and Airoidi, 2004), also has a lower sorption capacity. Only ponkan tangerine peel presents a higher sorption capacity, which could be related to the availability of carbonyl functional groups, in addition to the presence of hydroxyl groups (Pavan *et al.*, 2006). These values confirm that the presence of carbonyl groups favors copper sorption, but the additional presence of lignin in the epicarp fraction increases the sorption when compared with other babassu coconut components.

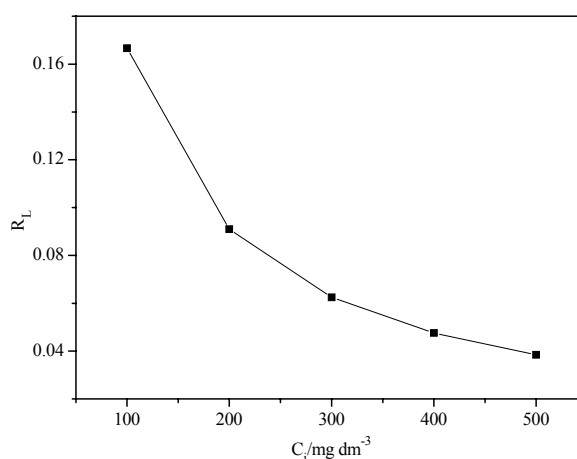


Figure 10: Effect of initial concentration of copper ions on the Langmuir parameter R_L .

Table 3: Comparison of different sorbents for copper sorption.

Sorbent	$Q_m / \text{mg g}^{-1}$	Reference
Babassu coconut mesocarp/ethylenesulfide	47.50	(Santana <i>et al.</i> , 2010)
Babassu coconut epicarp/ethylenesulfide	47.70	(Santana <i>et al.</i> , 2010)
Babassu coconut mesocarp/maleic anhydride	34.36	(Vieira <i>et al.</i> , 2010)
Babassu coconut mesocarp/phthalic anhydride	40.47	(Vieira <i>et al.</i> , 2010)
Babassu coconut mesocarp/succinic anhydride	40.98	(Vieira <i>et al.</i> , 2010)
Chitosan	24.14	Lima and Airolidi, 2004)
Ponkan peel	83.23	(Pavan <i>et al.</i> , 2006)
Pinhão wastes	32.20	(Lima <i>et al.</i> , 2007)
Olive pomace	4.26	(Pagnanelli <i>et al.</i> , 2003)
Grape stalks	10.10	(Villaescusa <i>et al.</i> , 2004)
Cork park	3.00	(Villaescusa <i>et al.</i> , 2004)
Granular activated carbon	38.00	(Babel and Kurniawan, 2003)
Pyrolyzed coffee residue	17.79	(Boonamnuayvitaya <i>et al.</i> , 2004)
Babassu coconut epicarp/maleic anhydride	55.09	This work

CONCLUSIONS

The maleation of the babassu coconut epicarp with molten maleic anhydride is an efficient chemical modification for obtaining a product with carboxylic groups. The new synthetic surface, with incorporation of pendant chains containing basic centers that are potentially available for cation removal, behaved as a promising material, with good sorption capacity for copper ion and potentially of great utility for ecosystem purification. The best conditions were established with respect to pH and contact time to saturate the available sites located on the sorbent surface. Kinetic models were used to adjust the sorption and both pseudo-first and second order models showed good fits.

The intra-particle diffusion model gave two linear regions, which suggested that the sorption could also follow multiple adsorption rates. The sorption process follows the Langmuir isotherm model, with a maximum sorbed amount of 55.09 mg g^{-1} .

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NOMENCLATURE

C_e	equilibrium copper concentration	mg dm^{-3}
C_i	initial copper concentration	mg dm^{-3}

C_{HCl}	hydrochloric acid concentration	mg dm^{-3}
C_{NaOH}	sodium hydroxide concentration	mg dm^{-3}
F_{error}	average percentage error	%
H	initial rate of sorption	$\text{mg g}^{-1} \text{ min}^{-1}$
k_1	rate constant of the pseudo-first order model	min^{-1}
k_2	rate constant of the pseudo-second order model	$\text{g mg}^{-1} \text{ min}^{-1}$
k_{id}	intra-particle diffusion rate constant	$\text{mg g}^{-1} \text{ min}^{-0.5}$
K_F	Freundlich constant representing sorption capacity	$\text{mg g}^{-1} (\text{dm}^3 \text{ mg}^{-1})^{1/n}$
K_L	Langmuir constant related to the apparent energy of sorption	$\text{dm}^3 \text{ mg}^{-1}$
K_T	Temkin equilibrium constant	$\text{dm}^3 \text{ mg}^{-1}$
M	mass of the sorbent	g
n_F	Freundlich exponent related to the sorption intensity	
n_T	Temkin constant related to heat of sorption	J mol^{-1}
P	the number of experimental data points	
q_e	amount of copper sorbed at equilibrium	mg g^{-1}
q_t	amount of copper sorbed at time t	mg/g
$q_{i \text{ exp}}$	experimental copper uptake amount	mg g^{-1}
$q_{i \text{ mod}}$	copper uptake amount calculated from kinetic or isotherm fitted models	mg g^{-1}

Q_{COOH}	amount of the carboxylic function	mg g^{-1}
Q_m	maximum Langmuir sorption capacity	mg g^{-1}
R^2	correlation coefficient	
R_L	Langmuir equilibrium parameter	
T	contact time	min
V	volume of the solution	dm^3
V_{HCl}	volume of hydrochloric acid	cm^3
V_{NaOH}	volume of sodium hydroxide	cm^3

Greek Letters

α	initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) of the Elovich equation	
β	Elovich constant related to the extent of surface coverage and also to the activation energy involved in chemisorption	g mg^{-1}

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