Chemical Engineering Journal 161 (2010) 99–105

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Copper sorption from aqueous solutions and sugar cane spirits by chemically modified babassu coconut (*Orbignya speciosa*) mesocarp

Adriana P. Vieira[a], Sirlane A.A. Santana[a,*], Cícero W.B. Bezerra[a], Hildo A.S. Silva[a], Júlio C.P. de Melo[b], Edson C. da Silva Filho[c], Claudio Airoldi[b]

[a] *Departamento de Química/CCET, Universidade Federal do Maranhão, Avenida dos Portugueses S/N, Campus do Bacanga, 65080-540 São Luís, MA, Brazil*
[b] *Institute of Chemistry, University of Campinas, P.O. Box 6154, 13084-971 Campinas, SP, Brazil*
[c] *Química, Universidade Federal do Piauí, 64900-000 Bom Jesus, Piauí, Brazil*

ARTICLE INFO

Article history:
Received 12 March 2010
Received in revised form 16 April 2010
Accepted 19 April 2010

Keywords:
Sorption
Babassu coconut mesocarp
Chemical modification
Heavy metal
Kinetic
Isotherm

ABSTRACT

The present investigation explores the chemical modification of natural dry babassu coconut (*Orbignya speciosa*) mesocarp (BM), using a quasi solvent-free procedure in which the precursor was added to molten succinic (S), maleic (M) or phthalic (P) anhydrides, to give new products named BMS, BMM and BMP (babassu coconut mesocarp modified with succinic, maleic and phthalic anhydride, respectively). These synthesized biopolymers were characterized by infrared spectroscopy and thermogravimetry and the degree of substitution was calculated, based on the number of carboxylic groups covalently attached to the lignocellulosic polymer. The chemically modified biopolymers suspended in aqueous or hydroalcoholic solutions have the ability to remove copper from aqueous or aqueous-alcohol solutions in the order BMS > BMP > BMM. The kinetic process followed a pseudo-second-order model and the results for sorbents were better represented by the Langmuir sorption model. The effectiveness of these biopolymers for application to real samples of sugar cane spirits reflected in using only 1.0 g dm^{-3} to reduce the copper to a value lower than 5.0 mg dm^{-3} for all sorbents. Thus, these inexpensive chemically modified biopolymers may be useful to permit sugar cane spirits to meet the requirements of Brazilian legislation with respect to copper contamination.

1. Introduction

Annually, agricultural residues, such as the class of lignocellulosic biomass, represent an abundant, inexpensive, and readily available source of sorbents. The potential uses attract increasing interest all over the world, particularly, for production of environmentally friendly, novel materials, mainly when industrially extractable by-products can be chemically modified [1,2]. For example, bagasse-based ion sorbents were prepared by chemically modifying the original materials with acrylonitrile and hydroxylamine, with the aim of enhancing the ability of heavy metal ion removal from wastewater [3].

Raw native wheat, soybean straw, corn stalk and corn cobs were studied to determine their efficiency in removing different heavy metal ions from contaminated samples. In attempting to increase their sorption capacities, efforts were directed to a variety of ways to chemically modify the original material and the effects of these treatments were evaluated in copper removal assays [4].

A great variety of reagents are able to react with lignocellulosic components, due to their high reactivity towards the available hydroxyl groups on the polymeric polysaccharide surfaces. For example, the chemical modification of sugar cane bagasse cellulose components with succinic anhydride in ionic liquids as the reaction medium was successfully accomplished with the carboxylic groups being covalently attached to the main polymeric structure [5]. Another aspect related to such chemical modification consists in the phthalation process under the same experimental condition, but in absence of any catalyst [6]. On the other hand, the ultrasound technique has improved the maleation of the free hydroxyl groups present in sugar cane bagasse, when the respective anhydride was used in pyridine as solvent [7].

Other important features associated with chemical modification are those related to lignocellulose esterification with dicarboxylic acid anhydrides, to yield synthesized material with improved abilities to trap heavy metals from aqueous solutions [8–10]. In addition, sugar cane bagasse was modified by mercerizing with aqueous sodium hydroxide solution, followed by reaction with succinic anhydride and the resulting materials were successfully applied for divalent copper, cadmium and lead sorptions [11,12].

---

* Corresponding author. Tel.: +55 98 33019233; fax: +55 98 33018245.
E-mail addresses: sirlane@ufma.br, sirlaneufma@hotmail.com (S.A.A. Santana).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.04.036

As a general procedure, the use of low-cost sorbents has been intensively investigated as sources of replacement materials for current costly methods of metal removal. Thus, this procedure was applied for copper with different natural sorbents such as lentil pods, wheat and rice husks. The sorption equilibrium level was determined as a function of the solution pH, temperature, contact time, initial sorbate concentration and sorbent quantity [13].

Babassu coconut mesocarp, an abundant agricultural lignocellulosic by-product, is a fibrous residue left after crushing and extracting the nuts. It is a non-toxic, renewable and modifiable material with wide potential as an excellent industrial material, as recently demonstrated by its high capacity for textile dye sorption from aqueous solutions [14]. From the structural point of view, its hydroxyl and phenolic chemical functions can be converted to carboxylic groups by using succinic, phthalic or maleic anhydrides. The great advantage in introducing some functional groups on these biopolymer structures is related to the increase in cation sorption capacity, which contrasts to the very low capacity before modification. A clear recent illustration is the chemical modification that was carried out by attachment of ethylenesulfide onto the surface; the final biopolymer demonstrated affinity to sorb copper from aqueous solution [15].

As far as the authors are aware, lignocellulosic esterification in the absence of both solvent and catalyst has not been reported. Thus, the present investigation deals with babassu coconut mesocarp chemically modified with succinic, phthalic or maleic anhydrides, which resulted in materials that were applied for copper sorption from aqueous and hydroalcoholic solutions. This last composition resembles sugar cane spirits that, in many cases, are distilled using pot stills made of copper, so that the distillate is contaminated with this metal [16,17]. The level of this undesirable metal is restricted to less than 5.0 mg dm^{-3} by Brazilian law and even lower amounts at the 2.0 mg dm^{-3} level, are permitted in distillates by northern hemisphere countries [18]. Based on these legal requirements, development of new inexpensive materials that can be useful for removing undesirable species from the environment is an important objective, as is proposed herein.

2. Methods

2.1. Materials and reagents

The mesocarp from raw babassu coconut and commercial sugar cane spirits were obtained in the city of São Luís, Maranhão state, in the northeast region of Brazil. The raw material was crushed to give particle sizes in the 0.088–0.177 mm range. N,N-dimethylacetamide (DMA) and the succinic, phthalic and maleic anhydrides were all of analytical grade.

2.2. Synthesis of derivatives

The lignocellulose derivatives containing free carboxylic groups were prepared by reaction of babassu coconut mesocarp (BM) with succinic, phthalic or maleic anhydrides in the absence of solvent [19]. This procedure consists in heating the dry mesocarp with an amount of each anhydride in an oil bath at the anhydride fusion temperature. In each case, the anhydride/mesocarp ratio was maintained in the 10:1 ratio, the mixture was stirred for 20 min and the reaction was stopped by addition of DMA. The solid was separated by filtration with a sintered filter, washed in sequence with acetone and distilled water to remove the unreacted anhydride, DMA and by products and dried at 353 K for 12 h. This resulted in the chemically modified biopolymers BMS, BMP and BMM after reaction with succinic, phthalic or maleic anhydrides, respectively. The complete scheme of the reactions is shown in Fig. 1.

2.3. Degree of substitution

The degree of substitution of the chemically modified biopolymers was 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 treated with 100.0 cm^3 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 cm^3 of each solution obtained were titrated with 365.0 mg dm^{-3} aqueous hydrochloric acid [11]. The concentration of the carboxylic function was calculated by Eq. (1):

$$C_{\mathrm{COOH}} = \frac{(C_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}}) - (5 \times C_{\mathrm{HCl}} \times V_{\mathrm{HCl}})}{m_{\mathrm{mat}}} \qquad (1)$$

where C_{NaOH} and C_{HCl} are the concentrations of hydroxide and acid (mg dm^{-3}), V_{NaOH} and V_{HCl} are the volumes of initial hydroxide and hydrochloric acid (dm^3) used in the titration of the excess of non-reacted base and m_{mat} (g) is the mass of the final chemically modified material.

2.4. Measurements

Infrared spectra were obtained by accumulating 32 scans in the 4000–400 cm^{-1} range on a MB-Bomem FTIR spectrophotometer using KBr pellets with a resolution of 4 cm^{-1}. Thermogravimetric curves (TG) were carried out with a Shimadzu TGA-50 instrument under a nitrogen flow rate of 0.50 cm^3 s^{-1}, in the temperature interval from 298 to 1000 K, with a heating rate of 0.167 K s^{-1} for a sample mass of about 10 mg. The experiments of the visible spectrophotometry were carried with VARIAN-AA 50 instrument.

2.5. Point of zero charge

The point of zero charge of the synthesized biopolymers was determined by the solid addition method [20]. To a series of 100.0 cm^3 conical flasks were transferred 50.0 cm^3 of solution with pH varying from 1 to 12 and the pH$_0$ values of each solution were adjusted by adding either 0.10 mol dm^{-3} of hydrochloric acid or sodium hydroxide. The pH$_0$ of the solutions was then accurately measured and 0.1000 g of one of the solids was added to each flask. The suspensions were then shaken for 24 h and the pH values of the supernatant were measured. The difference between the initial pH$_0$ and final pH$_\mathrm{f}$ values, given by pH = pH$_0$ − pH$_\mathrm{f}$, was plotted against pH$_0$ and the point of intersection of the resulting null ΔpH corresponds to the point of zero charge, pH$_{\mathrm{pzc}}$.

2.6. Sorption studies

2.6.1. Effect of pH

The precursor and the three chemically modified mesocarps were assayed. To determine the effect of pH on metal ion adsorption, an amount of 0.1000 g of each material was suspended in 100.0 cm^3 of copper solution having an initial concentration of 200 mg dm^{-3} under constant stirring for 24 h. The pH range studied was from 1.0 to 6.0 and these values were adjusted with 0.010–1.0 mol dm^{-3} aqueous hydrochloric acid solutions. After filtration, the cation concentration in the supernatant was determined by EDTA titration [21].

2.6.2. Kinetics

For this study 0.1000 g of each sorbent was mixed with 100.0 cm^3 of aqueous or 40% hydroalcoholic solution having concentrations of 200 mg dm^{-3} under stirring for different times. For all experiments in the aqueous solution the pH was adjusted at 6.0, using hydrochloric acid/sodium hydroxide solutions. After fil-

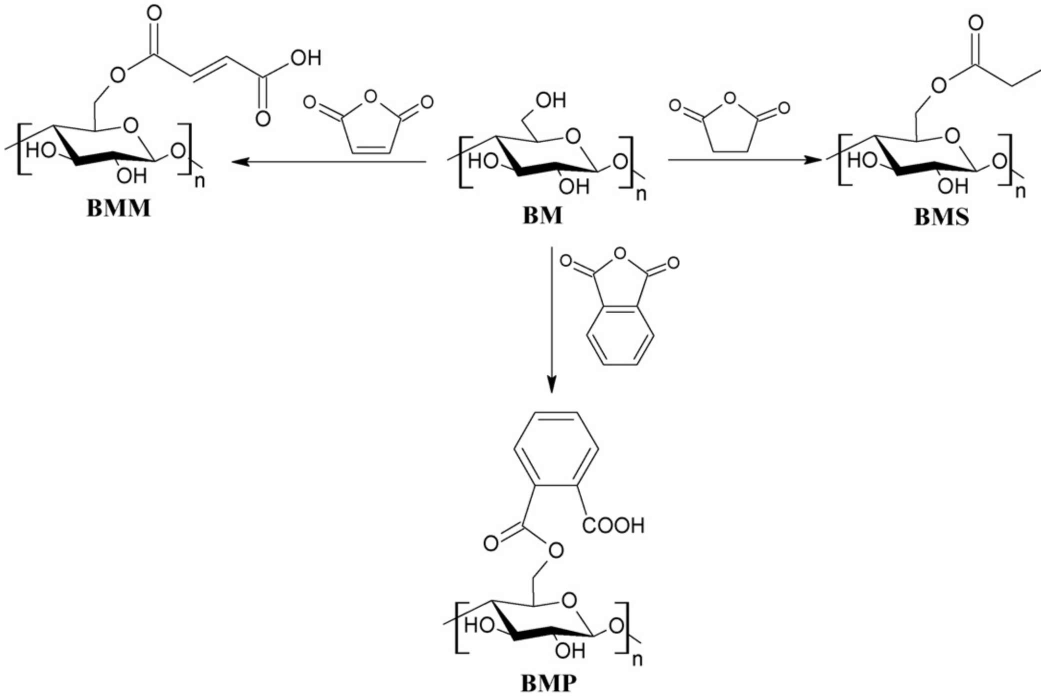

Fig. 1. A general scheme for synthesis of the biopolymers BMS, BMP and BMM.

tration, the cation concentration was determined as previously described [21].

2.6.3. *Sorption*

The batchwise sorption experiments used a series of flasks containing 0.1000 mg of each material suspended in 100.0 cm^3 of the aqueous or the 40% hydroalcoholic solutions having concentrations of copper cation that varied from 200 to 500 mg dm^{-3} at 298 ± 1 K. The suspensions were shaken for 30 min at the pH established from the previous experiments to ensure maximum adsorption. At the end of this process, the solid was separated by filtration and the metal ion amount sorbed was determined by difference between the initial solution concentration and that found in the supernatant by titration [21].

2.6.4. *Sorption from sugar cane spirit samples*

Sugar cane spirit samples obtained from a local market were doped with copper to simulate high levels of this metal. For this operation, an aliquot of 8.0 cm^3 of copper solution (40% ethanol) was diluted to 1 L of sugar cane spirits, to result in a sugar cane spirit having a final metal concentration of 8.0 mg dm^{-3}. The sorptions by 1.0–4.0 g of each chemically modified mesocarp BMS, BMP and BMM were assayed. For each biopolymer four independent determinations were performed, using 30 min of stirring. The concentration of copper remaining in the sugar cane sample was determined by a calibration curve in visible spectrophotometry. For each spectrophotometric determination 1.0 cm^3 of pyridine were added to aliquots of 9.0 cm^3 of the supernatant and the absorbance of the copper–pyridine complex formed was measured at a wavelength of 610 nm [16].

3. Results and discussion

3.1. *Characterization*

The amounts of carboxyl groups covalently attached to the synthesized biopolymers are shown in Table 1. A considerable increase in carboxylic groups is detected when compared to the unmodified precursor, confirming the success of the proposed chemical modification.

Table 1
Degree of substitution of the biopolymers.

Biopolymer	C_{COOH} (mg g^{-1})
BM	36.19 ± 0.03
BMS	176.99 ± 0.10
BMP	149.27 ± 0.05
BMM	141.79 ± 0.05

The infrared spectra of the unmodified and all chemically modified mesocarps are shown in Fig. 2. The precursor biopolymer BM in Fig. 2a shows a broad and intense band in the 3000–3700 cm^{-1}

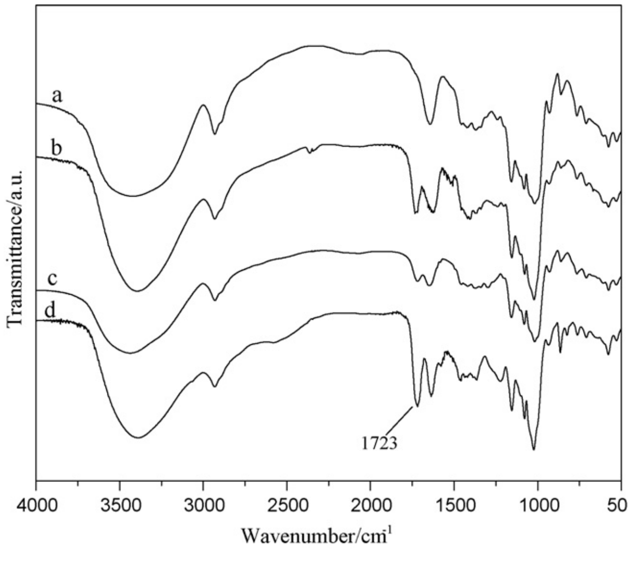

Fig. 2. Infrared spectra of the initial mesocarp BM (a), chemically modified biopolymers BMS (b), BMP (c) and BMM (d).

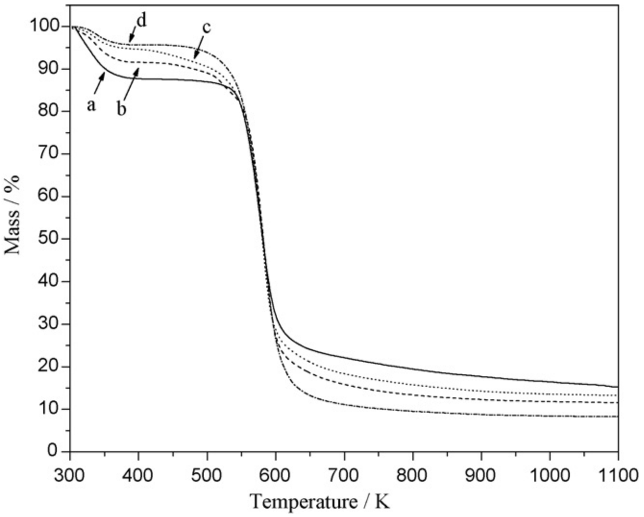

Fig. 3. Thermogravimetric curves for BM (a), BMS (b), BMP (c) and BMM (d).

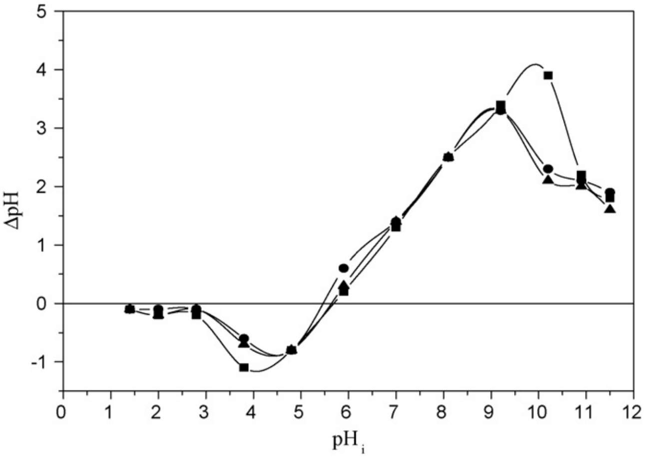

Fig. 4. Point of zero charge for BMS (■), BMP (●) and BMM (▲).

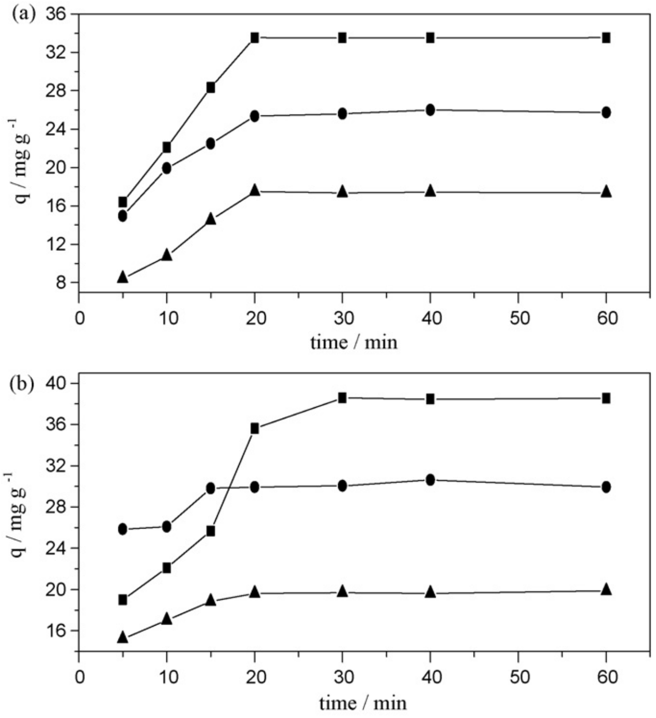

Fig. 5. Kinetics of copper sorption for BMS (■), BMP (●) and BMM (▲) in water (a) and hydroalcoholic (b) solution, both at pH 6.0 and at 298 ± 1 K.

range due to the presence of free and hydrogen bonded OH stretching vibrations. The hydroxyl groups bonded to the cellulosic structure correspond to the δ(O–H) band at 1640 cm^{-1} and those between 1200 and 1000 cm^{-1} are related to ν(C–O) [22]. The spectra of chemically modified biopolymers are very close to that of the precursor, however, the most remarkable differences are the strong band at 1723 cm^{-1} assigned to the C=O stretching vibration [10]. The presence of CH_2 and CH groups proceeding from the anhydrides added to the biopolymer backbone is shown by the stretching bands at 2930 and 2890 cm^{-1}, respectively [14]. Based on the difference from the precursor and the sorptions related to the modified biopolymers, mainly the carbonyl stretching frequency, these results clearly confirm the attachment of the anhydride molecules onto the polymeric structure.

The thermogravimetric curves for all biopolymers are shown in Fig. 3, from which a very similar behavior in decomposition is observed, in agreement to other lignocellulosic materials [23]. The first step of decomposition can be attributed to the release of water physically sorbed on the surface. This stage corresponds to a mass loss of 16.0, 4.3, 8.2 and 5.3% up to 375 K, for the BM, BMS, BMP and BMM, respectively. The second stage corresponds to the decomposition of organic material, as expected for the breakdown of fibers to give the final residue, and occurs in the 477 to 623 K temperature range. The mass loss that corresponds to this interval of temperature for BM is 60%, while for BMS, BMP and BMM, these percentages are 89.3, 81.2, and 82.7%, respectively.

3.2. 3.2 pH effect and point of zero charge

The unmodified mesocarp BM demonstrated a null sorptive capacity in the presence of copper cations under the conditions studied. As previously observed, its pH_{pzc} is 6.7 and the sorption of positively charged species will be favored only at $pH > pH_{pzc}$ [14]. However, it is expected that at pH higher than 6.7 species related to copper hydroxide can be formed, that will affect free cation sorption.

All anhydride-modified mesocarps presented an increase in the amount of copper sorbed with the increase of the pH of the solution with a maximum value at pH 6.0. The pH_{pzc} for these biopolymers are 5.6, 5.4 and 5.7 for BMS, BMP and BMM, respectively, as shown in Fig. 4. These values indicate that cation sorption is favored in solutions with pH higher than pH_{pzc} for each specific material. Under acidic conditions, the chemically modified biopolymers can be protonated, due to the higher concentrations of protons and the amount of cations sorbed decreases. On the other hand, the increase in pH deprotonates carboxylate groups, a condition that favors their chelating abilities and, consequently, the amount of sorbed Cu^{2+} ions is increased. An identical behavior was previously observed for other systems, in which the attached function, derived from succinic anhydride, chelated bivalent and trivalent cations [10–12,24,25].

3.3. Kinetics of sorption

The complete curves of sorbed amount versus time for the three chemically modified mesocarp biopolymers at pH 6.0 are shown in Fig. 5, where the sorption process in aqueous solution is compared with that of hydroalcoholic solutions, as observed in Fig. 5a and b, respectively. From these isotherms it is clearly evidenced that the equilibrium in aqueous solution is reached after 20 min of contact between copper and the suspended solids. However, in hydroalcoholic solution the amount adsorbed becomes constant after 30, 15 and 20 min for BMS, BMP and BMM, respectively. The results of the kinetic data were investigated by pseudo-first-order [20] and pseudo-second-order [26] models, as given by Eqs. (2) and (3), respectively. The initial rate of sorption, h (mg g^{-1} min^{-1}), can be obtained from Eq. (4):

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1 t}{2.303} \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \tag{3}$$

$$h = k2q_e^2 \tag{4}$$

where q_e and q_t are the amounts of metal sorbed on sorbent (mg g^{-1}) at equilibrium and at time t (min), respectively, k_1 and k_2 are the rate constants for first order (min^{-1}) and for second-order (g mg^{-1} min^{-1}) of such sorption processes.

The parameters obtained from these equations, based on the correlation coefficients for the best fit, are listed in Table 2. The sorption process described by the pseudo-second-order model is preferred. The correlation of this model for these systems corroborates with the studies when BM biopolymer was used as sorbent for textile dyes, demonstrating that all examined dyes showed better fit with the pseudo-second-order equation [14]. Other sorbents such as peat [27,28], chemically modified chitosan [29] and green coconut [30], that also present the ability to sorb copper, also showed a better adjustment to this model.

3.4. Sorption isotherms

The data used to build the sorption isotherms compared two well-known models Langmuir and the Freundlich models. The first model assumes that the sorbate forms a monolayer on a surface containing a finite number of sites with uniform strategies for sorption, without transmigration of sorbate on the plane of surface, while the Freundlich model assumes an energetic and heterogeneous surface. Based on the results obtained from the Langmuir equation, the energetic term varies as a function of surface coverage, as the sorption is in progress [31,32]. Taking into account the correlation coefficients, R^2, then the applicabilities of these isotherm equations can be compared. Both models permit the linearization of the isotherm data as indicated by Eqs. (5) and (6):

$$\frac{C_e}{q} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \tag{5}$$

$$\log q_e = \log K_f + \frac{1}{n \log C_e} \tag{6}$$

where C_e is the equilibrium concentration of the sorbate (mg dm^{-3}), q_e is the amount of sorbate per unit mass of sorbent (mg g^{-1}), Q_m (mg g^{-1}) and K_L (dm mg^{-1}) are Langmuir constants related to the capacity and rate of adsorption, respectively, K_f (dm mg^{-1}) and n are Freundlich constants and give an indication of how favorable the process and the capacity of the sorbent are, respectively. The values of the parameters of the isotherms and the related correlation coefficients are listed in Table 3, showing that the Langmuir model produces a better fit for all materials investigated. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [33], which is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of metal (mg dm^{-3}). The value of R_L indicates the type of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). For all biopolymers R_L values varied between 0 and 1, which confirms that the sorbents are favorable for copper sorption with the conditions used for this study. The sorption curves according to the Langmuir model for the system in aqueous and hydroalcoholic solutions are shown in Fig. 6a and b, respectively.

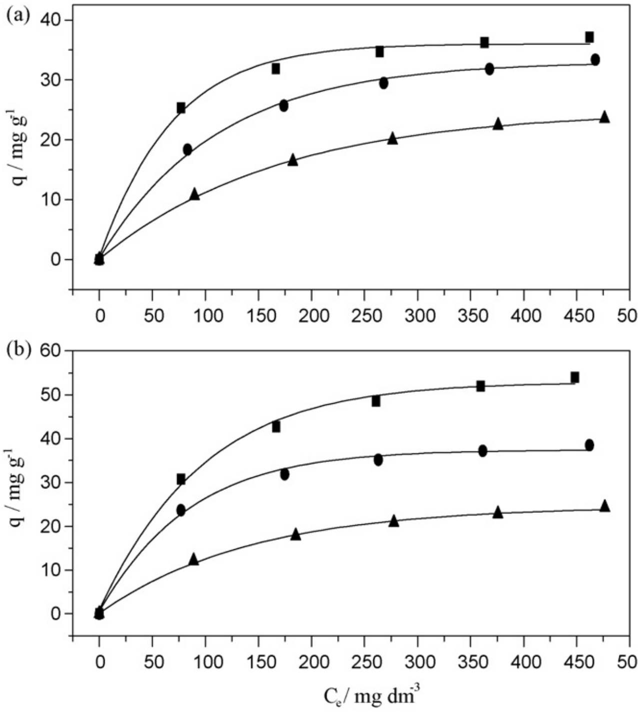

Fig. 6. Adjustment of the data to the Langmuir isotherms for copper sorption by BMS (■), BMP (●) and BMM (▲) in water (a) at pH 6.0 and hydroalcoholic solution (b), both at pH 6.0 and at 298 ± 1 K.

Earlier studies associated with copper sorption for a series of materials such as wheat and lentil and rice husks without modification [13] as well as materials such as sugar cane bagasse and cellulose [10–12] chemically modified with specific agents, revealed a tendency for Langmuir model adjustment. The parameters related to this model reflect the nature of the adsorbent and can be used to compare the performance of sorption, as regards the maximum capacity. According to the maximum sorption capacity for copper per gram of sorbent, Q_m, the order of amount adsorbed on the systems investigated was BMS > BMP > BMM. A similar sequence is found for the degree of functionalization with the carboxylic acids introduced into the mesocarp structure, 177.0, 149.3, 141.8 mg g^{-1} for the same sequence, respectively. This fact explains the sorption capacity of each material, because the presence of these functional groups is essential for cation sorption. The maximum capacity, Q_m, indicates for the hydroalcoholic solution that copper sorption is higher for these biopolymers than in the aqueous solutions. This can be explained based on the hydration energies of the hydrated copper ion with coordination number 6, as in alcohol solution, the solvation is hindered, which reduces the solubility of ions and can promote the sorption process [34].

3.5. Sorption from sugar cane spirit samples

The variation of the final copper concentrations according to the dosage of each sorbent, varying from 1.0 to 4.0 g dm^{-3}, is shown in Fig. 7. It is observed that the copper content in sugar cane spirits can be reduced to that permitted by Brazilian law, specified as 5.0 mg dm^{-3}, when only 1.0 g dm^{-3} of each sorbent was used. As

Table 2
Pseudo-first- and pseudo-second-order rate constants for copper sorption on chemically modified mesocarp at pH 6.0 and 298 ± 1 K.

Condition	Biopolymer	$q_{e,\mathrm{exp}}$ (mg g^{-1})	Pseudo-first order			Pseudo-second order			
			$q_{e,\mathrm{cal}}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,\mathrm{cal}}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
Water	BMS	33.53	62.80	0.202	0.928	37.19	0.005	7.586	0.992
	BMP	26.01	9.85	0.085	0.883	27.62	0.011	8.595	0.997
	BMM	17.50	15.54	0.127	0.952	19.46	0.009	3.625	0.988
Hydroalcoholic	BMS	38.58	45.98	0.126	0.951	44.86	0.002	5.720	0.982
	BMP	30.63	6.46	0.091	0.944	30.66	0.039	37.25	0.999
	BMM	19.88	4.66	0.092	0.753	20.43	0.033	13.94	0.999

Table 3
The Langmuir and the Freundlich parameters for copper adsorption on chemically modified mesocarps at pH 6.0 and 298 ± 1 K.

Condition	Biopolymer	Langmuir				Freundlich		
		R^2	Q_m (mg g^{-1})	K_L (dm^3 mg^{-1})	R_L	R^2	K_f (dm^3 mg^{-1})	N
Water	BMS	0.994	40.98	0.021	0.084	0.834	8.015	3.859
	BMP	0.986	40.47	0.010	0.166	0.901	3.221	2.557
	BMM	0.946	34.36	0.005	0.263	0.901	1.048	1.897
Hydroalcoholic	BMS	0.980	64.06	0.012	0.144	0.909	7.812	3.094
	BMP	0.995	44.11	0.015	0.120	0.939	6.526	3.373
	BMM	0.967	31.51	0.007	0.222	0.876	1.548	2.167

observed, the initial high concentration of cation of 8.0 mg dm^{-3} was reduced to 0.48, 1.41, 4.26 mg dm^{-3} for BMS, BMP and BMM, respectively, at the end of the sorption process. However, northern hemisphere countries permit only up to 2.0 mg dm^{-3} of copper in sugar cane spirits, which requires a dosage of 3.0 mg dm^{-3} of BMM to fit within the required standards.

The present chemically modified mesocarp has considerably higher sorption capacity when compared with other studied materials. For example, the most investigated sorbent activated carbon, has the ability for copper removal from sugar cane spirit [35], showing that it would require concentration of 12.0 g dm^{-3} and a stirring time of 60 min to obtain sugar cane spirits with copper levels below the limit allowed under Brazilian law.

Although the biopolymers of this study have demonstrated good efficiencies for copper removal from real samples of sugar cane spirits, a solid base for commercial application requires further studies on the changes in the profiles of inorganic and organic components of the sugar cane spirits, economic feasibility and the ideal flow conditions.

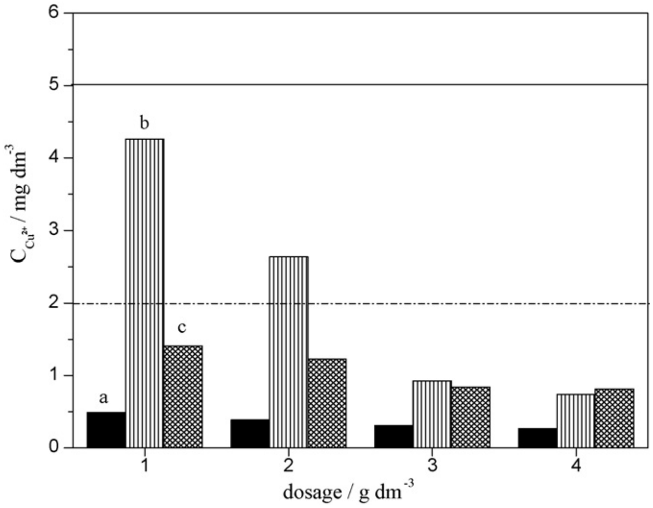

Fig. 7. Copper sorption form a sample of sugar cane spirit by BMS (a), BMM (b) and BMP (c) at 298 ± 1 K after 30 min of contact. (- - -) maximum allowed by the laws of countries of the northern hemisphere; (—) maximum allowed under Brazilian law.

4. Conclusion

Through a quick and ready methodology it was possible to devise a strategy to introduce chelating carboxylic acid functions onto natural babassu mesocarp. The synthesized biopolymers presented good sorption capacities for copper in hydroalcoholic and aqueous solutions, with maximum values obtained at pH 6.0. The corresponding kinetics of sorption is governed by a pseudo-second-order model, with better adjustment to the Langmuir model. The results also demonstrated the effectiveness of copper removal from a sample of sugar cane spirits, requiring only 1.0 g dm^{-3} of sorbent and 30 min of contact to meet the requirements of Brazilian law.

Acknowledgements

The authors are indebted to CAPES for financial support, to FAPEMA for a fellowship to APV and to CNPq for a fellowship to CA.

References

[1] A. Pandey, C.R. Soccol, P. Nigam, V.T. Soccol, Biotechnological potential of agro-industrial residues. I. Sugarcane bagasse, Bioresour. Technol. 74 (2000) 69–80.

[2] S. Richardson, L. Gorton, Characterisation of the substituent distribution in starch and cellulose derivatives, Anal. Chim. Acta 497 (2003) 27–65.

[3] Y. Jiang, H. Pang, B. Liao, Removal of copper (II) ions from aqueous solution by modified bagasse, J. Hazard. Mater. 164 (2009) 1–9.

[4] M. Šæiban, M. Klašnja, B. Škrbiæ, Adsorption of copper ions from water by modified agricultural by-products, Desalination 229 (2008) 170–180.

[5] C.F. Liu, R.C. Sun, A.P. Zhang, J.L. Ren, X.A. Wang, M.H. Qin, Z.N. Chao, W. Luo, Homogeneous modification of sugarcane bagasse cellulose with succinic anhydride using a ionic liquid as reaction medium, Carbohydr. Res. 342 (2007) 919–926.

[6] C.F. Liu, R.C. Sun, A.P. Zhang, J.L. Ren, Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium, Carbohydr. Polym. 68 (2007) 17–25.

[7] C.F. Liu, R.C. Sun, M.H. Qin, A.P. Zhang, J.L. Ren, F. Xu, J. Ye, S.B. Wu, Chemical modification of ultrasound-pretreated sugarcane bagasse with maleic anhydride, Ind. Crop. Prod. 26 (2007) 212–219.

[8] V. Marchetti, A. Clement, P. Gerardin, B. Loubinoux, Synthesis and use of esterified sawdusts bearing carboxyl groups for of removal cadmium (II) from water, Wood Sci. Technol. 34 (2000) 167–173.

[9] A.M.A. Nada, M.L. Hassan, Ion exchange properties of carbohydrate bagasse, J. Appl. Polym. Sci. 102 (2006) 1399–1404.

[10] O. Karnitz Júnior, V.A. L, J.C.P. Gurgel, V.R. Melo, T.M.S. Botaro, R.P.F. Melo, L.F. Gil, Adsorption of heavy metal ions from aqueous single metal solution by chemically modified sugarcane bagasse, Bioresour. Technol. 98 (2007) 1291–1297.

[11] L.V.A. Gurgel, R.P. Freitas, L.F. Gil, Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane

bagasse chemically modified with succinic anhydride, Carbohydr. Polym. 74 (2008) 922–929.

[12] L.V.A. Gurgel, O. Karnitz Jr., R.P.F. Gil, L.F. Gil, Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride, Bioresour. Technol. 99 (2008) 3077–3083.

[13] H. Aydın, Y. Bulut, C. Yerlikaya, Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents, J. Environ. Manag. 87 (2008) 37–45.

[14] A.P. Vieira, S.A.A. Santana, C.W.B. Bezerra, H.A.S. Silva, J.A.P. Chaves, J.C.P. Melo, E.C. Silva Filho, C. Airoldi, Kinetics and thermodynamics of textile dye adsorption from aqueous solutions using babassu coconut mesocarp, J. Hazard. Mater. 166 (2009) 1272–1278.

[15] S.A.A. Santana, A.P. Vieira, E.C. Silva Filho, J.C.P. Melo, C. Airoldi, Immobilization of ethylenesulfide on babassu coconut epicarp and mesocarp for divalent cation sorption, J. Hazard. Mater. 174 (2010) 714–719.

[16] B.S. Lima Neto, C.W.B. Bezerra, L.R. Polastro, P. Campos, R.F. Nascimento, S.M.B. Furuya, D.W. Franco, O cobre em aguardentes brasileiras: Sua quantificação e controle, Quím. Nova 17 (1994) 220–223.

[17] Y. Boza, J. Horii, Influência do grau alcoólico e da acidez do destilado sobre o teor de cobre na aguardente, Cienc. Tecnol. Aliment. 20 (2000) 279–284.

[18] M.B. Miranda, N.G.S. Martins, A.E.S. Belluco, J. Horri, A.R. Alcarde, Qualidade química de cachaças e de aguardentes brasileiras, Ciênc. Tecnol. Aliment. 27 (2007) 897–901.

[19] J.C.P. Melo, E.C. Silva Filho, S.A.A. Santana, C. Airoldi, Maleic anhydride incorporated onto cellulose and thermodynamics of cation-exchange process at the solid/liquid interface, Colloids Surf. A 346 (2009) 138–145.

[20] V.C. Srivastava, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA, J. Hazard. Mater. 134 (2005) 257–267.

[21] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, 5th ed. revised, John Wiley & Sons, New York, 1989.

[22] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., John Wiley & Sons, New York, 1986.

[23] V. Tserki, P. Matzinos, S. Kokkou, C. Panayiotou, Novel biodegradable composites based on treated lignocellulosic waste flour as filler. Part I. Surface chemical modification and characterization of waste flour, Composites: Part A 36 (2005) 965–974.

[24] A.D. Khasbaatar, Y.G. Ko, U.S. Choi, Adsorption and equilibrium adsorption modeling of bivalent metal cations on viscose rayon succinate at different pHs, React. Funct. Polym. 67 (2007) 312–321.

[25] A.D. Khasbaatar, Y.J. Chun, U.S. Choi, Trivalent metal adsorption properties on synthesized viscose rayon succinate, Polym. J. 40 (2008) 302–309.

[26] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process. Biochem. 34 (1999) 451–465.

[27] T. Gosset, J.L. Trancart, D.R. Thevenot, Batch metal removal by peat kinetics and thermodynamics, Water Res. 20 (1986) 21–26.

[28] Y.S. Ho, D.A.J. Wase, C.F. Forster, Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat, Environ. Technol. 17 (1996) 71–77.

[29] K.C. Justi, V.T. Fávere, M.C.M. Laranjeira, A. Neves, R.A. Peralta, Kinetics and equilibrium adsorption of Cu(II), Cd(II), and Ni(II) ions by chitosan functionalized with 2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formylphenol, J. Colloid Interface Sci. 291 (2005) 369–374.

[30] F.W. Sousa, S.A. Moreira, A.G. Oliveira, R.M. Cavalcante, R.F. Nascimento, M.F. Rosa, Uso da casca de coco verde como adsorvente na remoção de metais tóxicos, Quím. Nova 30 (2007) 1153–1157.

[31] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[32] H.M.F. Freundlich, Uber die adsorption in lösungen, Z. Phys. Chem. 57A (1906) 385–470.

[33] D.A. Fungaro, M.G. Silva, Utilização de zeólita preparada a partir de cinza residuária de carvão como adsorvente de metais em água, Quím. Nova 25 (2002) 1081–1085.

[34] L.B. Cantanhede, J.B. Lima, G.S. Lopes, R.F. Farias, C.W.B. Bezerra, Uso de sílica e sílica-titânia organofuncionalizada para a remoção de Cu (II) em aguardentes, Cienc. Tecnol. Aliment. 25 (2005) 500–505.

[35] A.J.B. Lima, M.G. Cardoso, M.C. Guerreiro, F.A. Pimentel, Emprego do carvão ativo para a remoção de cobre em cachaça, Quím. Nova 29 (2006) 247–250.