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Biosorbent of macadamia residue for cationic dye adsorption in aqueous solution

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ABSTRACT. This study evaluated the adsorption capacity of the methylene blue dye in macadamia residues, *in natura* and chemically modified. The waste characterization was performed using SME and spectroscopy in the infrared region, indicating the presence of carboxyl, carbonyl and hydroxyl groups. The equilibrium time for both residues was 240 minutes, following a kinetic described by models of the pseudo second-order and intra-particle diffusion. The maximum adsorption capacity was 117 mg g^{-1} to the residue *in natura* and 184 mg g^{-1} for the modified one, and was described by the Freundlich isotherm model. The system demonstrated to be spontaneous and favorable for both studied materials. Thus, these residues are promising for the adsorption of methylene blue dye in effluents.

Keywords: effluent, agro industrial waste, methylene blue, Macadamia biomass.

Resíduo de macadâmia como biossorvente para adsorção de corante catiônico em solução aquosa

RESUMO. O presente trabalho avaliou a capacidade de adsorção do corante azul de metileno em resíduos de noz-macadâmia *in natura* e quimicamente modificado. A caracterização dos resíduos foi realizada utilizando MEV e espectroscopia na região do infravermelho a qual indicou a presença de grupos carboxílicos, carbonila e hidroxila. O tempo de equilíbrio alcançado para ambos os resíduos foi de 240 min., seguindo a cinética descrita pelos modelos de pseudo segunda-ordem e difusão intrapartícula. A capacidade máxima de adsorção foi 117 mg g^{-1} para o resíduo *in natura* e 184 mg g^{-1} para o modificado, sendo descrita pelo modelo isotérmico de Freundlich. O sistema mostrou-se espontâneo e favorável para os dois materiais estudados. Desta forma, estes resíduos são promissores para a adsorção do corante azul de metileno em efluentes.

Palavras-chave: efluente, resíduo agroindustrial, azul de metileno, biomassa de macadâmia.

Introduction

One of the huge difficulties faced by the textile sector is to control and remove dyes present in their effluents. Textile dyes are often highly toxic and carcinogenic, and when released into rivers and lakes without treatment, they can affect transparency and water solubility of the gases that change the aquatic biota (Banat, Nigam, Singh, & Marchant, 1996; Cigdem, 2012; Kimura, Gonçalves Jr, Stolberg, Laranjeira, & Fávere, 1999; Kunz, Zamora, Moraes, & Durán, 2002). Thus, there is a need to remove them from the wastewater before their release into the environment. An alternative to this treatment is the adsorption; it is a physical process of great interest because of its high removal rates. In some cases, it is a non-destructive method and allows the recovery of the dye without loss of chemical identity (Cigdem, 2012; Dallago & Smaniotto, 2005). Among the adsorbent materials used in this technique, activated carbon stands out because of its excellent adsorptive properties; however, its high production cost is disadvantageous (Deng, Lu, Li, Zhang, & Wang, 2011). To achieve suitable materials that replace the activated carbon, several studies have been performed involving agro-industrial wastes. Such materials have shown efficient adsorbent properties, besides being easy to obtain and presenting low cost (Dos Santos, Tarley, Caetano, & Dragunski, 2010).

Among the agro-industrial wastes, stands out the macadamia nut. This product is highly appreciated by the international market, and has increased its consumption in Brazil, presenting approximately 6,000 ha planted; yet the growth in its production estimates high rates of residues of this agricultural product in the near future, being composed mainly of bark and carpel (Pimentel, Santos, Wagner Jr, Silva, & Bruckner, 2007).

The use of activated carbon from the macadamia shells have been used in adsorption dyes (methylene blue) (Pezoti Junior et al., 2014), and drugs (tetracycline) (Martins et al., 2015), obtaining excellent maximum adsorption capacity, of 194 and 455 mg g^{-1}, respectively. However, the production of active coal has a high cost. The use of macadamia waste was also studied for adsorption of metallic chromium (III) ions and lead (II) (Vilas Boas et al., 2015) with a maximum adsorption capacity of 82 and 91 mg g^{-1}, as well as copper ions with an adsorption of 28 mg g^{-1}(Vilas Boas et al., 2012).

Thus, this study aims at evaluating macadamia nut biomass as adsorbent for the methylene blue dye, considering that in the textile sector it is a widely used cationic dye.

Material and methods

Preparation and characterization of the biosorbent

The biomass formed by macadamia nut shells was dried in a greenhouse at 85°C for 24 hours and then was crushed and sieved (sieve Mesch Bertel 42) in order to obtain a homogeneous distribution of particle size. For the chemical modification, 20 mL of NaOH 0.1 mol L^{-1}were used for each gram of material, which were stirred for 2 hours at room temperature. At the end of this period, the material was filtered, washed and dried at 85°C for 24 hours (Rodrigues, Trevezoli, Santos, Leão, & Botaro, 2006).

The morphological characterization of materials were analyzed using scanning electron microscopy (SEM), infrared spectrometry measures were also obtained using KBr pellets in an equipment of Shimadzu Infrared Spectrophotometer FTIR-8300 Fourier Transform in the region of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}.

Experiment adsorption

The adsorption analyses as a function of pH, temperature and kinetics were performed using 50 mL of dye in the concentration of 100 mg L^{-1}; they were stirred with 0.5 g of adsorbent in an orbital shaker. To evaluate adsorption as function of pH, measurements were performed in a pH range between 3.0 to 11.0 (The solutions of 0.1 mol L^{-1} hydrochloric acid (HCl) and 0.1 mol L^{-1} sodium hydroxide (NaOH) were used to adjust the pH of the solutions), under stirring for 24 hours at room temperature. The measures of adsorption kinetics were performed at an interval of time from 10 to 1440 minutes, with the pH maintained at 7.0. For the isothermal test, the concentrations of the solutions varied between 10 and 3000 mg L^{-1} using 50 mL of these solutions in 0.5 g of the adsorbent; they remained under stirring for 4 hours as established by the kinetic assay. The temperature variation studied was 20 to 60°C and the stirring time was 4 hours in a thermostatic bath.

All measurements were performed in batch and at the end of each experiment, the supernatant liquid was filtered, diluted and analyzed using a Shimadzu UV-1601PC. The linear calibration line was obtained with the methylene blue concentration in the range of 0.1 to 5 mg L^{-1}, obtaining a correlation coefficient of R^2 = 0.999, in wavelength of 664 nm. The amount of dye adsorbed, q_{eq}, was calculated from Equation (1):

$$q_{eq} = \frac{(C_o - C_{eq}) * V}{M} \quad (1)$$

Ceq and C_0 are initial and equilibrium concentrations of methylene blue in the solution (mg L^{-1}), respectively, V is the volume (L) of the solution and M the dry mass of the adsorbent in the solution (g).

Results and discussion

Biosorbent characterization

The infrared spectra for the macadamia biomass are disposed *in natura* (Figure 1a) and modified (Figure 1b).

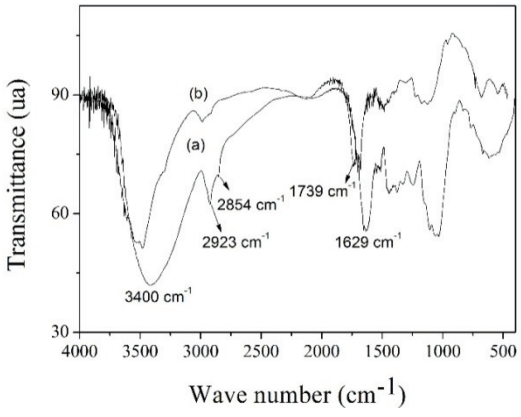

Figure 1. Infrared spectra for macadamia adsorbent *in natura* (a) and modified (b).

In Figure 1a, there is a strong and broad band in the region of 3400 cm^{-1}, which indicated the presence of O-H groups. Peaks in the region of 2923 and 2854 cm^{-1} can be assigned to the stretching vibration of C-H bonds (sp^3). There are peaks in 1739 and 1629 cm^{-1}, and according to the literature, they are correspondents to the vibrational stretching of the C-O bonds (Souza et al., 2012). However, after the chemical modification, a decrease in the intensity of the band at 3400 cm^{-1} was noticeable; furthermore it was demonstrated an absence of the small band in the region 1240 cm^{-1},

which confirmed the presence of lignin in the biomass *in natura* due to C-O vibration (Silva & Oliveira, 2012). Thus, it is possible to confirm the presence of hydroxyl, carbonyl and carboxyl groups in the macadamia biomass in both materials; nevertheless, after modification, there was extraction of lignin and hemicelluloses, which may have produced a more irregular material, resulting from the extraction of these substances, allowing the formation of gaps in the structure.

Adsorption studies

Influence of pH

Figure 2 shows a similar behavior of the curves; however, for the modified biomass, the values of Qeq were more constant, allowing a larger working range. The best values in the methylene blue adsorption occurred with pH between 5 and 9, results that corroborate those obtained by Silva and Oliveira (2012). For subsequent studies, it was decided to work with pH 7.00 because it is in the neutral pH region, since it may facilitate the use of adsorbents for the treatment of textile effluents.

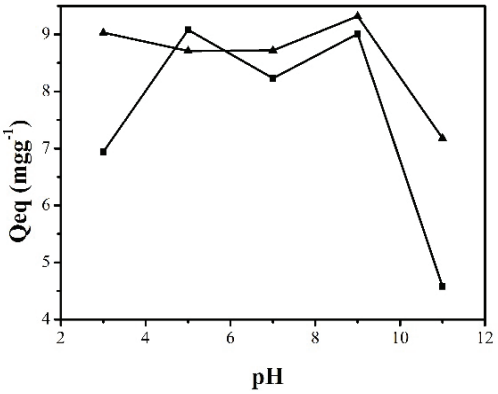

Figure 2. Influence of pH in the adsorption of methylene blue for the macadamia adsorbents (■) *in natura* and (▲) modified.

Influence of time on adsorption

The effect of time on the adsorption of methylene blue is showed in Figure 3. It can be seen that the adsorption capacity occurs initially rapidly and increasingly, and stabilization occurred in about 240 minutes for the two residues. According to Carvalho, Fungaro, and Izidoro, (2010), the rapid adsorption observed is initially due to the greater surface area available, so the dye molecules, after recoating the entire outer surface, follow slowly to the internal surface of the adsorbent. Furthermore, it should be noted that the adsorption capacity of the modified biomass was higher than the one *in natura*, confirming the efficiency of this material.

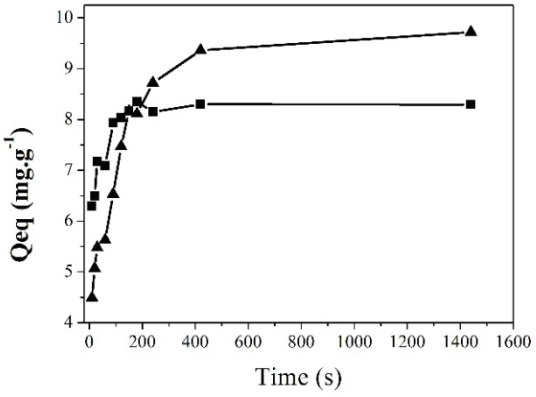

Figure 3. Influence of time on the adsorption of methylene blue by adsorbents (■) *in natura* and (▲) modified.

For better understanding of this mechanism, models of pseudo-first order, pseudo-second order, Elovich equation and intra-particle diffusion were applied (Doğan, Alkan, Türkyilmaz, & Özdemir, 2004; Gerola et al., 2013; Kalavathy, Karthikeyan, Rajgopal, & Miranda, 2005; Özcan, Özcan, Tunali, Akar, & Kiran, 2005; Pérez-Marín et al., 2007). The values found for each model are presented in Table 1.

Table 1. Kinetic parameters of models: pseudo first order, pseudo second order, Elovich and intra-particle diffusion.

Models		Samples	
		In natura	Modified
Pseudo fist Order $\log(q_{eq} - q_t) = \log q_{eq} - \frac{K_1 xt}{2{,}303}$	K_1 (min.$^{-1}$)	-21.923	-6.45E-3
	Qeq(mg g^{-1})	0.691	5.304
	R^2	0.428	0.982
Pseudo secondOrder $\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}}$	K_2 (10^{-3}) (g mg^{-1} min.$^{-1}$)	2.82E-2	3.17E-3
	Qeq(mg g-1)	8.32	9.93
	QeqExp(mg g-1)	8.15	8.72
	R^2	0.999	0.999
Elovich $Qt = A + B \ln t$	A	-8.07	1.434
	B	1.660	13.232
	R^2	0.769	0.920
Intra-particle diffusion $qt = K_{id} t^{1/2} + Ci$	K_{id} (mg g^{-1} min.$^{-1/2}$)	0.184	5.254
	C_i(mg g^{-1})	1.351	6.792
	R^2	0.997	0.997

Where: Qeq exp. is the maximum amount of methylene blue dye experimentally adsorbed (mg g^{-1}); q_t is the amount of methylene blue dye adsorbed (mg g^{-1}) in time t; k_1 is the velocity constant of pseudo-first order; k_2 is the velocity constant of pseudo-second order; A and B are Elovich constants; k_{id} is the intra-particle diffusion rate and C_i is the constant of the idea on the limiting layer thickness.

The experimental data showed that the mathematical models that fit better to this system are the pseudo-second-order and intra-particle diffusion. The first presented values of linear correlation coefficient (R2) near to 1. In addition, the values of Qeq calculated for the pseudo-second order model are very close to the obtained experimentally, indicating that the interaction of biosorbent with the dye was relatively high. The intra-particle diffusion model assumes that the adsorption rate decreases with the time due to the increased surface coverage (Tseng, Wu, Juang, 2003).

Adsorption isotherm

The comparison of the curves in Figure 4 showed that, in low concentrations, both residues have similar adsorption capacities; however, with the increased concentration, the modified adsorbent presented higher efficiency.

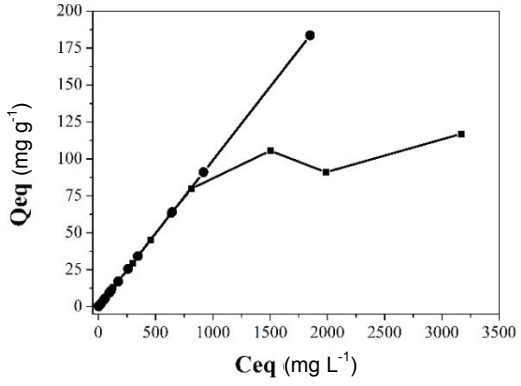

Figure 4. isotherms of adsorption of methylene blue by macadamia adsorbents (■) *in natura* and (▲) modified.

Nevertheless, in higher concentrations the methylene blue can form dimers. This occurs when the dye molecules have a tendency to aggregate in aqueous solutions due to the hydrophobic character of their molecular structure, influencing the physisorption of molecules on the adsorbent, so the adsorbate may find diffusion resistance until it reaches the adsorbent site (Ghanadzadeh, Zeini, Kashef, & Moghadam, 2008). Besides the possibility of formation of dimers, the modified adsorbent has higher adsorption capacity than the *in natura* adsorbent. The maximum adsorption capacity in equilibrium was 117 mg g^{-1} for the biomass *in natura* and 184 mg g^{-1} to the modified one, an increase of approximately 36%.

In order to evaluate the adsorption mechanism in relation to the concentration, the experimental data presented in Figure 4 were adjusted to mathematical models: Langmuir, Freundlich, Dubinine Radushkevich (DER) and Temkin (Kalavathy et al., 2005; Massocatto et al., 2013, Temkin & Pyzhev, 1960). The values obtained for the isothermal parameters are presented in the Table 2.

Analyzing the data in Table 2, it was found that the Freundlich model was more adjusted to this system, because it presents the linear correlation coefficient (R^2) 0.976 and 0.998 for the adsorbents *in natura* and modified, respectively. This model assumes that the adsorption occurs in multilayer at the surface of the adsorbent; therefore, it is widely used in heterogeneous surfaces (Kalavathy et al., 2005). The results corroborate the kinetic model of pseudo-second order, indicating a strong interaction between the adsorbent and the adsorbate.

Comparing q_m values for Macadamia shells with other biosorbents (Table 3), an advantage in terms of maximum adsorption capacity is attained by using the residue macadamia biomass. It can be seen that the capacity result in this study, 184 mg g^{-1} at pH 7.0, is relatively better than most of the results shown in the studies cited in Table 3. The q_m value was slightly lower than the $ZnCl_2$ activated carbon macadamia nut (Pezoti Junior et al., 2014), which uses a relatively expensive material.

Table 2. Isothermal parameters for the models of Langmuir, Freundlich, Temkin and Dubinine (DER).

Models		Samples	
		In natura	Modified
Langmuir $\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m}$	q_m (mg g^{-1})	221.23	-37878.88
	b (L mg^{-1}) (10^{-4})	4.840E-4	-2.540E-4
	R^2	0.721	0.056
Freundlich $\log q_{eq} = \log K_f + \left(\frac{1}{n}\right) \log C_{eq}$	K_f(mg g^{-1})	0.129	0.483
	N	1.07	3.52
	R^2	0.985	0.918
Temkin $q = B_1 \ln K + B_1 \ln_c$	K_t(K J mg^{-1})	0.031	0.879
	B_1 ($dm^3 mg^{-1}$)	20.29	117.63
	R^2	0.803	0.294
Dubinini (DER) $\ln q_e = \ln q_d - B_d E^2$	q_d(mg^2 kJ^{-2})	20.26	277.78
	B_d(mg^2 kJ^{-2})	5.125E-5	1.984E-6
	R^2	0.379	0.758

Where: q_m is the measure of the capacity that indicates the adsorption intensity; b is the constant that indicates the adsorption intensity; K_f is Freundlich constant; n is a constant that relates the adsorption intensity; K is the linking equilibrium constant; B_1 is related to the adsorption heat; q_d is the capacity of theoretical saturation; B_d is a constant related to the average free energy of adsorption by methylene blue dye mols.

Table 3. The list of adsorbents available for adsorption of methylene blue dye.

Adsorbents	q_m (mg g^{-1})	pH	mass (g)	References
Biochars palm bark	2.95	7.0	0.4	(Sun, Wana, & Luo, 2013)
Biochars eucalyptus	2.00	7.0	0.4	(Sun et al, 2013)
Peach palm waste	78.98	7.0	0.5	(Honorato et al., 2015)
Corn straw	106.00	7.0	0.5	(Honorato et al., 2015)
$ZnCl_2$-activated carbon Macadamia nut	194.00	7.0	0.025	(Pezoti Junior et al., 2015)
Daucuscarota plant Waste	66.60	7.0	0.1	(Kushwaha, Gupta, & Chattopadhyaya, 2013)
Macadamia shell	184.00	7.0	0.5	This study

Thermodynamic parameters

Thermodynamic parameters related to the energy changes associated with the adsorption process between the adsorbate and adsorbent including ΔH (enthalpy variation), ΔS (entropy variation), and ΔG (variation of Gibbs' energy) were also determined. Therefore, at pH 7.0, 0.5 g of adsorbents were stirred with 50.0 mL of solution at 100.0 mg L^{-1} concentration in the temperature range of 10-60°C for 240 minutes. Using the graphic of $\ln K_d$ *versus* 1 T^{-1}, the value $\Delta H\left(\frac{-\Delta H}{R}\right)$was calculated from the angular coefficient of the straight line, which provided $T\Delta S$ $\left(\frac{\Delta S}{R}\right)$, according to Equation 2 (Vilas Boas et al., 2015).

$$\ln K_d = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{R}\right)\frac{1}{T} \quad (2)$$

where:

K_d is the adsorbate distribution coefficient (L g^1), which corresponds to the ratio between q_{eq} and C_{eq}, T is the temperature in Kelvin (K), R is the universal gases constant (8.314 JK^{-1} mol^{-1}). With the calculated values of enthalpy and entropy, it is possible to determine ΔG values in Equation 3, which refer to the adsorption spontaneity, where the more negative the ΔG value, the more spontaneous the adsorption process (Vilas Boas et al., 2015).

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

The thermodynamic parameters show that, for both adsorbents, the adsorption is energetically favorable, since it showed negative values for the Gibbs free energy with 0.33 kJ mol^{-1} for in natura residue and -337.00 kJ mol^{-1} for the modified one. However, it can be noted that after the chemical modification, the process has become more spontaneous, which corroborates the higher adsorption capacity. It was also found that the process is exothermic due to the negative enthalpy (-49.55 kJ mol^{-1} *in natura* and -390.00 kJ mol^{-1} modified) and an ordering on the surface of the adsorbent by negative values of entropy occurred (-19.54 $JK^{-1}mol^{-1}$ *in natura* and -20.70 $JK^{-1}mol^{-1}$ modified). The values were calculated at 30°C.

Conclusion

The Macadamia biomass, *in natura* and modified, presented good adsorption capacity, obtaining a value closer to the activated carbon material, which is considered the best adsorbent, with a kinetic described by models of the pseudo-second order and intra-particle diffusion. In the isotherm study, the Freundlich model was the best adjusted for both models, with a higher efficiency of the modified biomass than the *in natura* one for the removal of methylene blue. Furthermore, the adsorption in this study occurred spontaneously and was energetically favorable.

Acknowledgements

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