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Malachite green adsorption by mango (*Mangifera indica* L.) seed husks: Kinetic, equilibrium and thermodynamic studies

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ABSTRACT

Mango seed husks (MSH), an agricultural waste, was evaluated as an adsorbent for removal of malachite green (MG) from aqueous solutions. Batch adsorption tests were performed at room temperature and the effects of contact time and initial solution pH were investigated. Equilibrium was attained after 2 h for all the tested initial MG concentrations (100–500 mg L^{-1}). Adsorption kinetics was determined by fitting pseudo first and second-order kinetic models to the experimental data, with the pseudo second-order model providing the best description of MG adsorption by MSH. The experimental adsorption equilibrium data were fitted to Langmuir and Freundlich adsorption models, with Freundlich providing the best fit. Evaluation of thermodynamics parameters indicated that the adsorption is spontaneous (ΔG^o = –4190 J mol^{-1} at 30°C) and exothermic (ΔH^o = –66.2 KJ mol^{-1}). Maximum adsorption capacity was 47.9 mg g^{-1}, comparable to other untreated agricultural residues such as rattan sawdust and lemon peel. The experimental data obtained in the present study indicate that this type of waste material is a suitable candidate for use as a biosorbent in the removal of cationic dyes.

Keywords: Adsorption; Agri-food waste; Toxic pollutants

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1. Introduction

Malachite green (MG) is an *N*-methylated diaminotriphenylmethane dye widely used by fish (topical fish treatment against protozoal and fungal infections), food (coloring agent, food additive), textile (dye in silk, wool, jute, and leather cotton), paper and acrylic industries [1]. Toxicological studies have shown that, in the tissues of fish and mice, this dye is reduced to persistable leucomalachite green, which acts as a tumor promoter [2]. Also, MG degradation products present carcinogenic potential [3].

Given the high toxicity of MG and its employment by a wide variety of industries, several studies are available regarding its removal from wastewater. Employed techniques include photo-degradation [4], photo-catalytic degradation [5] and adsorption [1,6–11]. Though the removal of dyes through activated carbon adsorption is quite effective, the large-scale application of activated carbon is still restricted due to both fabrication and regeneration high costs [6]. Lately, there has been a growing interest in using low cost adsorbents for dye removal and

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recent studies have demonstrated that a wide variety of agricultural residues can be employed, with minimum treatment (drying, grinding), as biosorbents for the removal of dyes from wastewaters [12].

Mango (*Mangifera indica* L.) is a fruit grown in almost all tropical and sub-tropical regions of the world, and Brazil is the ninth producer and the second exporter in the world [13]. Mango production solid wastes represent 28–43% of the fruit weight and include the peel, stalk trimmings, fibrous material and the pit [14]. The mango pit is formed by three constituents: the husk (MSH), the thin seed coat and the embryo or seed (MS). A few recent studies have shown that both MS and MSH can be employed for removal of methylene blue (MB) from aqueous solutions [15,16]. In the case of MSH, the maximum value of uptake capacity was 27.8 mg g^{-1}, high in comparison to values encountered in the literature for other untreated agricultural by-products and wastes, including spent coffee grounds (18.7 mg g^{-1}) and wheat shells (16.6 mg g^{-1}) [17,18]. Adsorption was fast and effective even at high initial MB concentrations, indicating that this agricultural waste is a potential adsorbent for the removal of cationic dyes in wastewater treatments. No other studies were found regarding kinetics and equilibrium data for mango seed husks as biosorbents.

In view of the aforementioned, and the fact that there are no studies available on the use of mango seed husks (MSH) for the removal of malachite green (MG), the objectives of this study were (i) to evaluate the kinetics, equilibrium and thermodynamic aspects of this process, and (ii) to confirm the potential of such residue as a biosorbent for the removal of basic dyes in wastewater treatment.

2. Materials and methods

2.1. Materials

Mango seed husks were removed from mango fruits (Palmer variety) employing a kitchen knife and submitted to overnight (~20 h) drying at 55°C in a convective oven. The dry mango seed husks (MSH) were then cut into small pieces, ground and sieved. The cationic dye used as target adsorbate was malachite green (malachite green oxalate salt — $C_{23}H_{25}N_2 \cdot C_2HO_4 \cdot 0.5C_2H_2O_4$), purchased from Sigma-Aldrich (São Paulo, Brazil). MG stock solutions were prepared in distilled water. Working solutions (100–500 mg L^{-1}) were prepared by diluting the stock solution with distilled water prior to each adsorption test.

2.2. Adsorbent characterization

The point of zero charge (pH_{PZC}) was obtained by employing a mass titration method [19]. Three aqueous solutions of different pH´s (3, 6 and 11) were prepared. Different amounts of adsorbent (0.05%, 0.1%, 0.5%, 1.0%, 3.0%, 7.0% and 10.0% w/w) were added to 20 mL of each solution to get different rates of adsorbent amounts/volume of solution. The aqueous suspensions were then let to equilibrate for 24 h under agitation (100 rpm) at 25°C. The pH of each solution was measured using a digital pH meter (Micronal, São Paulo, Brazil) and the pH_{PZC} was determined as the converging pH value from the pH vs. adsorbent mass curve. Surface functional groups determination was based on the Boehm titration method [20]. Solutions of $NaHCO_3$ (0.1 mol L^{-1}), Na_2CO_3 (0.05 mol L^{-1}), NaOH (0.1 mol L^{-1}), and HCl (0.1 mol L^{-1}) were prepared with distilled water. A volume of 50 mL of these solutions was added to vials containing 1 g of the adsorbent, shaken for 24 h (100 rpm) and then filtered. Five solution blanks were also prepared. The excess of base or acid was determined by back titration using NaOH (0.1 mol L^{-1}) and HCl (0.1 mol L^{-1}) solutions.

2.3. Adsorption studies

Batch experiments of adsorption were performed using 250 mL Erlenmeyer flasks agitated on a shaker at 100 rpm for pre-determined time intervals. In all sets of experiments, a pre-determined mass of MSH was thoroughly mixed with 100 mL MG solution. Particle size (diameter = D) was defined as $D < 0.43$ mm, based on the results presented by Franca et al. [16] for methylene blue adsorption. Effect of initial solution pH was evaluated in the range of 3–11 at a fixed initial dye concentration (100 mg L^{-1}). Effect of adsorbent dosage was verified in the range of 5–50 g L^{-1} at a fixed initial dye concentration (100 mg L^{-1}). Effect of contact time was evaluated at time periods ranging from 15 min to 24 h, initial dye concentration ranging from 100 to 500 mg L^{-1} and at the following temperatures: 30, 40 and 50°C. All tests were performed in three replicates.

2.4. Analysis of malachite green

After the specified time periods, 2 mL aliquots were taken from the Erlenmeyer flasks and the concentration of MG was determined by a spectrophotometer (Cole Parmer 1100 RS) at 620 nm. The amount of dye adsorbed was evaluated according to the difference between the initial dye concentration and the concentration of the solution at the time of sampling. All determinations were performed in a total of three replicates per experiment and the average values were reported.

2.5. Adsorption kinetics

The controlling mechanism of the adsorption process was investigated by fitting pseudo first and second-order kinetic models to the experimental data [21]. The kinetic rate equations can be written as:

$$\frac{dq_t}{dt} = k_n \left(q_e - q_t\right)^n \tag{1}$$

where q_e and q_t represent the amount of dye adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium and at time t, respectively; k_n is the rate constant for nth order adsorption (k_n units are min^{-1} for $n = 1$ and g $mg^{-1}min^{-1}$ for $n = 2$). Selection of the best-fit model was based on both linear regression correlation coefficient values (R^2) and the difference between calculated and experimental q_e values. The linear integrated forms of Eq. (1) are:

Pseudo first-order kinetics ($n = 1$):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

Pseudo second-order kinetics ($n = 2$):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

It is noteworthy to mention that the application of the pseudo first order model in its linear integrated form requires previous knowledge of the equilibrium capacity (q_e). Such value was obtained by a trial and error procedure, in order to obtain the highest possible correlation coefficient (R^2) values.

2.6. Adsorption equilibrium

Langmuir, Freundlich and Tempkin models were tested for equilibrium description [22]. Langmuir isotherm is a theoretical model based on the assumption of monolayer adsorption over an energetically and structurally homogeneous adsorbent surface. It can be represented by the following equation:

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

where q_e (mg g^{-1}) is the amount adsorbed per gram of adsorbent and C_e (mg L^{-1}) corresponds to the solute concentration in the aqueous solution, after reaching equilibrium conditions. $q_{\max}$ and K_L are constants related to the maximum adsorption capacity (mg g^{-1}) and the adsorption energy (L mg^{-1}), respectively. Another characteristic parameter of the Langmuir isotherm, the separation factor r, is related to the shape of the isotherm. Its value indicates either unfavorable ($r > 1$), linear ($r = 1$), favorable ($0 < r < 1$) or irreversible ($r = 0$) adsorption. It can be calculated as:

$$r = (1 + K_L C_0)^{-1} \qquad (5)$$

where C_0 is the highest value for initial sorbate concentration (mg L^{-1}).

Freundlich´s equation, on the other hand, is an empirical model based on heterogeneous adsorption over independent sites. It can be represented by the following equation:

$$q_e = K_F C_e^{1/n} \qquad (6)$$

where K_F is the relative adsorption capacity ($mg1^{-(1/n)}$ $L^{1/n}$ g^{-1}) and $1/n$ is related to the intensity of adsorption. This model does not account for adsorbent saturation, given that no limit is imposed on the adsorption capacity.

The Tempkin isotherm assumes a linear decrease in sorption energy as the adsorption sites are filled, with the heat of adsorption decreasing linearly with surface coverage due to adsorbent–adsorbate interactions. Adsorption is also characterized by a uniform distribution of binding energies, up to a maximum value. It can be represented by the following equation:

$$q_e = \frac{RT}{b} \ln\left(K_T C_e\right) \qquad (7)$$

where b is the Tempkin constant related to the heat of sorption (J mol^{-1}), K_T is the Tempkin isotherm constant (L g^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

The best-fit model selection was based on both linear regression correlation coefficient (R^2) and a non-linear χ^2-statistic (SS) determination test, with SS providing a measure of the difference between experimental and calculated qe values:

$$\mathrm{SS} = \sqrt{\sum \left(q_{e,\mathrm{calc}} - q_{e,\mathrm{exp}}\right)^2 / N} \qquad (8)$$

where N corresponds to the number of experimental points.

2.7. Thermodynamic parameters

The free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were determined in order to evaluate the effect of temperature on MG adsorption by mango seed husks. The Gibbs free energy was evaluated as:

$$\Delta G^o = -RT \ln K^o \qquad (9)$$

where $\Delta G°$ is the standard Gibbs free energy change (J), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K) and K^0 is the standard thermodynamic equilibrium constant of the adsorption system. It can be obtained by calculating the apparent equilibrium constants (K) at different initial concentrations of dye and extrapolating the data to zero [23]. The equilibrium constant is defined as:

$$K = \frac{C_{ad,e}}{C_e} \qquad (10)$$

where C_e and $C_{ad,e}$ correspond to the equilibrium concentration of MG on the solution and on the adsorbent, respectively. Enthalpy ($\Delta H°$) and entropy ($\Delta S°$) values were obtained from the slope and intercept of a van't Hoff equation of $\Delta G°$ vs. T:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (11)$$

3. Results and discussion

3.1. Adsorbent characterization

The experimental titration curves for evaluation of the point of zero charge converged to a pH_{PZC} value of approximately 4.5 (Fig. 1) and therefore pH values should be maintained over 5 to ensure a predominant negatively charged surface. The functional groups at the surface of the adsorbent, characterized by the Boehm method, were predominantly acidic (phenolic: 0.97 mmol/$g_{sorbent}$; lactonic: 0.84 mmol/$g_{sorbent}$; carboxylic: 0.26 mmol/$g_{sorbent}$; basic: 0.02 mmol/$g_{sorbent}$). The acidic character of the surface is in agreement with the low pH_{PZC} value and also with available literature data regarding chemical characterization of this specific residue [15].

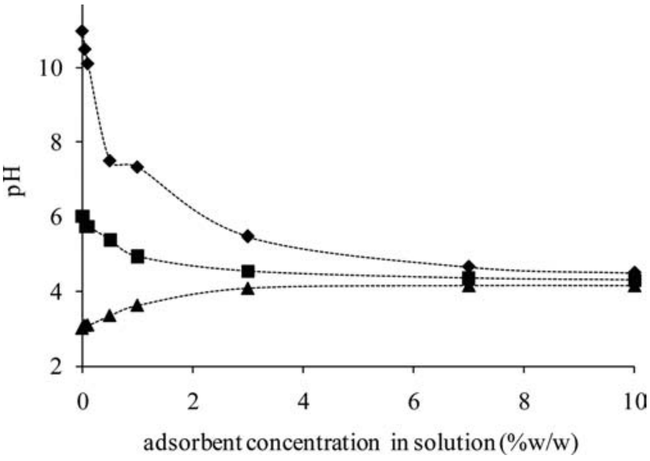

Fig. 1. Experimental curves for pH_{PZC} determination. ▲ Initial pH = 3, ■ Initial pH = 6, ◆ Initial pH = 11.

3.2. Influence of initial solution pH

The aqueous solution pH is expected to affect the adsorption of dyes due to its impact on both the surface binding-sites of the adsorbent and the ionization process of the dye molecule [24]. In the present study, the effect of pH was investigated for values between 3 and 11 (Fig. 2a). The adsorption capacity was higher in the pH range of 5–9, without significant differences in this pH range (based on the Tuckey test at 5% probability). Such results indicated that, above the pH_{PZC} value, the adsorbent surface became predominantly negatively charged (i.e., with most of the oxygenated acidic groups being present in their deprotonated form), thus, enhancing the electrostatic attraction between the surface and MG cations. Given the fact that in this pH range the dye molecule will present its nitrogen end positively charged, it is most likely that the adsorption of the dye molecule will be of the end-on type, due to the electrostatic interaction with the negatively charged oxygenated acidic groups at the surface. Possible hydrophobic interactions between the husks surface and the dye molecule are not to be ruled out, considering that the husks contain a certain amount of lignin [15] which is comprised of aromatic alcohols and, thus, will present a certain amount of delocalized π-electrons on the carbon surface. pH measurements after the adsorption tests indicated that the final solution pH showed a tendency towards the pH_{PZC} value, and that such pH value was only attained after 2 h adsorption for the tests with initial pH in the range of 5–9. Similar results were reported by Gong et al. [8] for MG adsorption by rice straws. Based on these results, the remaining tests were conducted at pH = 5, since it is the value closest to the natural pH of the MG solution (~3) that provided satisfactory adsorption performance.

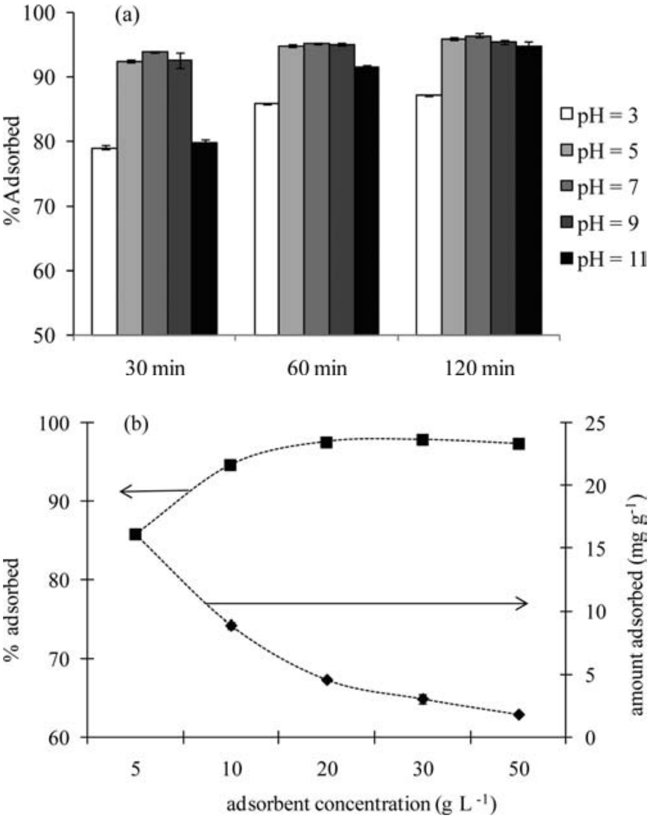

Fig. 2. Effect of (a) initial solution pH and (b) adsorbent concentration on MG adsorption by mango seed husks (30°C, initial MB concentration 100 mg L^{-1}).

3.3. Influence of adsorbent dosage

The influence of adsorbent dosage on the efficiency of MG removal is shown in Fig. 2b. MG removal efficiency increased with an increase in adsorbent dosage. After 2 h, the percent removal of MB varied from 88 to 97% with an increase in adsorbent concentration from 5 to 20 g L^{-1}. This is attributed to the increase in surface area (and corresponding increase in the number of active adsorption sites) resulting from the respective increase in adsorbent mass. However, MG removal efficiency did not change with the increase in adsorbent dosage from 20 to 50 g L^{-1}. This is attributed to the fact that mixing and consequent mass transfer is hindered by the increase in adsorbent dosage. The amount of dye adsorbed per unit mass of adsorbent decreased with increasing adsorbent mass. This was expected, since the dye amount remained constant as the adsorbent mass was increased. Based on the results presented in Fig. 2b, the remaining experiments were conducted for an adsorbent dosage of 5 g L^{-1}.

3.4. Adsorption kinetics

The results obtained for varying contact time and initial dye concentration are displayed in Fig. 3. Experiments were conducted employing the following parameters: adsorbent dosage of 5 g L^{-1}, initial solution pH adjusted to 5 and D < 0.43 mm. The results presented in Fig. 3 show that a contact time of 2 h assured attainment of equilibrium conditions, regardless of the initial MG concentration. An evaluation of all curves shows that adsorption presented a two-stage kinetic behavior, with a rapid initial adsorption during the first 15 min, followed afterwards by a slower rate. The amount of MG adsorbed ranged from 15.7 to 46.5 mg g^{-1} after 15 min and from 19.9 to 50.3 mg g^{-1} after 2 h. A similar behavior was reported for MG adsorption by chitosan beads [1]. The initial fast adsorption is an indication that MG adsorption occurs mainly on the surface of the adsorbent, given its acidic characteristic. Results presented in Fig. 3 also show that sorption of MG by MSH presents a strong dependency on dye initial concentration. The amount adsorbed increased with an increase in initial MG concentration, given the corresponding increase in driving force, i.e., MG concentration gradient between the solution and the adsorbent.

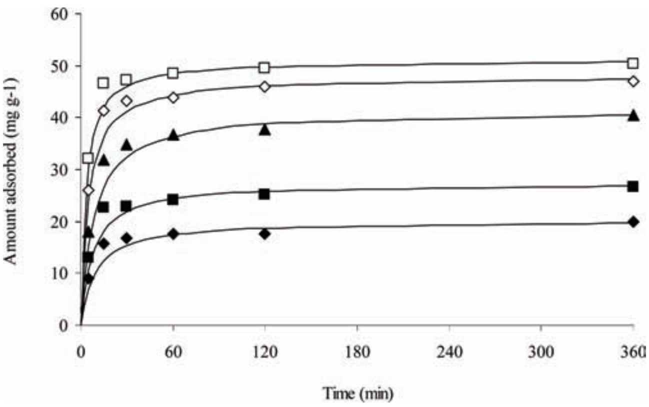

Fig. 3. Effect of contact time on MG adsorption by mango seed husks (30°C, initial pH = 5). Initial dye concentration: ◆ 100 mgL^{-1}, ■ 200 mgL^{-1}, ▲ 300 mgL^{-1}, ◇ 400 mgL^{-1}, □ 500 mgL^{-1}. Solid lines correspond to pseudo-second order kinetics model fits.

The controlling mechanism of MG adsorption by MSH was investigated by fitting pseudo first and second-order models to the experimental data for the adsorption dynamics at room temperature (30°C). The results of the kinetic parameters are displayed in Table 1. The pseudo first-order model did not provide a good fit, with lower correlation coefficients in comparison to the pseudo second-order model. Furthermore, q_e values were significantly underestimated. Such poor estimate could be improved by employing a non-linear regression procedure. An evaluation of both the correlation coefficients and estimated q_e values indicates that MG adsorption by MSH can be satisfactorily described by the pseudo second-order model, in agreement with other MG biosorption studies [1,11] and also suggesting chemisorption as the rate controlling mechanism [21]. The values of q_e increased with increasing concentration of MG, as a consequence of the enhanced mass transfer rate at the adsorbent surface, indicating that boundary layer resistance is not the rate limiting step [25].

3.5. Adsorption equilibrium

The adsorption isotherms at 30, 40 and 50°C are presented in Fig. 4. The shape of the curves confirms favorable adsorption, as can be also corroborated by the calculated value of the separation factors (r) displayed in Table 2. Coefficients for the Langmuir, Freundlich and

Table 1
Kinetic parameters for MG adsorption by MSH

Initial dye concentration (mg L^{-1})	q_e (exp.)	Pseudo first-order				Pseudo second-order			
		qe	% dif.*	k_1	R^2	q_e	% dif.*	k_2	R^2
100	20.28	9.11	–55	0.0203	0.9537	20.41	0.6	0.0051	0.9999
200	27.38	11.19	–59	0.0238	0.9727	27.59	0.8	0.0047	0.9999
300	41.56	15.45	–63	0.0193	0.9732	41.77	0.5	0.0028	0.9999
400	48.03	12.08	–75	0.0226	0.9802	48.17	0.3	0.0042	1.0000
500	51.22	8.16	–84	0.0209	0.9694	51.31	0.2	0.0057	0.9999

*percent difference between calculated and experimental q_e values

Table 2
Langmuir and Freundlich isotherm constants for MG adsorption by MSH

Model	Temperature		
	30°C	40°C	50°C
Langmuir			
K_L (L mg^{-1})	0.0369	0.0370	0.0167
$q_{\max}$ (mg g^{-1})	47.85	43.48	31.25
r	0.05–0.21	0.05–0.21	0.11–0.37
R^2	0.8656	0.7738	0.9034
SS	5.63	3.79	3.21
Freundlich			
K_F (mg1$^{-(1/n)}$L$^{1/n}$ g^{-1})	6.547	6.322	2.136
$1/n$	0.36	0.36	0.47
R^2	0.9494	0.8882	0.9249
SS	2.91	2.78	2.06
Tempkin			
K_T (L g^{-1})	0.228	0.239	0.086
b (J mol^{-1})	212.3	243.9	295.6
R^2	0.8955	0.8717	0.8358
SS	3.86	2.99	2.64

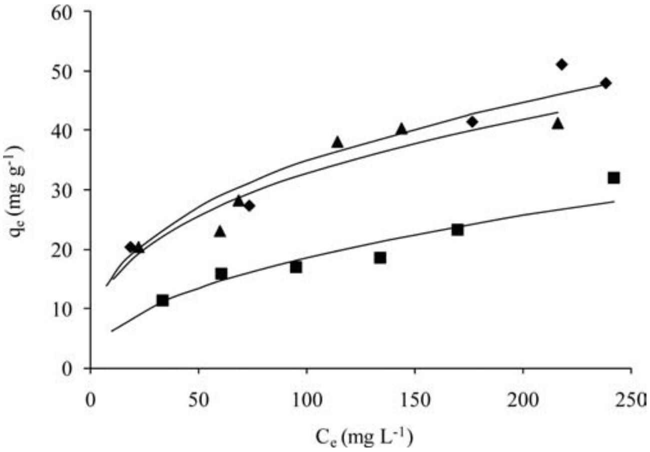

Fig. 4. Adsorption isotherms of MG by mango seed husks: ◆ 30°C, ▲ 40°C, ■ g 50°C. Solid lines correspond to Freunlich model fits.

Table 3
Langmuir based maximum adsorption capacity of some biosorbents for MG adsorption at room temperature

Adsorbent	q_0 (mg g^{-1}) (Temperature, °C)	Reference
Rice straw	94.3 (20)	[8]
Chitosan bead	93.6 (30)	[1]
Rattan sawdust	62.7 (30)	[11]
Mango seed husks	47.9 (30)	This study
Lemon peel	43.5 (32)	[9]
Marine algae	19.9 (25)	[10]
Bentonite clay	7.7 (30)	[26]

Tempkin adsorption models are displayed in Table 2. MG adsorption from aqueous solutions by MSH was better described by Freundlich model in comparison to both Langmuir and Tempkin, indicating heterogeneous adsorption. The best fit of the Freundlich model was determined both by its higher value of R^2, the linear regression correlation parameter, and lower value of SS, the parameter that measures the difference between the experimental and the estimated qe values. Maximum MG uptake capacity, represented by qmax in Langmuir equation, was 47.9 mg g^{-1}, a comparable value to other agricultural residue-based biosorbents reported in the literature for MG adsorption at room temperature (Table 3). Adsorption capacity was low compared to some residues, such as sawdust, rice straws and chitosan beads. However, such results do not preclude the feasibility of employing MSH as adsorbents for MG removal from aqueous solutions, since it presented good adsorption capacity in comparison to other low cost residues. It is noteworthy to mention that the equilibrium data from the previously mentioned biosorbents, e.g. rattan sawdust and chitosan beads, were better described by Langmuir as opposed to the better fit obtained for Freundlich employing mango seed husks. This can be attributed, in the case of rattan sawdust and chitosan beads, to the monolayer adsorption of MB molecules occurring both on the surface and also inside micropores of those adsorbents [27], thus confirming that, in the case of mango seed husks, adsorption occurs mainly on the surface. Such results are also in agreement with the faster MG adsorption of mango seed husks in comparison to the previously mentioned biosorbents.

3.6. Thermodynamic parameters

Results for thermodynamic parameters evaluation are displayed in Table 4 and Fig. 5. The negative $\Delta G°$ values obtained for MG adsorption at various temperatures confirm the spontaneous characteristic of the process. The standard enthalpy and entropy changes of biosorption were –50 kJ mol^{-1} and –0.15 kJ mol^{-1} K^{-1}, respectively. The negative value of $\Delta H°$ confirms the exothermic nature of MG biosorption by mango seed husks and the negative $\Delta S°$ value confirms the decreased randomness at the solid–solute interface during biosorption.

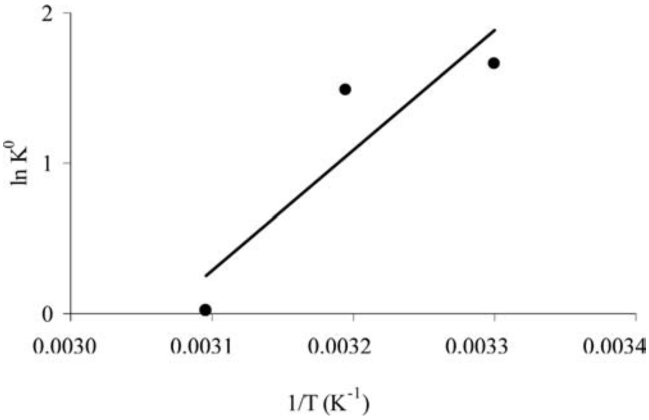

Fig. 5. Van't Hoff plot for determination of ΔH^o and ΔS^o (ln K^0 vs. 1/T).

Table 4
Thermodynamic parameters for MG adsorption by MSH

	Temperature (°C)		
	30	40	50
K^o	5.37	4.52	1.57
ΔG^o (J mol^{-1})	–4234	–3929	–1214
ΔH^o (KJ mol^{-1})		–50.4	
ΔS^o (J mol^{-1} K^{-1})		–0.15	

4. Conclusions

Experiments were conducted to investigate the potential of mango seed husks (MSH) as adsorbents for the removal of malachite green (MG) from aqueous solutions. The adsorbent presented a better adsorption performance at pH values above its pH_{PZC} value (4.5), which suggests that the adsorption of the dye molecule will be of the end-on type, due to the electrostatic interaction with the negatively charged oxygenated acidic groups at the surface in that pH range. Equilibrium data demonstrated favorable adsorption and were better described by Freundlich model, indicating heterogeneous adsorption. The maximum value of uptake capacity obtained for the MSH/MG system was comparable to values encountered in the literature for other untreated agricultural by-products and wastes. Although MSH presented lower uptake capacity than other residues, adsorption was quite fast and effective, even at higher initial MG concentrations. Adsorption kinetics was well described by the pseudo-second-order kinetic model equation. The results presented in this study confirm that mango seed husks presents great potential as a fast, inexpensive and easily available alternative adsorbent for the removal of cationic dyes in wastewater treatments.

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References

[1] Z. Bekci, C. Ozveri, Y. Seki and K. Yurdakoc, Sorption of malachite green on chitosan bead, J. Hazard. Mater., 154 (2008) 254–261.

[2] S.J. Culp and F.A. Beland, Malachite green: A toxicological review, J. Am. Coll. Toxicol., 15 (1996) 219–238.

[3] S. Srivastava, R. Sinha and D. Roy, Aquat.Toxicol., Toxicological effects of malachite green, 66 (2004) 319–329.

[4] K. Rajeshwar, M.E. Osugi, W. Chanmanee, C.R. Chenthamarakshan, M.V.B. Zanoni, P. Kajitvichyanukul and R. Krishnan-Ayer, Heterogeneous photocatalytic treatment of organic dyes in air, aqueous media, J. Photoch. Photobio., C 9 (2008) 171–192.

[5] F. Sayilkan, M. Asilturk, P. Tatar, N. Kiraz, E. Arpac and H. Sayilkan, Preparation of re-usable photocatalytic filter for degradation of Malachite Green dye under UV and vis-irradiation, J. Hazard. Mater., 148 (2007) 735–744.

[6] R. Gong, M. Feng, J. Zhao, W. Cai and L. Liu, Functionalization of sawdust with monosodium glutamate for enhancing its malachite green removal capacity, Bioresource Technol., 100 (2009) 975–978.

[7] A. Mittal, Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers, J. Hazard. Mater., 133 (2006) 196–202.

[8] R. Gong, Y. Jin, F. Chen, J. Chen and Z. Liu, Enhanced malachite green removal from aqueous solution by citric acid modified rice straw, J. Hazard. Mater., 137 (2006) 865–870.

[9] K.V. Kumar, Optimum sorption isotherm by linear and nonlinear methods for malachite green onto lemon peel, Dyes Pigments, 74 (2007) 595–597.

[10] Z. Bekci, Y. Seki and L. Cavas, Removal of malachite green by using an invasive marine alga *Caulerpa racemosa* var. *cylindracea*, J. Hazard. Mater., 161 (2009) 1454–1460.

[11] B.H. Hameed and M.I. El-Khaiary, Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modeling, J. Hazard. Mater., 159 (2008) 574–579.

[12] L.S. Oliveira and A.S. Franca, Low-cost adsorbents from agrifood wastes, In: L.V. Greco and M.N. Bruno, eds., Food Science and Technology: New Research, Nova Publishers, New York, 2008, pp. 171–209.

[13] FAO Agricultural production: crops primary-production mangoes. Available in:http://www.fao.org/es/ess/top/commodity.html?lang=en&item=571&year=2005 (2008) Accessed on 29/12/2008.

[14] D. Puravankara, V. Boghra and R.S. Sharma, Effect of antioxidant principles isolated from mango (*Mangifera indica* L.) seed kernels on oxidative stability of buffalo ghee (butter-fat), J. Sci. Food Agr., 80 (2000) 522–526.

[15] M.P. Elizalde-Gonzalez and V. Hernandez-Montoya, Characterization of mango pit as raw material in the preparation of activated carbon for wastewater treatment, Biochem. Eng. J., 36 (2007) 230–238.

[16] A.S. Franca, L.S. Oliveira, P.I.A. Santos, S.A. Saldanha and S.A. Salum, Mango seed husks as biosorbents for basic dyes, J. Biotech., 136 (2008) S655.

[17] A.S. Franca, L.S. Oliveira and M.E. Ferreira, Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds, Desalination, 249 (2009) 267–272.

[18] Y. Bulut and H. Aydin, A kinetic and thermodynamic study of methylene blue adsorption on wheat shells., Desalination, 194 (2006) 259–267.

[19] H. Valdés, M. Sánchez-Polo, J. Rivera-Utrilla and C.A. Zaror, Effect of ozone treatment on surface properties of activated carbon, Langmuir, 18 (2002) 2111–2116.

[20] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks on other carbons, Carbon, 32 (1994) 759–769.

[21] Y.S. Ho and G. McKay, A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Process Saf. Environ., 76 (1998) 332–340.

[22] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London, 1998.

[23] Z. Aksu, A. I. Tatli and O. Tunc, A comparative adsorption/biosorption study of Acid Blue 161: Effect of temperature on equilibrium and kinetic parameters, Chem. Eng. J., 142 (2008) 23–39.

[24] M.C. Ncibi, B. Mahjoub and M. Seffen, Kinetic and equilibrium studies of methylene blue biosorption by *Posidonia oceanica* (L.) fibres, J. Hazard. Mater., 139 (2007) 280–285.

[25] X.-F. Sun, S.-G. Wang, X.-W. Liu, W.-X. Gong, N. Bao, B.-Y. Gao and H.-Y. Zhang, Biosorption of Malachite Green from aqueous solutions onto aerobic granules: Kinetic and equilibrium studies, Bioresource Technol., 99 (2008) 3475–3483.

[26] S.S. Tahir and N. Rauf, Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay, Chemosphere, 63 (2006) 1842–1848.

[27] A.S. Franca, L.S. Oliveira, A.A. Nunes and C. C. Alves, Microwave assisted thermal treatment of defective coffee beans press cake for the production of adsorbents, Bioresource Technol., 101 (2010) 1068–1074.