An Acad Bras Cienc (2023) 95(Suppl. 2): e20210124 DOI 10.1590/0001-3765202320210124
Anais da Academia Brasileira de Ciências | *Annals of the Brazilian Academy of Sciences*
Printed ISSN 0001-3765 I Online ISSN 1678-2690
www.scielo.br/aabc | www.fb.com/aabcjournal

CHEMICAL SCIENCES

A ‘green’ adsorbent: effect of chemical modification of biosorbents on the adsorption of methylene blue and malachite green

STEPHANY B. FRANCESCHINI, CAROLINE P. SENDESKI, KETHLEENN D. DE LIMA, KELLER P. NICOLINI & JAQUELINE NICOLINI

Abstract: The dyes methylene blue and malachite green were adsorbed onto the as-prepared and chemically-modified biosorbents obtained from the mesocarp of crushed calabash *(Lagenaria siceraria)*. The aim was to investigate the adsorption capacity of the natural biosorbent, neutralized biosorbent (0.1 mol L^{-1} NaOH, followed by 0.1 mol L^{-1} HCl), acid biosorbent (0.1 mol L^{-1} HCl) and basic biosorbent (0.1 mol L^{-1} NaOH). The maximum adsorption capacities for methylene blue were, in ascending order: 11.37 mg g^{-1} for acid biomass < 11.87 mg g^{-1} for basic biomass < 16.55 mg g^{-1} for neutralized biomass < 18.83 mg g^{-1} for natural biomass. In ascending order, for malachite green the maximum adsorption capacities were: 12.80 mg g^{-1} for basic biomass < 13.31 mg g^{-1} for acid biomass < 18.74 mg g^{-1} for natural biomass < 19.67 mg g^{-1} for neutralized biomass. A comparison of the thermodynamic parameters Gibbs free energy, enthalpy and entropy obtained for the natural biosorbent with those obtained for the chemically-modified biosorbents indicated that the chemical modification proposed led to a change in the materials. The removal capacity, the Freundlich isotherms and the pH of the biosorbents underwent changes with the chemical modification carried out, promoting a novel approach for the use of this biosorbent.

Key words: cationic dyes, residual biomass, physico-chemical parameters, *Lagenaria siceraria*.

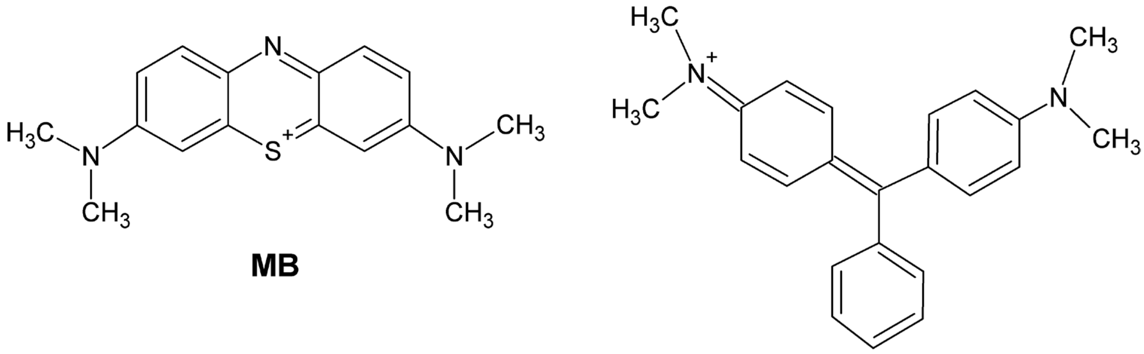
INTRODUCTION

The dyes malachite green and methylene blue are cationic dyes (Figure 1) (PubChem 2021), used for dyeing fabrics (Gupta et al. 2016, Tahir & Rauf 2006). However, the main use of malachite green is as a fungicide in fish farming (Culp & Beland 1996, Hu et al. 2021) and methylene blue is used in basic medicine (Roldan et al. 2021, Wainwright 2003). The colored effluents generated by the textile industry require treatment and this can be carried out using the adsorption technique.

In this regard, alternative biosorbents have been investigated to replace activated carbon, aimed at reducing the cost of the treatment process (Choi & Cho 1996, Grassi et al. 2021). One of the simplest representations of the adsorption phenomenon assumes the migration of the adsorbate (A) to a site (S) at the surface or inside the adsorbent matrix (generally a solid). This can be represented by an equilibrium described as follows (Davis et al. 2003):

$$\mathrm{S} + \mathrm{A} \leftrightarrow \mathrm{SA}, \text{ and : } K_{ads} = \frac{[SA]}{[S][A]}$$

where S is a site on the adsorbent surface and A is the adsorbate.



MB

MG

Figure 1. Structures of methylene blue (MB) and malachite green (MG).

Researchers have studied various absorbents for different adsorbates (Ndiaye et al. 2019, Zheng et al. 2020, Zhu et al. 2020), seeking to reduce the costs of the adsorption processes and obtain good efficiency. Examples include the use of lemongrass leaf for crystal violet and methylene blue (cationic dyes) adsorption (Putri et al. 2021) and the use of *Capparis flexuosa* to remove blue methylene and bright blue (de O. Salomón et al. 2021). In the southern region of Brazil, it is common to cultivate calabash (*Lagenaria siceraria*) of the Cuburbitaceae family. This plant is used all over the world and in Brazil it is employed for the production of gourds ("cuias") for the consumption of a typical drink named "chimarrão" or "mate" (Bracesco et al. 2011). Regarding the morphology of *Lagenaria*, in the internal part, the fruit presents the mesocarp (pulp) and endocarp (placenta and seeds) and more externally the exocarp (Trevisol 2013). For the production of gourds, the internal part of the calabash (mesocarp), which is porous and similar to wood, is subjected to sanding down until it becomes homogenous, generating a biomass residue that is not usable (residual biomass). The skin or shell (exocarp or pericarp) and the internal part, now smooth (center of the mesocarp) (Nejeliski 2015), form the gourds, which are hollow fruits (Bracesco et al. 2011). The residual biomass of calabash, which has no use in the regional matrix, was the biosorbent employed in this study (Figure 2a, b, c and d).

In this study, we used the dyes methylene blue and malachite green as a model, since their adsorption in the presence of *Lagenaria siceraria* as a biosorbent has been little explored in the literature. The adsorption capacity of this specific adsorbent (*Lagenaria*) has been investigated for the removal of nitrate (Nikolić et al. 2021), alizarine dye (de Lima et al. 2021), toxic metals from industrial wastewaters (Ahmed et al. 2018), chromium (VI) using HCl-modified *Lagenaria* (Achary et al. 2020, Ghosh & Mishra 2016) and methylene blue (Biswal et al. 2023, Bojić et al. 2013). However, it is important to note that biosorption studies involving combinations of malachite green and methylene blue dyes with *Lagenaria*, raw or modified with HCl or NaOH and acid–base chemical modification, could not be found in a literature survey.

The aim of this study was to investigate the effect of the chemical modification of a biosorbent in relation to the adsorption of methylene blue and malachite green. The biosorbent used originated from the mesocarp of *Lagenaria* as a residual byproduct produced in the southern region of Brazil. This allows the addition of value to a biomass present in the regional matrix.

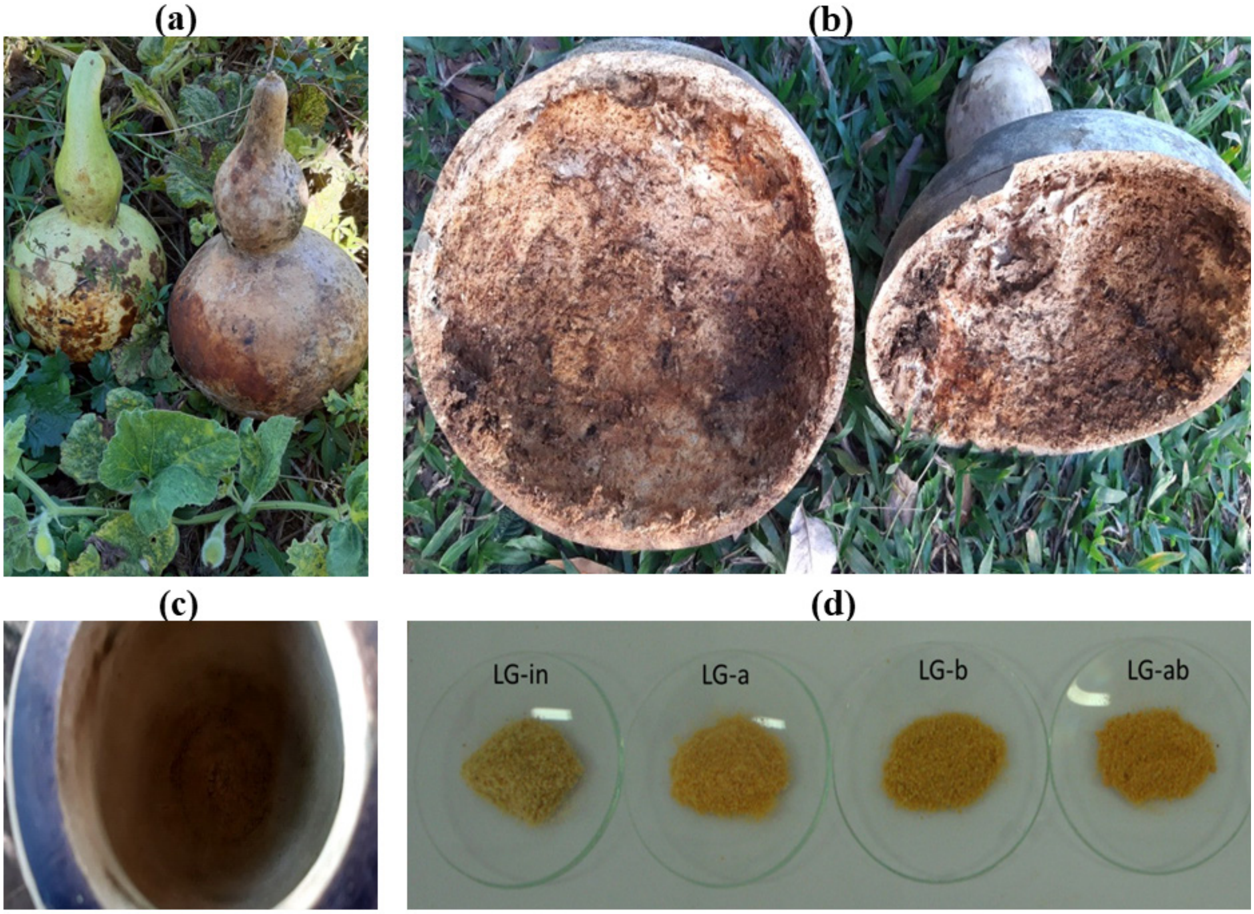


Figure 2. (a) Calabash cultivation. (b) Open calabash before sanding down. (c) Internal part of an open calabash (“cuia”) after sanding down. (d) Biosorbents.

MATERIALS AND METHODS

Reagents and equipaments

The dyes methylene blue (MB) and malachite green (MG) were acquired from Neon (Brazil). All chemical products were used as received, without additional purification. Distilled water was used in all tests. In the determination of the pH of the samples, a digital bench pH meter (Kasvi) was employed, using buffer solutions (Vetec) pH 4.00 and pH 7.00 in order to calibrate the pH meter, with an error of ± 0.02. The absorbances were obtained with a PerkinElmer spectrophotometer (Lambda 365).

Preparation of biosorbents

Lagenaria (LG) is a creeping and resistant plant. The example used in this study was obtained in the region around the municipality of Palmas, Paraná state, southern Brazil (Latitude: -26.47880 S and Longitude: -51.99583 W). Four different materials derived from *Lagenaria* were prepared: (1) natural LG (LG-in); (2) LG chemically modified through acid and basic treatment employing hydrochloric acid and sodium hydroxide (LG-ab); (3) LG chemically modified through treatment with hydrochloric acid (LG-a); and (4) LG chemically modified through treatment with sodium hydroxide (LG-b). The internal part of the LG biomass used was crushed to give a granulometry of 150 µm (0.15 mm), since the smaller the particle size the larger the contact surface and the adsorption capacity of the material (Stanković et al. 2016). The skin, that is, the external part of the LG biomass, was discarded and only the internal part (mesocarp) was used, free from any other parts of the fruit. After the preparation of the material, all of the LG biomass samples were crushed again in order to eliminate small granules formed during the drying process.

(1) *Preparation of LG-in:* the crushed biomass was washed extensively with distilled water until constant pH.

(2) *Preparation of LG-ab*: the crushed and dry biomass was immersed for 24 h in a 0.1 mol L^{-1} NaOH solution and washed extensively again with water. The LG biomass was then left in a 0.1 mol L^{-1} HCl solution for a period of 2-3 h to remove traces of NaOH.

(3) *Preparation of LG-a*: the crushed and dry biomass was immersed in a 0.1 mol L^{-1} HCl solution for 24 h.

(4) *Preparation of LG-b:* the crushed and dry biomass was immersed in a 0.1 mol L^{-1} NaOH solution for 24 h.

All of the LG biosorbents were then washed extensively in distilled water and filtered until the water used for washing became colorless and with a constant pH. Lastly, the biosorbents were dried in oven at 313-328 K until constant mass.

Potentiometric titration and pH of biosorbents

The potentiometric titrations were carried out in Erlenmeyer flasks at 298 K. The tests were conducted using 0.01 mol L^{-1} NaOH with 20 mL of 0.01 mol L^{-1} HCl in the presence of 0.1500 g ± 0.0003 g of each biosorbent, after 30 min of contact between the biosorbent and the 0.01 mol L^{-1} HCl solution. The same procedure was carried out using 0.01 mol L^{-1} NaOH with 20 mL of 0.01 mol L^{-1} HCl in the absence of the biosorbent (reference sample).

The pH of the biosorbents was measured based on a suspension containing 0.1500 g (± 0.0003 g) of each biosorbent added to 20 mL of distilled water after 30 min of contact.

Adsorption experiments

In order to determine the removal of each dye from the aqueous solution, 0.1500 g (± 0.0003 g) of each biosorbent was added to 20 mL of MB (4.80 mg L^{-1}) and to 20 mL of MG (3.65 mg L^{-1}) and left to adsorb for 10 min (Hasany et al. 2002) at temperatures of 298 K, 313 K and 328 K (± 2.5). After the adsorption, each biosorbent (LG-in, LG-ab, LG-a and LG-b) was separated through centrifugation at 3500-4000 rpm, and the absorbance of the supernatant was then measured with the aid of a UV-Vis spectrophotometer at 619 nm for MG and 666 nm for MB. The percentage of dye adsorption was calculated using Equation (1):

$$Adsorption\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

where Co (mg L^{-1}) is the initial concentration of the dye and Ce (mg L^{-1}) is the equilibrium concentration of the dye in the solution after the biosorption.

The saturation of the biosorbents was monitored for 30 min and the results demonstrated that saturation occurred within 10 min. In order to determine the maximum biosorption capacity of each biosorbent derived from LG, 20 mL of the solution of each dye (MB and MG) at the concentrations of 4.80 mg L^{-1} for MB and 3.65 mg L^{-1} for MG, at 298 K, was used (Namane et al. 2005) with 6 different masses of LG (0.005, 0.010, 0.0250, 0.0500, 0.1000 and 0.1500 g ± 0.0002 g), and the treatment time was 10 min. In the next step, the biosorbents LG-in, LG-ab, LG-a and LG-b were separated by centrifugation at 3500-4000 rpm. The absorbance of the supernatant was then measured with a UV-Vis spectrophotometer at 666 nm for MB and 619 nm for MG and the corresponding adsorption capacity (qe, mg g^{-1}) was calculated using Equation (2):

$$qe = \frac{(C_o - C_e) \times V}{m} \tag{2}$$

where qe (mg g^{-1}) is the adsorption capacity of each biosorbent, V (L) is the initial volume, m (g) is the mass of each biosorbent and Co (mg L^{-1}) and Ce (mg L^{-1}) were described previously.

Adsorption isotherms and thermodynamic parameters

Only the Freundlich equation (Equation 3) allowed an analysis of the data reported in this manuscript. This equation (Freundlich 1932, Girods et al. 2009) is generally employed to study adsorption isotherms (Freundlich 1907) as well as their linearized form (Equation 4) (Souza et al. 2013, Yao et al. 2010).

$$q_e = K_f C_e^{1/n} \tag{3}$$

$$lnqe = lnKf + \frac{1}{n} lnCe \tag{4}$$

In the Freundlich equation, qe (mg g^{-1}) is the equilibrium adsorption capacity, Ce (mg L^{-1}) is the equilibrium concentration and K_f and 1/n are adsorption constants of the Freundlich equation, where n describes the adsorption intensity (Khorasani & Shojaosadati 2019).

The adsorption phenomenon is dependent on the temperature and the characteristics of thermodynamic parameters describe the viability of the adsorption process. The spontaneity of a system is defined by the variation of the standard free energy of the system (ΔG^o). At equilibrium, ΔG^o is defined as represented in Equation 5 (Tran et al. 2016):

$$\Delta G^o = -RTln\,K_c \tag{5}$$

where R is the universal gas constant (8.314 J/mol.K), T is the absolute temperature in Kelvin (K) and K_c is the thermodynamic equilibrium constant (Tran et al. 2016).

RESULTS AND DISCUSSION

Adsorption isotherms

The adsorption isotherms for MG, for the four biosorbents investigated (LG-in, LG-ab, LG-a and LG-b), were fitted by the adsorption model described by Freundlich, an exponential model proposed to investigate the adsorption in solutions (Freundlich 1907). This model considers the adsorption energy to be heterogeneously distributed on the surface of the adsorbent and since the surface is heterogenous the adsorption sites have different adsorption energies (Walker & Weatherley

Table I. **Equilibrium parameters for MB and MG adsorption onto LG-in, LG-ab, LG-a and LG-b.**

Biosorbents (*Lagenaria* derivatives)	**T (K)**		**Freundlich Parameters**			
		1/n	K_F (mg g^{-1} L mg^{-1})/$^{(1/n)}$	n	R^2	χ^2
Methylene Blue (MB)						
LG-in	298	0.969	0.130	1.03	0.998	1.81×10^{-2}
	313	0.993	0.133	1.01	0.998	6.34×10^{-3}
	328	0.991	0.130	1.01	0.998	1.17×10^{-2}
LG-a	298	0.815	1.61	1.23	0.992	4.43×10^{-2}
	313	0.667	1.04	1.50	0.998	2.42×10^{-2}
	328	0.673	0.400	1.49	0.974	7.66×10^{-2}
LG-b	298	0.792	2.28	1.26	0.998	1.46×10^{-2}
	313	0.523	1.23	1.91	0.998	2.38×10^{-2}
	328	0.749	1.69	1.33	0.994	3.54×10^{-2}
LG-ab	298	0.469	0.576	2.13	0.998	1.83×10^{-2}
	313	0.751	0.585	1.33	0.998	2.22×10^{-2}
	328	0.778	0.555	1.29	0.998	3.34×10^{-2}
Malachite Green (MG)						
LG-in	298	1.001	0.910	0.999	0.994	3.73×10^{-2}
	313	1.041	0.118	0.961	0.998	1.35×10^{-2}
	328	1.026	0.125	0.974	0.998	1.66×10^{-2}
LG-a	298	0.761	1.69	1.31	0.996	3.45×10^{-2}
	313	1.026	0.124	0.975	0.998	1.58×10^{-2}
	328	1.015	0.128	0.985	0.998	1.18×10^{-2}
LG-b	298	0.837	2.20	1.19	0.982	7.62×10^{-2}
	313	1.098	0.123	0.910	0.998	1.74×10^{-2}
	328	1.013	0.132	0.987	0.998	7.08×10^{-2}
LG-ab	298	0.877	0.557	1.14	0.992	5.15×10^{-2}
	313	0.973	0.107	1.03	0.994	4.38×10^{-2}
	328	0.981	0.121	1.02	0.998	1.55×10^{-2}

2001). The results gave a value of $R^2 \geq 0.974$ (Table I), suggesting a heterogeneous distribution of the adsorbate on the surface of the material.

The linearization of the Freundlich isotherm (Figures 3 and 4) leads to a slope 1/n varying between 0 and 1, which is a measure of the adsorption intensity or the surface heterogeneity, the surface becoming more heterogenous as the value moves closer to 0 (Yao et al. 2010). It can be observed that for MB (Table I), the chemical modification of the biosorbents led to a more

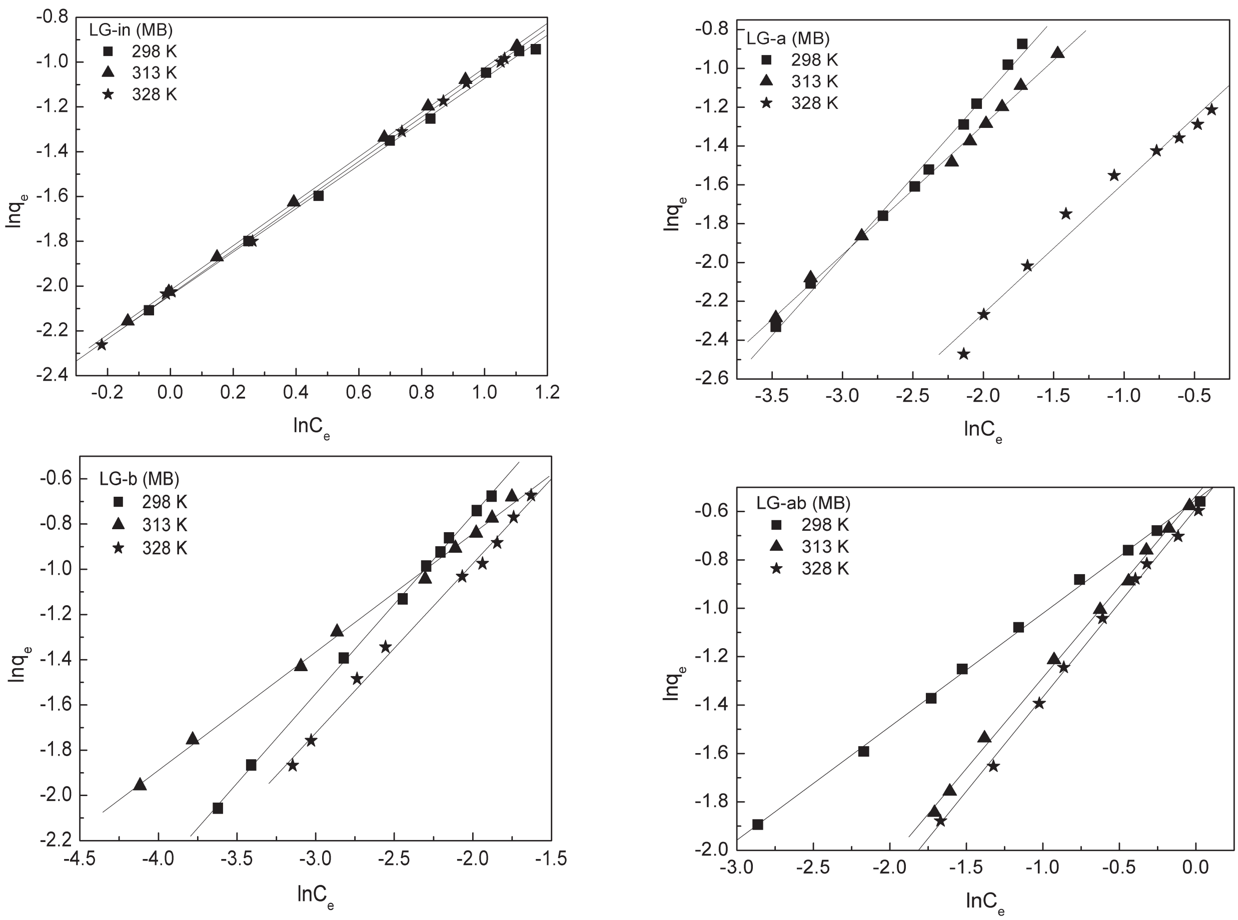


Figure 3. Freundlich isotherms for MB dye adsorption onto *Lagenaria* biosorbents at different temperatures.

heterogenous adsorption. On the other hand, in general, the 1/n values are equal to 1 for the natural LG biomass (LG-in), for all working temperatures. On plotting $\ln q_e$ against $\ln C_e$, straight lines with a 1/n slope are obtained for all biosorbents investigated in the presence of MG and MB, with values of $R^2 \geq 0.974$ for MB and $R^2 \geq 0.982$ for MG (Table I). The n values obtained within the range of 2 to 10 represent a good adsorption capacity. Values between 1-2 indicate intermediate adsorption capacity and values below 1 indicate low adsorption capacity of the material (Yao et al. 2010). In general, the chemical modification generates an increase in the n values in the presence of MB (Table I) and n values between 1-2 are obtained, particularly at temperatures of 298 K and 313 K. The biosorbent LG-in has the lowest n values, however, they are not lower than 1. In the presence of MG (Table I), the chemical treatment of the biosorbents did not lead to significant changes in the n value, which was found to be close to 1 at all temperatures. Thus, all of the biosorbents tested show, according to the n value, intermediate adsorption capacity for the dyes MB and MG.

The maximum biosorption percentages for MB, at 298 K, for the biosorbents were: 99.4 % for LG-in, 98.8% for LG-ab, 95.9 % for LG-a and 98.7 for LG-b while for MG, at 298 K, the maximum adsorptions were 89.0 % for LG-in, 96.8 % for LG-ab, 95.9 % for LG-a and 92.3 % for LG-b. The values for the maximum biosorption capacity for MB, employing the chemically-modified biosorbents, were lower compared with the biosorbent without chemical treatment: 11.37 mg g^{-1} for LG-a < 11.87 mg g^{-1} for LG-b < 16.55 mg

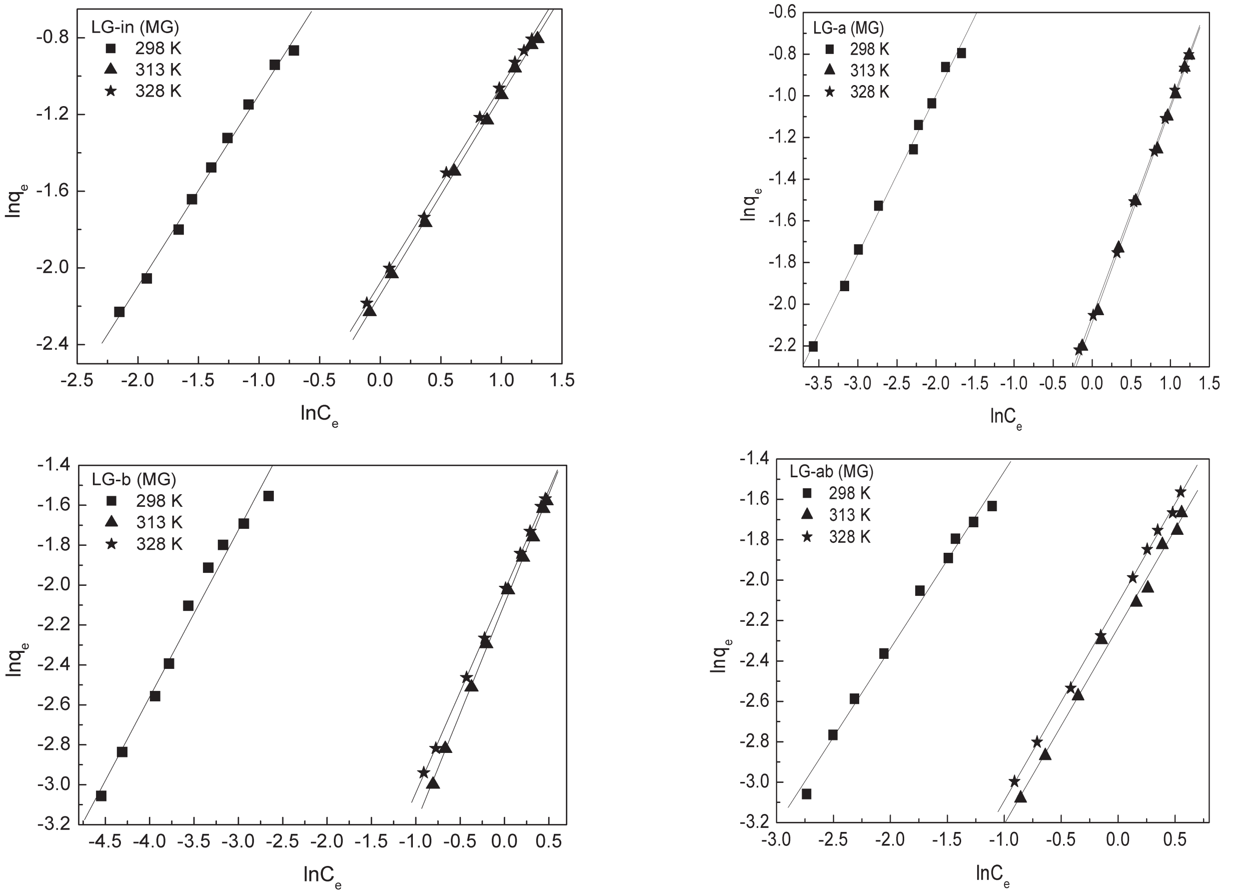


Figure 4. Freundlich isotherms for MG dye adsorption onto *Lagenaria* biosorbents at different temperatures.

g^{-1} for LG-ab < 18.83 mg g^{-1} for LG-in. The maximum biosorption capacity for MG is similar to that for MB. In ascending order, the values for the MG biosorption were: 12.80 mg g^{-1} for LG-b < 13.31 mg g^{-1} for LG-a < 18.74 mg g^{-1} for LG-in < 19.67 mg g^{-1} for LG-ab. In this study, the biomass of *Lagenaria* (mesocarp) adsorbed MB in concentrations similar to those reported for wheat husks (16.56–21.50 mg g^{-1}) (Bulut & Aydın, 2006) and it absorbed MG in concentrations similar to those observed for stems of *Solanum tuberosum* (27.0 mg g^{-1}) (Gupta et al. 2016). Table II shows a comparison of the adsorption capacities (mg g^{-1}) observed for MB and MG with those reported in the literature for several adsorbents. Bojić *et al.* (2013) studied *Lagenaria vulgaris* shell and reported an adsorption capacity of 39.3-49.6 mg g^{-1} for MB (Bojić et al. 2013) (Table II). Another material, pectin-*Chlorella vulgaris* (Table II), showed higher adsorption of 175.66 mg g^{-1} for MB and 247.23 mg g^{-1} for MG (Khorasani & Shojaosadati 2019). Neem sawdust showed low adsorption values of 2.12-3.62 mg g^{-1} for MB and 2.04-3.42 mg g^{-1} for MG (Khattri & Singh 2000) (Table II). The data indicate that the adsorption capacity of the biosorbent investigated in this study (11.37-18.83 mg g^{-1} to MB and 18.80-19.67 mg g^{-1} to MG) is similar to results reported for other lignocellulosic agricultural wastes (Table II).

Table II. Previously reported adsorption capacities for various adsorbents in studies using methylene blue (MB) and malachite green (MG) as adsorbents.

Adsorbent	**q_o, mg g^{-1}**			
	MB	**Ref.**	**MG**	**Ref.**
Wheat shells	16.56–21.50	(Bulut & Aydın 2006)	-	-
Carbon nanotubes	35.4–64.7	(Yao et al. 2010)	-	-
Lagenaria vulgaris shell	39.3-49.6	(Bojić et al. 2013)	-	-
Neem (*Azadirachta indica*) leaf powder	3.67-19.61	(Bhattacharyya & Sharma 2005)	-	-
Coconut activated carbons	-	-	83.06-91.24	(Qu et al. 2019)
Coal activated carbons	-	-	74.91-83.47	(Qu et al. 2019)
Apricot activated carbons	-	-	69.59-74.18	(Qu et al., 2019)
Peach activated carbons	-	-	69.93-73.53	(Qu et al. 2019)
Pectin-*Chlorella vulgaris*	175.66	(Khorasani & Shojaosadati 2019)	247.23	(Khorasani & Shojaosadati 2019)
Neem sawdust	2.12-3.62	(Khattri & Singh 2000)	2.04-3.42	(Khattri & Singh 2000)
Sugar Cane Dust	2.18-3.74	(Khattri & Singh 1999)	2.32-4.00	(Khattri & Singh 1999)
Zeolite	53.3	(Zhu et al. 2014)	48.6	(Zhu et al. 2014)
Leaves of *Solanum tuberosum*	51.2	(Gupta et al. 2016)	33.3	(Gupta et al. 2016)
Stem of *Solanum tuberosum*	41.6	(Gupta et al. 2016)	27.0	(Gupta et al. 2016)
Lagenaria spp.	11.37-18.83	This study	18.80-19.67	This study

Thermodynamic parameters

The fundamental concept of thermodynamics assumes that, in an isolated system, energy can be neither acquired nor lost and a variation in entropy is the only driving force (Aravindhan et al. 2007). In practical terms, both the energy and the entropy factors must be considered in order to determine whether the process will occur spontaneously. Reactions occur spontaneously at a certain temperature if the G value is negative.

The equilibrium constant (K_{eq} or K_C) needs to be considered for the determination of the thermodynamic parameters, that is, the variations in the standard enthalpy (ΔH°), standard entropy (ΔS°) and Gibbs free energy (ΔG°). In the case of nonionic solutes or dilute ionic solutions, the equilibrium constant (K_{eq}) (Ghosal & Gupta 2017) is equivalent to K_C (Tran et al. 2016) and it can also be defined as the distribution coefficient (K_d) (Aravindhan et al. 2007).

The data obtained in this study can be fitted using the linearized Freundlich model. The Freundlich equation is consistent with the thermodynamics of heterogenous adsorption and the different units of K_F can be reciprocally converted by Equation 6, as described by Tran et al. (Tran et al. 2016) :

$$K_F = \left(K_F^* M_w \right)^{1-1/n} \tag{6}$$

where M_w is the molar mass of the dye (MB or MG), K_F is in (mg g^{-1}) (mg $L^{-1})^{1/n}$ with C (mg L^{-1}) and q (mg g^{-1}), and the unit of K^*_F is (mmol g^{-1}) (mmol $L^{-1})^{1/n}$ (Tran et al., 2016). Thus, the equilibrium constant (K_C) can be obtained from the Freundlich constant (K_F), as described in Equation 7, and subsequently ΔG° (Equation 8), ΔH° and ΔS° (Equation 9) can be obtained (Tran et al. 2016):

$$K_C = \left(K_F \rho \left(\frac{10^6}{\rho}\right)^{\left(1-\frac{1}{n}\right)} \right) \tag{7}$$

$$\Delta G^o = -RTln\, K_F \rho \left(\frac{10^6}{\rho}\right)^{\left(1-\frac{1}{n}\right)} \tag{8}$$

$$ln\left(K_F \rho \left(\frac{10^6}{\rho}\right)^{\left(1-\frac{1}{n}\right)} \right) = \frac{-\Delta H^o}{R} \times \frac{1}{T} + \frac{\Delta S^o}{R} \tag{9}$$

where ρ is the density of pure water (assuming a value of ~1.0 g mL^{-1}). Employing the linearized form of the van't Hoff equation (Equation 9), the plot of $\ln K_{eq}$ against 1/T provides ΔH^o and ΔS^o as the slope and intercept, multiplied by R (Ghosal & Gupta 2017).

The change in the Gibbs free energy (ΔG^o) gives an indication of the spontaneity of a chemical reaction (Job & Rüffler 2016). The thermodynamics parameters of ΔH^o and ΔS^o were obtained from Equation 9 ($\ln K_{eq}$ against 1/T) and are given in Table III. The values of ΔG^o were calculated based on Equation 8 (Table III). Considering MB as an analyte, a negative ΔH^o value is observed for the biosorbents chemically modified with a base (LG-b), suggesting the adsorption shows exothermic behavior. In contrast, the natural biosorbents (LG-in), biosorbent chemically modified with an acid (LG-a) and the biosorbent neutralized with acid and base (LG-ab) show endothermic behavior ($\Delta H > 0$).

In the case of MG, all biosorbents show endothermic behavior. In exothermic reactions (ΔH^o negative), the equilibrium constant decreases with an increase in temperature (that is, when 1/T decreases). Also, in endothermic reactions (ΔH^o positive), the equilibrium constant increases with an increase in temperature (Keszei 2013). The ΔH^o and ΔS^o values are dependent on temperature. The positive ΔS^o value suggests an increase in the randomness of the solid/solution interface (Özcan et al. 2005) in the adsorption of MB onto the biosorbent LG-b. This is not observed for MB adsorption onto LG-a, LG-in or LG-ab or for MG in the presence of any of the biosorbents ($\Delta S < 0$). A positive ΔS^o value reflects an increase in the degree of freedom of the adsorbed species and lower affinity of the adsorbent for the adsorbed species, with a prevalence of randomness in the system. A negative ΔS^o value suggests that the adsorption process is driven by enthalpy and it also implies a reduction in the disorder of the solid/liquid interface during the adsorption process, favoring the migration of the molecules from the solid phase to the liquid phase (Saha & Chowdhury 2011).

The materials LG-a, LG-b and LG-ab in the presence of MB show negative ΔG^{o} values at all temperatures and in the presence of MG these materials only have a negative ΔG^{o} value at 298 K. The ΔG^{o} values provide a general insight into the order and disorder of adsorption systems (Sellaoui et al. 2017). In general, through comparison with the natural material (LG-in), the values for the thermodynamic parameters ΔG^{o}, ΔH^{o} and ΔS^{o} obtained for the chemically-modified biosorbents (LG-a, LG-b and LG-ab), in the presence of MB and MG, indicate that the chemical modification proposed herein caused alterations in the materials.

Table III. **Thermodynamic parameters for MB and MG calculated using the Freundlich constant.**

Biosorbents	**T (K)**	**K_c**	ΔG^{o} **(kJ mol^{-1})**	ΔH^{o} **(kJ mol^{-1})**	ΔS^{o} **(J mol^{-1} K^{-1})**
Methylene Blue (MB)					
LG-in	298	0.167	4.430	4.917	-31.575
	313	0.141	5.104		
	328	0.140	5.363		
LG-a	298	7.155	-4.876	6.009	-1.478
	313	15.170	-7.076		
	328	5.574	-4.685		
LG-b	298	12.175	-6.192	-2.454	33.024
	313	57.016	-10.522		
	328	12.690	-6.929		
LG-ab	298	41.483	-9.230	69.313	-204.088
	313	4.331	-3.814		
	328	3.308	-3.263		
Malachite Green (MG)					
LG-in	298	0.904	0.251	60.400	-206.724
	313	0.085	6.410		
	328	0.101	6.251		
LG-a	298	11.577	-6.068	127.263	-412.820
	313	0.101	5.975		
	328	0.114	5.932		
LG-b	298	8.150	-5.198	116.950	-382.308
	313	0.056	7.513		
	328	0.119	5.811		
LG-ab	298	1.503	-1.010	65.059	-218.048
	313	0.133	5.240		
	328	0.141	5.335		

The pH and potentiometric titration results for biosorbents

The pH of the distilled water changed when it was placed in contact with the biosorbents, except in the case of LG-ab, and the values obtained, in ascending order, were: 6.2 (LG-a) < 7.2 (LG-ab) < 8.4 (LG-in) < 11.4 (LG-b). The pH value of 8.4 reveals the basic characteristics of the LG-in surface while the value of pH 7.2 for LG-ab is equivalent to the pH of distilled water, suggesting that there is chemical modification when 0.1 mol L^{-1} NaOH is used after 0.1 mol L^{-1} HCl, generating the neutralization of the surface of the natural biomass, as expected. The pH value of 6.2 for LG-a reveals a slightly acidic characteristic of the biomass surface. The chemical modification that led to the greatest change in pH was that of LG-b (pH of 11.4), demonstrating the basic character of the surface of this material, probably due to the presence of basic groups.

The potentiometric titration tests, carried out using 0.01 mol L^{-1} NaOH and 0.01 mol L^{-1} HCl solutions containing the biosorbents, indicated that the potentiometric jump point for the basic materials was associated with the lowest volumes of titrant, which was 17.2 mL for LG-in (± 0.3 mL) and LG-b (± 0.8 mL). The corresponding volumes were 20.5 mL (± 0.5) for LG-a and 20.3 mL (± 0.4)

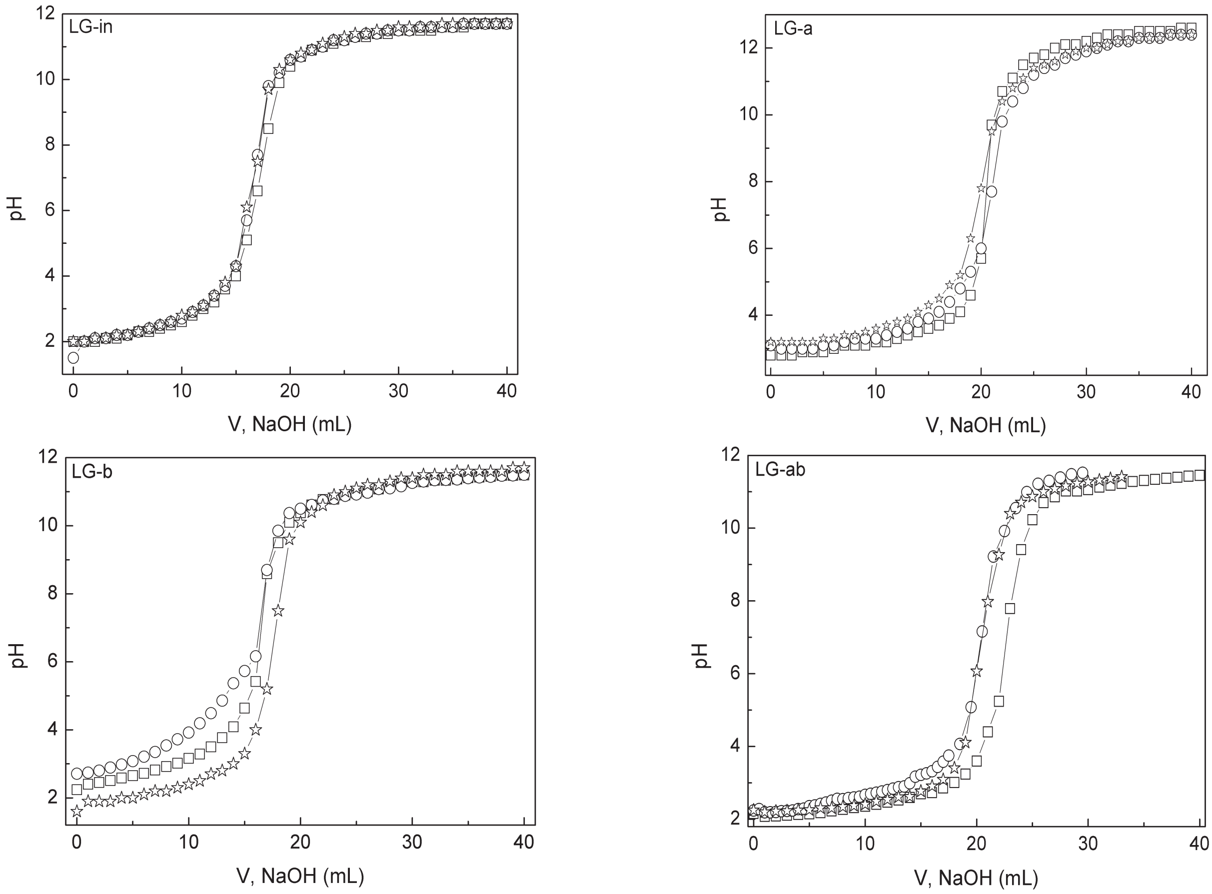


Figure 5. **Results for potentiometric titration of the protonated *Lagenaria* biosorbents using base solutions (NaOH) of 0.01 mol L^{-1}.**

for LG-ab, values equal to or very close to the result for the reference (i.e., 20.5 mL (± 0.5)), that is, the procedure carried out in the absence of LG. The equivalence points can be located precisely by employing the first derivative of the experimental data (Figure 5). The results obtained verified that the chemical modification changed the surface of the biosorbents.

The *Lagenaria* biomass is a lignocellulosic material (Nikolić et al. 2021) with irregular shape and porous structure, containing pores of different shapes and sizes (Marković-Nikolić et al. 2019). The process to obtain the LG-in biosorbent is called pre-hydrolysis and is used to remove hemicelluloses and the ash content (Santos et al. 2016). Acid hydrolysis was used to obtain the LG-a biosobent. HCl promotes greater agglomeration of fibers of lignocellulosic materials and, depending on the surface load of the fibers, their stability decreases (Teixeira et al. 2010), reducing the pH of the material to 6.2. The use of alkalinizers, such as NaOH, changes the lignocellulosic structure of the material, causing delignification (Santos et al. 2016) and increasing the material pH to 11.4. It was observed that the potentiometric titrations changed the surface of the biosorbents (Figure 5) and the acid and basic hydrolysis negatively affected the adsorption capacity of the materials, demonstrating that after acidic and basic treatment the biosorbents LG-a and LG-b have a lower adsorption capacity than the natural biomass. The results shows that adsorption occurs preferentially on surfaces containing basic groups that can interact with the dye structures. The results indicate that pH 8.4 (pH of the natural biomass) is the optimal pH for the adsorption of MB and MG using *Lagenaria* as a biosorbent. This is because the anionic groups of lignocellulosic biomass, present on the surface of the natural biomass (LG-in), interact with cationic groups present in structures of the MB and MG dyes (Figure 1). The basic and acid chemical surface modification promotes the removal or neutralization of the anionic surface groups of the biomass, reducing the adsorption rate. Also, in the LG-in and LG-n biosorbents, the hydrogen bond interactions between nitrogens in the MB and MG dye structures and hydrogens from surface composition of the *Lagenaria* biomass are favored.

CONCLUSIONS

The chemically-modified biosorbents, derived from the mesocarp of *Lagenaria*, named LG-in, LG-a, LG-b and LG-ab, are alternative materials with the potential to be used in the removal of cationic dyes, such as malachite green (MG) and methylene blue (MB), in aqueous matrixes. The Freundlich model provided a good fit with the MG and MB adsorption data, with the slope of 1/n suggesting adsorption with a less heterogeneous character (1/n = 1) for the natural biosorbent LG-in (without chemical modification) and with a higher degree of heterogeneity (1/n < 1) for the chemically-modified materials (LG-a, LG-b and LG-ab). The n values indicate low to intermediate levels of adsorption (1 > n < 2). In general, the biosorbents present basic characteristics, except for LG-a. With regard to the thermodynamic parameters, positive ΔS^o values were observed for the biosorbent LG-b for MB, suggesting an increase in the randomness of the solid/solution interface, which was not observed for LG-a, LG-in or LG-ab or for any of the biosorbents in the presence of MG ($\Delta S^o < 0$). The negative ΔS^o values for these materials suggest that the adsorption process is driven by enthalpy, with a reduction in the disorder of the solid/liquid interface. The mesocarp of *Lagenaria* is a biosorbent obtained from a residual biomass widely available in the southern region of Brazil. The results obtained in this study indicate that this biomass has good potential for use as an alternative biosorbent (a green adsorbent) of low cost for cationic dyes.

Acknowledgments

Laboratório de Corantes e Processos Pirolíticos (LACOPPI), Instituto Federal do Paraná (IFPR, DIPE/PROEPI/PIAP Edital N° 05/2019) for scholarships: Fundação Araucária (FA), Programa de Bolsas de Iniciação Científica (PIBIC-FA, PIBIC/CNPq), PIBIC-Jr/CNPQ/IFPR, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Brazil).

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How to cite

FRANCESCHINI SB, SENDESKI CP, DE LIMA KD, NICOLINI KP & NICOLINI J. 2023. A 'green' adsorbent: effect of chemical modification of biosorbents on the adsorption of methylene blue and malachite green. An Acad Bras Cienc 95: e20210124. DOI 10.1590/0001-3765202320210124.

Manuscript received on January 26, 2021;
accepted for publication on June 1, 2021

STEPHANY B. FRANCESCHINI
https://orcid.org/0000-0001-6353-9378

CAROLINE P. SENDESKI
https://orcid.org/0000-0003-3433-4669

KETHLEENN D. DE LIMA
https://orcid.org/0000-0002-2107-6544

KELLER P. NICOLINI
https://orcid.org/0000-0003-1185-6229

JAQUELINE NICOLINI
https://orcid.org/0000-0002-3446-9275

Instituto de Educação, Ciência e Tecnologia do Paraná/IFPR,
Laboratório de Corantes e Processos Pirolíticos/Lacoppi,
Av. Bento Munhoz da Rocha Neto, s/n, Trevo da Codapar,
PRT-280, Universitário, 85555-000 Palmas, PR, Brazil

Correspondence to: **Jaqueline Nicolini**
E-mail: jaqueline.nicolini@ifpr.edu.br

Author contributions

Stephany B. Franceschini, Caroline P. Sendeski and Kethleenn D. De Lima: Investigation, Preliminary analysis. Keller Paulo Nicolini: Investigation, Preliminary analysis Writing- Reviewing. Jaqueline Nicolini: Supervision, Investigation, Preliminary analysis, Formal analysis, Writing-Reviewing and Editing.