A MECHANISTIC APPROACH TO METHYLENE BLUE SORPTION ON TWO VEGETABLE WASTES: CORK BARK AND GRAPE STALKS

M. Àngels Olivella,[a] Núria Fiol,[b] Florencio de la Torre,[b] Jordi Poch,[c] and Isabel Villaescusa [b]

Two vegetable wastes, cork bark and grape stalks, were investigated for the removal of methylene blue from aqueous solution. The effects of contact time, dye concentration, pH, and temperature on sorption were studied relative to adsorption on a commercially-activated carbon. The highest adsorption yield was obtained within the pH range 5 to 10 for grape stalks and 7 to 10 for cork bark. The sorption kinetics of dye onto activated carbon and grape stalks was very fast. Kinetics data were fitted to the pseudo-first and second order kinetic equations, and the values of the pseudo-second-order initial rate constants were found to be 1.69 mg g^{-1} min^{-1} for activated carbon, 2.24 mg g^{-1} min^{-1} for grape stalks, and 0.90 mg g^{-1} min^{-1} for cork bark. Langmuir maximum sorption capacities for activated carbon, grape stalks, and cork bark for methylene blue estimated by the Orthogonal Distance Regression method (ODR) were 157.5 mg g^{-1}, 105.6 mg g^{-1}, and 30.52 mg g^{-1}, respectively. FTIR spectra indicated that carboxylic groups and lignin play a significant role in the sorption of methylene blue. Electrostatic forces, n-π interactions, cation-π, and π-π stacking interactions contribute to methylene blue sorption onto grape stalks and cork bark. Grape stalks can be considered an efficient biosorbent and as a viable alternative to activated carbon and ion-exchange resins for the removal of methylene blue.

Contact information: (a) Department of Chemistry, University of Girona, Campus Montilivi s/n, 17071 Girona, Spain; (b) Department of Chemical Engineering, Escola Politècnica Superior, University of Girona, Avda. M. Aurèlia Campmany, s/n 17071, Girona, Spain; (c) Department of Applied Mathematics, Escola Politècnica Superior, Universitat de Girona, Avda. Lluís Santaló, s/n, 17071 Girona.
Corresponding author: angels.olivella@udg.edu

INTRODUCTION

Dyes are commonly used in many industries such as food, paper, carpets, rubbers, plastics, cosmetics, and textiles in order to colour their products. The discharge of coloured wastes into streams not only affects the aesthetic nature but also interferes with the transmission of sunlight into streams and therefore reduces photosynthetic activity (Doğan and Alkan 2003; Mall *et al.* 2006). Methylene blue is a cationic dye widely used in paper colouring, cotton and wool dyeing, and coating for paper stock. Although it is not considered as a very toxic dye, it can have various harmful effects on living organisms (Cengiz and Cevas 2008) and once inhaled it may cause several disorders to human health (*i.e.* nausea, vomiting, mental confusion, and difficulties in breathing). The release of coloured wastewater from these industries may present an eco-toxic hazard and

introduce the potential danger of bioaccumulation, which may affect man through the food chain.

Activated carbon is widely used as an adsorbent due to its high adsorption abilities in removing organic pollutants from wastewater; however, the cost of activated carbon is relatively high and the regeneration is difficult, which limits its usage in dye waste treatment (Waranusantigui *et al.* 2003). As a result, many researchers have investigated low-cost, biodegradable substitutes made from natural resources to remove organic contaminants such as dyes from wastewater (Gupta and Suhas 2009; Sharma *et al.* 2011). Different types of these low-cost biosorbents have been tested in either batch or column tests (Sharma *et al* 2011; Zhang *et al.* 2011).

Recently, our group has tested the efficiency of cork bark for the removal of some organic compounds (Olivella *et al.* 2011; Villaescusa *et al.* 2011) and grape stalks (GS) for the removal of metal ions (Fiol *et al.* 2003; Villaescusa *et al.* 2004). These low-cost sorbents are abundant, inexpensive, and require little processing. In the case of cork bark wastes, the annual world production reaches around 50.000 tons, which corresponds on average to 25 to 30% of the quantity used in cork stopper manufacturing (Silva *et al.* 2005). In the case of GS, only one medium-sized wine producer may generate 1000 tons of GS waste per year. The use of these sorbents for MB sorption would valorize them, and the resulting low volume of secondary waste would be burnt or disposed of in appropriate landfills.

The aim of this work was to study the adsorption of MB onto CB and GS and to compare the obtained results with those obtained with a commercial activated carbon. The effect of pH, contact time, and temperature on MB adsorption has been investigated. Kinetic and equilibrium data were submitted to the corresponding models to determine rate constants and maximum adsorption capacities of the studied sorbents. With the aim to elucidate the functional groups on sorbent surface involved in the sorption process, Fourier transfer infrared (FTIR) analysis was carried out. The chemical evidence found in this research worked together with the knowledge of functional groups determined by FTIR analysis and allowed us to suggest the possible mechanisms for MB sorption onto GS and CB.

EXPERIMENTAL

Materials

GS and CB were kindly supplied by two industries from the Girona region (Spain) dealing with wine production and tap manufacturing, respectively. Activated carbon (AC) was supplied by Panreac (Granulated n.3 QP). GS were previously rinsed with abundant distilled water to remove dirty particles and colour and then dried in an oven at 100°C. No water treatment was needed for the CB. The GS and CB were milled in a Taurus MS 50.

Both sorbents and activated carbon were sieved (Screener FT-91) for a particle size between 0.63 mm and 0.75 mm.

Stock solutions of MB (Chemical formula: $C_{16}H_{18}ClN_3S$; molecular weight: 319.86 g mol^{-1}; solubility: 40 g L^{-1}) were dissolved in deionized water (Millipore Direct Q4 Water Purification System) to get the required initial concentrations. When required, pH adjustments were made by using 0.1 M hydrochloric acid or sodium hydroxide. The pH values were recorded with a pH meter (Crison GLP-21). All reagents were analytical grade and purchased from Panreac, Barcelona, Spain.

Methods

Sorption procedure

Batch equilibrium experiments were conducted at room temperature (20 ± 2°C) on a rotary shaker (rotator STR4, Stuart Scientific Bibby) at 30 rpm, using 25 mL glass tapered tubs. In all experiments, 0.1 g of the sorbents (particle size 0.63 to 0.75 mm) was put into contact with 15 mL of dye solutions under continuous agitation. At the end of the adsorption time, the separation of the sorbent was performed by centrifugation (Jouan C R312) at 4000 rpm for 10 min; the final pH was recorded, and the dye concentrations in the filtrates were analysed by spectrophotometry (Shimadzu UV-160) at the λ_{max} value of 664 nm.

The residual concentration of dye was obtained by calculating the difference between the initial, C_i, and the final, C_f, dye concentration in solution. The following equation was used to compute the specific uptake by the sorbent,

$$q = (C_i - C_f) \; V / w \tag{1}$$

where V (in L) is the solution volume and w (in g) is the amount of dry sorbent used.

When studying the effect of pH, the dye solution initial pH was varied within the range 1 to 10. For these experiments, the initial dye concentration was 100 mg L^{-1}, and the chosen agitation time was 90 min.

Sorption kinetics of dye onto the sorbents was investigated at three different temperatures: 15, 20, and 30 ± 2°C. For these experiments, the initial dye concentration was 100 mg L^{-1}, and the pH was around 6.5.

Dye solutions of different initial concentrations (50 to 2000 mg L^{-1}) within the pH range of 6.0 to 6.5 were used to obtain sorption isotherms at 20 ± 2ºC. For these experiments, the agitation time was 500 minutes.

Sorption mechanism

FTIR analysis was used to determine the functional groups involved in the sorption process of MB onto CB and GS. Spectra were obtained using KBr pellets and were recorded on a Galaxy 5000 FTIR spectrometer (Mattson Instrument Co., Madison, WI).

To prepare the pellets, about 2 mg of the sample was ground for 1 to 2 minutes together with about 200 mg of KBr (FT-IR grade, Acros Organics). All FTIR spectra were measured in the 3500 to 400 cm^{-1} range by co-addition of 32 scans with a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

Effect of pH

MB adsorption as a function of pH is shown in Fig. 1. As seen in the figure, the removal of the dye by activated carbon was insignificantly affected over the wide pH range of 1 to 10. Conversely, pH influenced the MB sorption onto GS and CB. The optimum adsorption yields were obtained within the initial pH range 5 to 10 for GS and within 7 to 9 for CB. Bhattacharyya and Sharma (2005) found that pH variation had only little effect on the amount of MB sorbed onto Neem leaf powder.

The pH at point zero charge (*i.e.* the pH at which the net surface charge is zero) of GS (5.0) and of CB (3.6) were determined in a previous work (Fiol and Villaescusa 2009). Above the point zero charge, the surface of the sorbent becomes negatively charged, which favors the electrostatic interaction between the sorbent and the positively charged sorbate MB (Vadivelan and Kumar 2005). MB is positively charged over the studied pH range ($pK_a > 18$) (Montes-Navajas and Garcia 2009). The lower point zero charge of CB (3.6) compared to GS (5.0) could explain the differences in MB sorption.

Protons are released as a consequence of CB deprotonation at relatively low pH values in which the H^+ concentration is already high. In such a situation, MB cations must compete with protons for the sorbent active sites and therefore dye sorption is unfavoured. The complex nature of the cork matrix involves weak and strong carboxylic groups, whose acidity depends on the proximity of carboxyl groups to each other and to other functional groups (Leenheer *et al.* 1995). As pH increases, the surface charge of CB becomes more negatively charged, mainly due to deprotonation of both weak and strong carboxylic groups from extractives (pK_a between 3 and 6), while phenolic groups from lignin (pK_a about 9.5 to 10.5) are not expected to make a significant contribution.
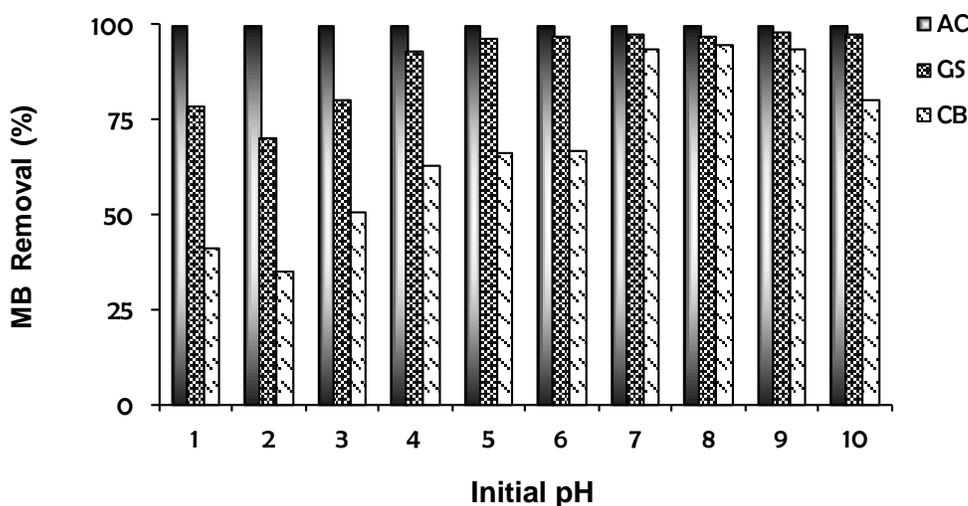
Fig. 1. Removal percentage of methylene blue (MB) as a function of solution initial pH by activated carbon (AC), grape stalks (GS), and cork bark (CB). Concentration: 100 mg L^{-1}; agitation time: 90 min

The change in pH when solutions at different initial pH values were contacted for 90 minutes with the selected sorbents in the absence and in the presence of the dye was recorded. Initial pH versus final pH values are plotted in Fig. 2. As seen in the figure, from an initial pH value that is specific for each sorbent, the final pH tends to increase or decrease to reach a plateau. The sorbent exerts a kind of buffering, and the value of the final pH appeared to be independent of the initial pH value within a specific range (*i.e.* solutions of initial pH values in the range 4 to 10 reach a pH around 10 when in contact with AC). In the cases of CB and GS, two plateaus were observed. The first was found at a final pH of 4.2 and 5.1 for CB and GS (initial pH range 4 to 6) and the latter at around 6.5 for both sorbents (initial pH range 8 to 10). This trend is shown for both series of experiments, that is, in the presence and in the absence of MB. This fact might lead to the deduction that the presence of MB does not cause pH variation. The explanation for the two plateaus observed might be attributed to the different acidities of the functional groups on the CB and GS surfaces. Besides this, the presence of MB and therefore the dye sorption process provoked a slight decrease in the final pH when the initial pH was within the range of 5.5 to 7.5 and the sorbents are GS and CB (see solid symbols in Fig. 2). In the case of AC, these differences were found for a larger range of initial pH values (4 to 10).
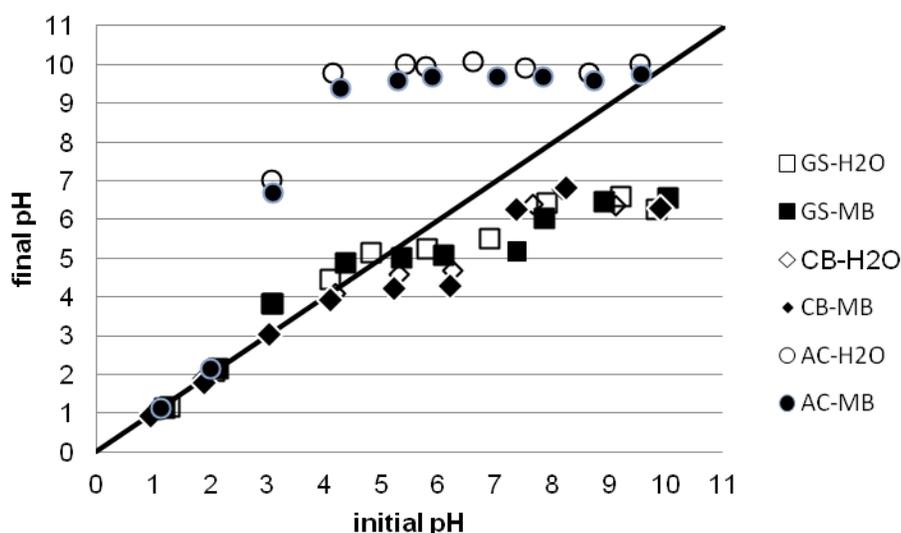
Fig. 2. Plot of initial versus final pH solution after contact with activated carbon (AC), grape stalks (GS) and cork bark (CB) in the presence of methylene blue (-MB) and in the absence of MB (-H$_2$O). Concentration: 100 mg L^{-1}; agitation time: 90 min

As mentioned above, the MB maximum sorption onto CB appeared at 3 units of pH higher than that of the pH$_{pzc}$. The explanation for this must be found in the pH variation. When contacting CB with solutions at an initial pH within the range 4.2 to 6.3 for 90 minutes, the pH decreased to reach the final pH values within the range 3.9 to 4.3. These observations confirm the release of protons from the sorbent and explain the unfavoured conditions for MB being sorbed onto CB at these initial pH values. In the

case of GS, when considering the same interval of initial pH, the pH after 90 minutes did not change.

Taking into account the discussed results, further experiments were performed at a pH of 6.5 which is the natural pH of 100 mg L^{-1} MB in water. This coincided with the final pH value (second plateau) at which the maximum MB sorption onto CB and GS occurred.

Sorption Kinetics

Sorption kinetics profiles of MB obtained at $20 \pm 2^{o}C$ are shown in Fig. 3. In the case of AC, experimental data was not well fitted to the pseudo-first-order model (R^2=0.898). It shows that at the beginning, MB sorption was fast: removal of 50% of the dye was attained in 15 min in the case of activated carbon and grape stalks and 20 min in the case of CB. Equilibrium was achieved at 240 min for activated carbon and at 480 min for both GS and CB at initial MB concentration of 100 mg L^{-1}. Therefore, to ensure that equilibrium is reached, a contact time of 500 minutes was used for subsequent experiments.

The obtained kinetics data plotted in Fig. 3 were fitted to pseudo-first and pseudo-second order models.

The sorption kinetics following the pseudo-first order model (Ho and McKay 1998 and Sivaraj *et al.* 2001) and pseudo-second order kinetics (Ho 2003) are given by Eqs. (2) and (3),

$$\frac{dq}{dt} = K_1(q_e - q_t) \tag{2}$$

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \tag{3}$$

where q_e and q represent the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time t, and K_1 and K_2 represent the sorption rate constant (min^{-1}). K_1 and K_2 can be obtained by plotting $\log[q_e/(q_e - q)]$ versus time (t) and by plotting t/q versus t, respectively.

The initial sorption rate (h) was calculated as follows:

$$h = K_2 q_e^{\;2} \tag{4}$$

Table 1 shows the kinetics models parameters for MB sorption onto the three studied sorbents. GS showed a higher initial sorption rate than activated carbon but a smaller amount of dye sorbed at equilibrium. CB showed the lowest sorption initial rate and also the lowest amount of MB sorbed at equilibrium time. The highest regression coefficient values obtained when using a pseudo-second-order model indicates that this model provides the best fit of the experimental data; therefore the uptake process can be postulated as chemisorption that may occur at the polar functional groups of lignin and/or cellulose (Ho 2003). Besides, the fact that sorption capacities of CB and GS are inversely

proportional to their specific surface areas 52.04 m^2 g^{-1} and 21.8 m^2 g^{-1} determined in a previous work (Fiol 2005) indicates that physical sorption was not the dominant sorption process.

Table 1. Pseudo-First-Order Rate and Pseudo-Second-Order Rate Constants for Methylene Blue (MB) Sorption onto Activated Carbon (AC), Grape Stalks (GS), and Cork Bark (CB)

MB	Pseudo-First order			Pseudo-second order			
Sorbent	K_1 (min^{-1})	q_e (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	h mg (g min)$^{-1}$	R^2
AC	0.1289	27.11	0.898	0.0105	15.22	1.69	0.999
GS	0.0764	15.80	0.991	0.0116	14.99	2.24	0.999
CB	0.0294	13.20	0.911	0.0069	12.29	0.90	0.999

In Fig. 3 the theoretical curves calculated from the model parameters are superimposed with the experimental data.
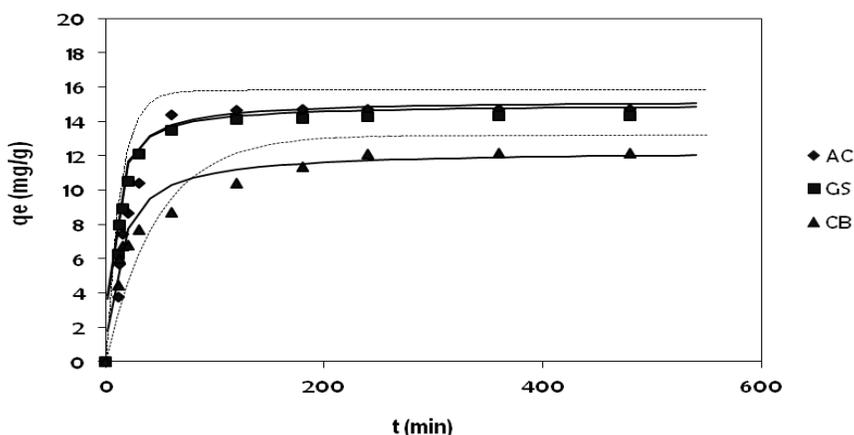
Fig. 3. Methylene blue (MB) sorption onto activated carbon (AC), grape stalks (GS), and cork bark (CB) as a function of time. Initial metal concentration: 100 mg L^{-1}; initial pH: 6.5. Symbols are the experimental data, solid lines represent predicted data by the pseudo-first model, and dashed lines represent predicted data by the pseudo-second model.

During kinetic sorption experiments, the pH was recorded at different intervals of time. As mentioned, for these experiments, the initial pH was 6.5. After 10 minutes, the solution pH reached almost a stable pH value of 10 for AC, 5.0 for GS and 4.4 for CB.

The kinetics of MB sorption was also studied at 15°C and 30°C (results not shown). It was observed that temperature change has almost no effect on the sorption of MB onto the studied sorbents; therefore, a thermodynamic study of MB sorption was not undertaken. Similar observations about the weak effect of temperature were reported by other researchers (Elass *et al.* 2010; Malash and El-Khaiary 2010; Ofomaja 2007).

Sorption Isotherms

Equilibrium sorption data shown in Fig. 3 were fitted to the Langmuir-type adsorption isotherm model,

$$q = \frac{q_{\max}bC_{eq}}{1+bC_{eq}} \tag{5}$$

where q is the adsorbed amount (mg g^{-1}), $q_{\max}$ is the maximum metal uptake (mg g^{-1}), C_{eq} is the equilibrium concentration of adsorbate in solution after adsorption (mg L^{-1}), and b is the equilibrium constant related to the energy of sorption which quantitatively reflects the affinity between the sorbent and sorbate.

The Langmuir isotherm parameters, $q_{\max}$ and b, were obtained using two regression methods: (1) the Ordinary Least Squares (OLS) method, the most commonly used, which assumes that all the experimental error is in the dependent variable q and the equilibrium concentration (C_{eq}) is known without error; and (2) the Orthogonal Distance Regression method (ODR) in which it is assumed that C_{eq} and q are known with some experimental error. The latter method better represents the real situation in which C_{eq} and C_0 are determined experimentally by chemical analysis and therefore should be observed with error. On the other hand, q is calculated using Eq. 1, and thus both C_{eq} and C_0 errors contribute to q error; therefore, errors in both C_{eq} and q must be taken into account. Recently, Poch and Villaescusa (2012) reported that the Orthogonal Distance Regression method (ODR) gives the most accurate estimates of the isotherm parameters among the different methods when the experimental data have error.

The OLS method relies on minimizing the sum of square errors (Eq. 6), and ODR uses the sum of square relative errors with regard to both C_{eq} and q (Eq. 7). Regression computations were carried out using Matlab R2008b. Specifically, the optimization was performed by applying the Generalized Reduced Gradient method, and the library GRG2 (Lasdon and Warren 1979) was employed.

$$SSR_{OLS} = \sum_{i=1}^{N}\left(\frac{q_{i,\exp}-q_{i,calc}}{q_{i.\exp}}\right)^2 \tag{6}$$

$$SSR_{ODR} = \sum_{i=1}^{N}\left(\frac{C_{eq,i,\exp}-C_{eq,i,calc}}{C_{eq,i,\exp}}\right)^2 + \left(\frac{q_{i,\exp}-q_{i,calc}}{q_{i.\exp}}\right)^2 \tag{7}$$

In order to compare the results obtained by both regression methods, the sum of the square residuals for each pair of q_{max} and b were calculated as well as the sum of normalized residues (SNR) (Eq. 8). The obtained results are presented in Table 2.

$$SNR_i = \sum_{i=1}^{2} \frac{SSR_{OLS,i}}{\max(SSR_{OLS,1}, SSR_{OLS,2})} + \frac{SSR_{ODR,i}}{\max(SS_{ODR,1}, SSR_{ODR,2})} \qquad (8)$$

The obtained results for q_{max} and b for MB sorption onto the three studied sorbents estimated by the ODR and OLS methods, as well as the corresponding SSR and SNR values, are presented in Table 2. From the estimated model parameters, the calculated curves were superimposed to the experimental values in Fig. 4.

Table 2. Langmuir Parameters for Methylene Blue (MB) Sorption by Activated Carbon (AC), Grape Stalks (GS), and Cork Bark (CB)

		Sorbent	AC	GS	CB
ODR	q_{max}	(mg g^{-1})	157.5	105.6	30.52
	b	(L mg^{-1})	0.94	0.019	0.012
	SSR $_{OLS,1}$		94.7	836.0	257.6
	SSR $_{ODR,1}$		0.00073	0.0041	0.014
	SNR$_1$		1.988	1.414	1.269
OLS	q_{max}	(mg g^{-1})	157.8	99.9	26.1
	b	(L mg^{-1})	0.91	0.039	0.35
	SSR $_{OLS,2}$		92.3	510.8	69.9
	SSR $_{ODR,2}$		0.00074	0.0099	0.052
	SNR$_2$		1.975	1.611	1.271

When comparing the sum of normalized residues (SNR), the results in Table 2 show that SNR was lower when applying the ODR method for GS and CB, and almost similar in the case of AC. In consequence, the values of q_{max} and b estimated by the ODR method are considered to be the more accurate. The improvement of parameters estimation is remarkably observed in the corresponding fitting of the experimental data (Fig. 4).

As seen in Table 2, from the two vegetable wastes investigated, GS show the highest sorption capacity for MB. Though this capacity is 1.5 times lower than that obtained for AC in the present work, its capacity is 1.3 folds higher than this of an exchange resin (Wawrzkiewicz and Hubicki 2009) and also higher than those of many biosorbents, such as *Paspalum notatum* (31.4 mg g^{-1}) (Kumar and Porkodi 2007), yellow passion fruit waste (44.7 mg g^{-1}) (Pavan *et al.* 2008), orange peel (18.6 mg g^{-1}) (Annadurai *et al.* 2002), rice husk (40.58 mg g^{-1}) (Vadivelan and Kumar 2005), charcoal (62.7 mg g^{-1}) (Banat *et al.* 2007), and olive pomace (42.3 mg g^{-1}) (Banat *et al.* 2007) and similar to several other sorbents such as phoenix tree leaves (80.9 mg g^{-1}) (Han *et al.* 2007), giant duckweed (119 mg g^{-1}) (Waranusantigul *et al.* 2003), teak leaves (120 mg g^{-1}) (Kumar *et al.* 2010), and teak sawdust (96 mg g^{-1}) (Kumar *et al.* 2010). Nevertheless,

the capacity of GS is lower than those reported for activated carbons (300 to 980 mg g^{-1}) (Gupta and Suhas 2009), teak wood bark (914 mg g^{-1}) (Gupta and Suhas 2009), and honey tree leaves (417 mg g^{-1}) (Kumar *et al.* 2010).
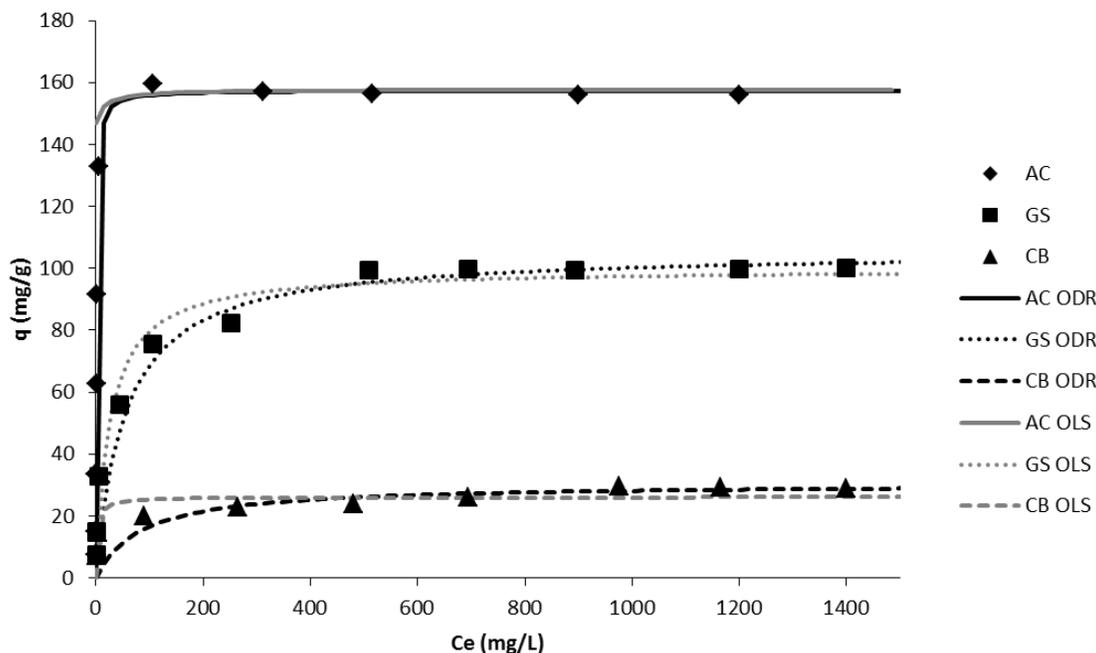
Fig. 4. Sorption isotherms of methylene blue (MB) using activated carbon (AC), grape stalks (GS), and cork bark (CB). Solid lines represent predicted data by the Langmuir model, and the symbols are the experimental data. Initial pH = 6.5; contact time (AC) = 240 min; Contact time (AC and GS) = 480 min; T = 20±2°C.

FTIR and Proposed Adsorption Mechanisms

FTIR spectroscopy was applied to identify the functional groups responsible for MB sorption (Fig. 4). A decrease was observed for the band corresponding to aromatic vibrations from 1612.2 cm^{-1} to 1598.7 cm^{-1} in the case of GS and a minor shift from 1512.9 cm^{-1} to 1511.9 cm^{-1} in the case of CB. The interaction between carboxylic groups, negatively charged (-COO^{-}) and MB^{+} cations would be difficult due to the proximity between the aromatic rings of lignin moieties and MB, resulting in a shift of the band corresponding to aromatic vibrations. In addition, the FTIR spectra indicate that the band at around 1035 cm^{-1} attributed to C-O stretching of the methoxy group (-OCH$_3$) of the aromatic ring of lignin (Herbert 1971) or to the C-O bonds of cellulose/hemicelluloses constituents (Haussard *et al.* 2003) was shifted. Other hydroxyl groups and carboxyl groups (*i.e.* phenolic, aliphatic extractives), also negatively charged, could also be involved in the sorption of MB via electrostatic interaction.

Recent studies performed by Liu *et al.* (2010) and Khraisheh *et al.* (2005) reported that carboxyl and hydroxyl groups were identified as the most important groups responsible for the sorption of MB. The higher MB sorption yield of GS compared to CB at the studied pH (6.5) could be attributed to the higher lignin content of GS and/or to the difference in water extractives which contain tannins (*i.e.* OH groups): 3 to 8% in cork bark (Jové *et al.* 2011) *vs.* 24% in grape stalks (Prozil *et al.* 2012).

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Concerning the band characteristic of C-O bonds (corresponding to the methoxy group of lignin) it was observed that it shifted from 1034.6 cm^{-1} and 1035.6 cm^{-1} to 1039.5 cm^{-1} and 1038.5 cm^{-1} in the case of GS and CB, respectively. In the CB spectrum, another band characteristic of C-O bonds of cellulose/hemicelluloses also significantly shifted from 1166.7 cm^{-1} to 1161.9 cm^{-1}.

It must be noted that the strong peaks at about 1598 cm^{-1}, 1391 cm^{-1}, 1334 cm^{-1}, and 886 cm^{-1} (Fig. 5) are characteristic bands of the MB spectrum.
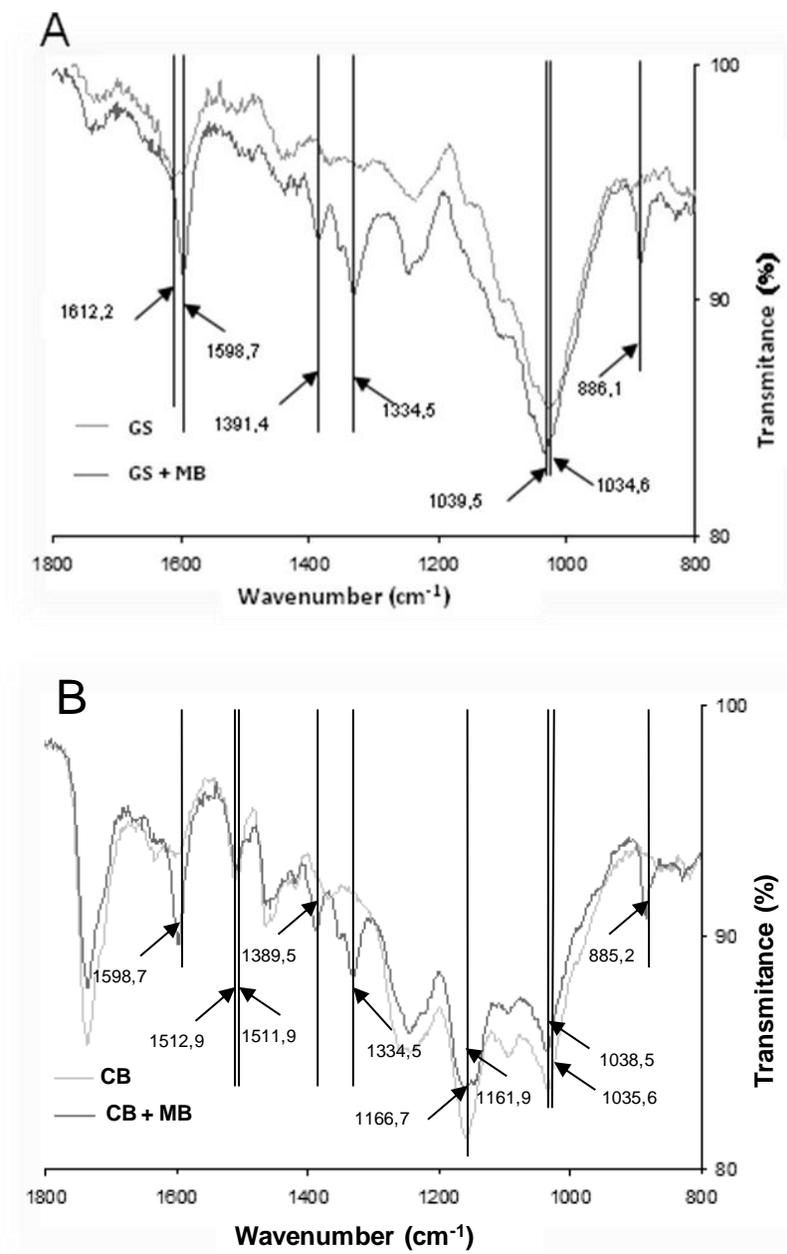

Fig. 5. FTIR spectra of A) grape stalks (GS) and B) cork bark (CB) loaded with methylene blue

Taking into consideration the abovementioned, the following sorption mechanisms are proposed:

1) Electrostatic interactions between the negative groups of carboxylic groups from GS and CB and the cation groups N^+ of the MB.
2) n-π interactions between deprotonated carboxyl groups (-COO^-) of the sorbents as n-donors with the π-acceptor sites of the aromatic ring of the MB (Keiluweit and Kleber 2009).
3) Cation–π interactions: the cationic center N^+ of MB can make favorable interactions with the π-electron cloud of aromatic side chains (Aschi *et al.* 2002; Crowley and Golovin 2005).
4) π-π interactions between π aromatic ring donors of MB and π acceptor groups in the sorbents (*i.e*. the aromatic rings of lignin) (Keiluweit and Kleber 2009).

CONCLUSIONS

Sorption of methylene blue onto grape stalks, cork bark, and activated carbon have been studied. The following conclusions arise from this work:

1. Grape stalks served as a good source for activated carbon that exhibited efficient adsorption of methylene blue sorption at low dye concentrations. Such material may be a good alternative to the use of conventional activated carbon to remove methylene blue from water. Cork bark showed the lowest efficiency and the highest influence of pH for the sorption of methylene blue. The lower point zero charge of CB (3.6) compared to GS (5.0) could explain the difference in MB sorption.

2. Langmuir parameters estimated by the Orthogonal Distance Regression method (ODR) provided the best fit of the experimental data. Maximum sorption capacities were found to be 157.5 mg g^{-1} for activated carbon, 105.6 mg g^{-1} for grape stalks, and 30.52 mg g^{-1} for cork bark.

3. FTIR spectra indicated that apart from the dominant electrostatic interactions in which carboxylic groups play a significant role, lignin moieties also influence the sorption process of methylene blue. Proposed mechanisms also include n-π interations, cation-π interactions, and π-π interactions. In addition, the higher the number of active sites reported in the literature for GS compared to CB could be responsible for the highest sorption.

ACKNOWLEDGMENTS

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