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Kinetic, isotherm and thermodynamic studies of the adsorption of methylene blue dye onto agro-based cellulosic materials

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ABSTRACT

The purpose of this work is to establish the optimal experimental conditions for the removal of methylene blue (MB-as model basic dye) from aqueous solution by adsorption onto four agro-based materials, namely, cedar sawdust, pine sawdust, wheat straw, and Provence cane *Arundo donax*. Results show that an increase in acidity or ionic strength of the medium has generally a negative effect on the discoloration yield. From the data of pH effect, there is no need to change the initial pH of the MB solution to be treated. Equilibrium was reached after 20−30 min of agitation when cedar sawdust, pine sawdust, and Provence cane are used as adsorbents. However, in the case of wheat straw, an agitation for 40 min is required. The pseudo-second-order model was found as the best to explain the adsorption kinetics effectively. The adsorption may be controlled by external mass transfer followed by intra-particle diffusion mass transfer. The adsorption equilibrium data were fitted well by the Langmuir isotherm and the maximum adsorption capacity was estimated to be about 100, 71.4, 143, and 91 mg g^{-1} for cedar sawdust, pine sawdust, straw, and Provence cane, respectively. For all the adsorbents tested, adsorption decreases with the increase in solution temperature. The values of the thermodynamic parameters of each system adsorbent/MB indicated that adsorption is a spontaneous and exothermic process. The comparison of the characteristics of the supernatants recovered after adsorption shows clearly that cedar sawdust leads to the production of a liquid with minimum values of turbidity, conductivity, and permanganate index.

Keywords: Adsorption; Methylene blue; Agro-based materials; Kinetic study; Thermodynamic parameters

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1. Introduction

The problem of decontamination of water and wastewater has grown with rapid industrialization. Various kinds of synthetic dyestuffs appear in the effluents of industries, such as dyestuffs, textiles, leather, paper, plastics, etc. [1,2]. The presence of dyes in the effluents is a major concern due to their effect on photosynthetic activity in aquatic systems. In addition, some dyes and their degradation products have toxic, mutagenic, or carcinogenic influences on living organisms [3]. There are several dyes with different chemical structures commercially available; they are classified as anionic, cationic, and non-ionic depending on the ionic charge on the dye molecules. Cationic dyes are more toxic for water ecosystems than anionic dyes [4]. MB has wider applications, which includes coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, etc. [5] being one of the most important synthetic dyes that can negatively affect photosynthesis [6].

Various techniques have been employed for the removal of dyes from wastewaters, The conventional methods are coagulation and flocculation [7], oxidation or ozonization [8,9], membrane separation [10–12], and activated carbon adsorption [13,14]. Adsorption technology is one of the widely used treatments to remove synthetic dyes from wastewater because of the negligible one-time investment, easy separation, and convenient use [15].

Currently, adsorption on activated carbon is extensively used for the removal of dyes, but, it is still considered an expensive adsorbent, especially in large-scale water [16]. Consequently, the search for low-cost adsorbents, especially derived from locally available waste materials has nowadays become a main research focus. There has been a growing interest in utilizing non-conventional, low-cost adsorbents, such as agriculture and industrial wastes, natural materials, and bioadsorbents. These materials are assumed to be low-cost adsorbents because they are abundant in nature, inexpensive, and require little processing [17]. Crude biomass, chemically modified biomaterials and some industrial wastes were investigated by several researchers in order to provide a competitive substitute for activated carbon in purifying the dyeing wastewater [18–20].

The main objectives of this study were to: (i) evaluate the feasibility of removing the MB from aqueous solution by adsorption onto four untreated agro-based materials: cedar sawdust, pine sawdust, wheat straw, and Provence cane *Arundo donax*; (ii) investigate the effect on adsorption process of various operational conditions, including adsorbent mass, pH, ionic strength, contact time, dye's initial concentration, and temperature; (iii) describe the adsorption process using mathematic models and discuss the adsorption mechanism of MB onto adsorbents; (iv) evaluate the effect of temperature in order to determine the thermodynamic parameters, and (v) examine the effect of the adsorbents tested on the quality of the aqueous medium in order to choose the adequate material that can lead to a complete discoloration without affecting the quality of the water being treated.

2. Materials and methods

2.1. Adsorbents and adsorbate

The adsorbents used in this study are the following: cedar sawdust, pine sawdust, wheat straw, and Provence cane. These agro-based materials were used directly for adsorption experiments without any treatment. Their specific surface areas, measured by the use of a Micromeritics ASAP2010 instrument, are 0.99 ± 0.04, 1.14 ± 0.04, 2.40 ± 0.03, and 1.47 ± 0.03 m^2/g, respectively.

Methylene blue ($\lambda_{max} = 664$ nm), a cationic dye, was chosen in this study as an adsorbate because of its known strong adsorption onto solids, and its recognized usefulness in characterizing adsorptive material. The solutions at the desired concentration were prepared with distilled water.

2.2. Adsorption procedure

Adsorption experiments were carried out at room temperature. Agitation was made using magnetic stirrer (500 rpm) for 5 h which is more than sufficient. At the end of the equilibrium period, the supernatant was subsequently analyzed for residual concentration of MB. The amount of MB adsorbed Q_e (mg g^{-1}), was obtained as follows:

$$Q_e = \frac{(C_0 - C_e)\,V}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid phase concentrations of MB (mg L^{-1}), respectively; V is the volume of the solution (L) and m is the amount of adsorbent used (g).

The effect of pH on the equilibrium uptake of MB was studied over a pH range from 2 to 12. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions. The effect of adsorbent dosage and that of initial concentration of dye (ranging from 50 to 2000 mg L^{-1}) were investigated. In the kinetic study, the adsorption experiments were carried out by agitating the selected amount of each adsorbent (cedar sawdust, pine sawdust, straw, or Provence cane) in 1 L aqueous solution of MB at a concentration of 20 mg L^{-1}. MB content in the solutions was analyzed at regular intervals. The pseudo-first-order and the pseudo-second-order models were used to evaluate the adsorption kinetics. The Langmuir and Freundlich isotherms were selected in this study to model adsorption equilibrium and the characteristic parameters for each isotherm were determined. The effect of temperature on adsorption was investigated at several temperatures (25, 30, 40, 50, and 60℃).

2.3. Analysis

When the adsorption procedure was completed, the residual concentration of MB was analyzed using ATI Unicam UV2 UV/vis Spectrometer (Cambridge, UK). Sometimes, appropriate dilution was processed to ensure that the concentration of the solution was within the dynamic range of the calibration curve.

An environmental scanning electron microscope (SEM) equipped with an EDAX system PHILIPS XL 30 ESEM (Einhoven, Netherlands) was used to observe the structure of each adsorbent material. IR spectra of adsorbents tested in this work were recorded using a Tensor 27 FTIR spectrometer from Bruker (Karlsruhe, Germany) equipped with a DLaTGS detector. Spectra were obtained in the attenuated total reflectance (ATR) mode by coadding 50 scans per spectrum at a resolution of 4 cm^{-1} and a scanner velocity of 10 kHz HeNe frequency, from 4,000 to 550 cm^{-1}. For instrumental and measurement control, spectra treatment and data manipulation, the OPUS program (version 6.5) from Bruker was employed. Spectra recorded are the average of 3 spectra of each sample with a smoothing of 9 points.

Adsorbents were analyzed by atomic spectrometry with a Thermo Finnigan EA 1110 CHNS (Waltham, MS, USA) elementary analyzer. Dry samples were analyzed after homogenization and milling using a ball mill until the proper particle size was obtained. Few milligrams of each sample was analyzed per duplicate using sulfanilamide as calibration standard.

The chemical analysis of cellulose, hemicellulose, and lignin were conducted as per the standards of American Society for Testing and Materials.

The supernatants recovered after adsorption, under optimal operating conditions, were characterized. The parameters mainly analyzed were pH, turbidity, conductivity, and permanganate index (PI). The pH and conductivity were measured directly by the use of Fisher Scientific Accumet Basic AB15 pH Meter (USA) and Conductivity Meter Model 101 (Orion Research, Cambridge, MA, USA), respectively. Turbidity was measured using a device (TN-100/T-100, Eutech Instruments). PI was measured as stated in AFNOR NF T 90-050 standard.

2.4. Point of zero charge (pH_{PZC})

The point of zero charge (pH_{PZC}) can be used to characterize an adsorbent material, since it indicates the pH at which the adsorbent material has a net zero surface charge [21]. The adsorbent surfaces have a net positive charge at $pH < pH_{PZC}$, while at $pH > pH_{PZC}$, the surfaces have a net negative charge [22].

The determination of pH_{PZC} of cedar sawdust, pine sawdust, straw, and Provence cane was performed according to the solid addition method [23] described as follows: 50 mL of 0.01 M KNO_3 solution was placed in conical flasks. The initial pH of the solutions was adjusted to a value between 2 and 12 by adding 0.1 M HCl or NaOH solutions. Then, 1 g of each adsorbent was added, the mixture was stirred, and the final pH of the solutions was measured after 24 h. The value of pH_{PZC} can be determined from the curve that cuts the pH_i line of the plot $pH_f - pH_i$ vs. pH_i (Fig. 1). The pH value for the potential of zero charge for cedar sawdust, pine sawdust, straw, and Provence cane was 5.7, 6.7, 7.7, and 7.0, respectively.

3. Results and discussion

3.1. Characterization of adsorbents

Fig. 2 shows the SEM of cedar sawdust, pine sawdust, straw, and Provence cane. It is clear that all adsorbents have a highly ordered structure; they are in the form of a multilayer composite. Images

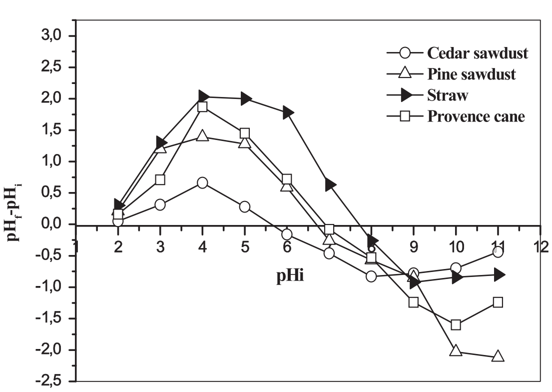

Fig. 1. Point of zero charge pH_{PZC} of cedar sawdust, pine sawdust, straw, and Provence cane.

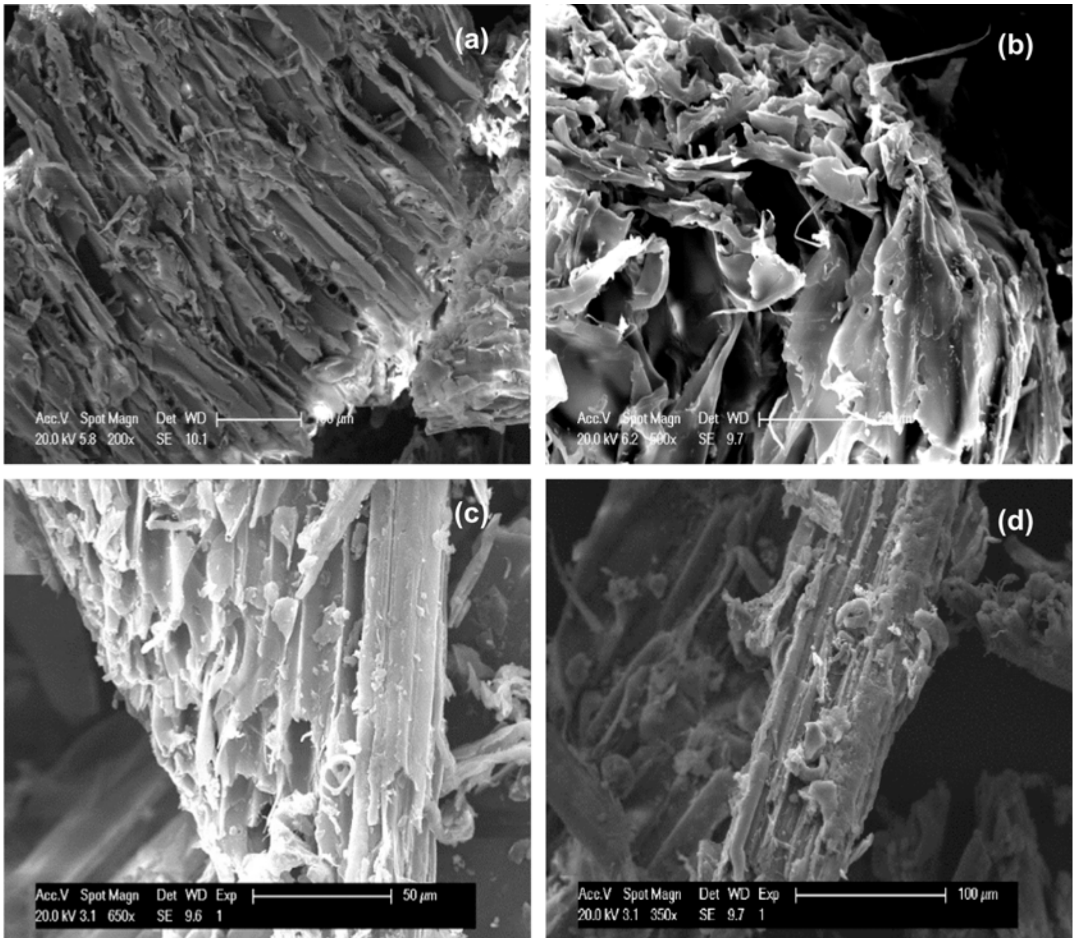

Fig. 2. SEM of cedar sawdust (a), pine sawdust (b), straw (c), and Provence cane (d).

obtained from SEM revealed that the studied agro-based materials have considerable layers of pores where there is a good possibility for the dye to be adsorbed. The morphology of these materials can facilitate the retention of adsorbate, due to their irregular surfaces. Furthermore, the surface roughness is indicative of high surface area. So, based on morphology, it can be concluded that these materials present an adequate morphological profile to retain dyes.

The infrared spectra of cedar sawdust, pine sawdust, straw, and Provence cane shown in Fig. 3 indicate a strong peak at 3,445 cm^{-1} attributed to the stretching vibrations of O–H. The band at 2,800–3,000 cm^{-1} is attributed to the stretching vibrations of C–H. Obtained spectra also show several distinct peaks in the fingerprint region between 500 and 1,750 cm^{-1}. Most of the observed bands of agro-based materials represent major cell wall components and have contributions from both carbohydrates (cellulose and hemicellulose) and lignin [24]. The comparison of the IR spectrum of each adsorbent before and after adsorption of MB did not show a clear difference (data not shown).

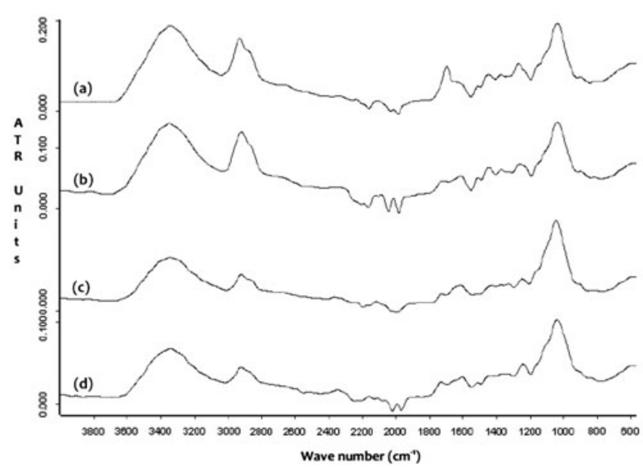

Fig. 3. FTIR spectra of pine sawdust (a), cedar sawdust (b), straw (c), and Provence cane (d).

The elementary analysis of cedar sawdust, pine sawdust, straw, and Provence cane was performed and results are presented in Table 1. As it can be seen, CHNS analysis illustrates that carbon is the major component of agro-based materials. The elements detected can be classified according to their percentage content in the following order: Carbon > Hydrogen > Nitrogen. It must also be noticed that sulfur was not detected in any of the products assayed.

The chemical composition (cellulose, hemicellulose, and lignin) of the cedar sawdust, pine sawdust, straw, and Provence cane is shown in Table 2. The composition of the aforementioned materials was compared to that of some agro-based products presented in the literature [25,26]. However, the accurate composition of each material can vary from cultivar to cultivar, the nature of soil, fertilizer to be used, and climatic conditions.

3.2. Effect of adsorbent dosage

In order to evaluate the effect of the adsorbents mass for the removal of MB from aqueous solutions, we carried out adsorption tests with different adsorbent dosages in 100 mL of MB solution at 20 mg L^{-1}. The results of the experiments with varying adsorbent mass are presented in Fig. 4. Maximum removal percentages were observed with an adsorbent dosage of about 5 g L^{-1} for cedar sawdust, straw, and Provence cane and about 10 g L^{-1} for pine sawdust. These optimal weights have been taken into consideration to conduct the experiments presented hereinafter. The percentage of MB removal increases by increasing the adsorbent mass for each adsorbent. It is clearly understood that the effect of adsorbent mass plays a very vital role in the adsorption process of MB onto agro-based materials. In fact, the number of available adsorption sites increases by increasing the adsorbent dose. The use of high adsorbent mass results in a low adsorption capacity value Q_e (mg/g) at a fixed MB concentration (20 mg L^{-1}). At a low adsorbent mass, all types of sites are entirely exposed and the adsorption on the surface is saturated faster, showing high Q_e values.

3.3. Effect of pH

The influence of the aqueous solution pH on the adsorption behavior of the dye onto various adsorbents was considered by many authors [21–23], because, this parameter is one of the most important factors affecting the adsorption process. In order to investigate the influence of pH on the MB removal by cedar sawdust, pine sawdust, straw, and Provence cane, experiments were carried out at pH values ranging from 2 to 12 at a fixed MB concentration of 20 mg L^{-1}. Fig. 5 shows that the increase in the acidity of the medium has generally a dramatic effect on the yield of MB adsorption and that removal percentage increases with the increase in pH.

The very low adsorption capacity at strong acidic pH is mainly due to the presence of an excess of H^+ ions which compete with the cationic dye for the active sites [27]. When the pH is increased to values higher than the pH_{PZC} of cedar sawdust, pine sawdust, and straw, the number of negatively charged sites on the surface of the three adsorbents increases and the removal percentage of MB also increases. This could be attributed to the increase in the electrostatic attractions between the MB cation and the adsorbent's functional groups. However, the decrease in adsorption at high pH values for Provence cane might be due to its partial hydrolysis. Therefore, the normal pH of MB solution, without correction, was selected to be the best for further studies.

3.4. Effect of ionic strength

The effect of the ionic strength on the biosorption process of MB was studied using various ratio weights of NaCl (g)/volume of MB solution (mL). Different amounts of sodium chloride ranging from 0 to 1.0 g were added to 100 mL of the dye solution at 20 mg L^{-1}. As it can be seen in Fig. 6, an increase in the ionic strength of the solution decreases the discoloration yield for all adsorbents. The reason for this is that, hydrated cations in the aqueous phase compete effectively for the active sites of the adsorbents. The ionic atmosphere which may be progressively formed

Table 1
Elementary analysis of cedar sawdust, pine sawdust, straw, and Provence cane

Element	Cedar sawdust	Pine sawdust	Straw	Provence cane
% C	50.1 ± 0.1	49.3 ± 0.2	42.47 ± 0.34	43.4 ± 0.1
% H	6.6 ± 0.3	6.2 ± 0.1	5.9 ± 0.4	5.6 ± 0.2
% N	0.21 ± 0.01	0.475 ± 0.007	0.43 ± 0.02	0.356 ± 0.025
% S	n.d	n.d	n.d	n.d

Note: n.d: not detected.

Table 2
Average chemical composition of cedar sawdust, pine sawdust, straw, and Provence cane compared with other materials

Materials	Lignine (%)	Cellulose (%)	Hemicellulose (%)	Reference
Cedar sawdust	28.8	39.3	12.0	In this study
Pine sawdust	26.2	34.0	34.6	In this study
Straw	22.5	33.0	23.8	In this study
Provence cane	22.7	36.6	26.6	In this study
Wheat straw	16.9	36.6	29.8	[25]
Barley straw	12.7	40.4	25.6	[25]
Rice straw	9.8	35.3	26.7	[25]
Sugar cane bagasse	17.9	40.1	26.3	[25]
Pine sawdust	28.5	40.0	28.5	[26]

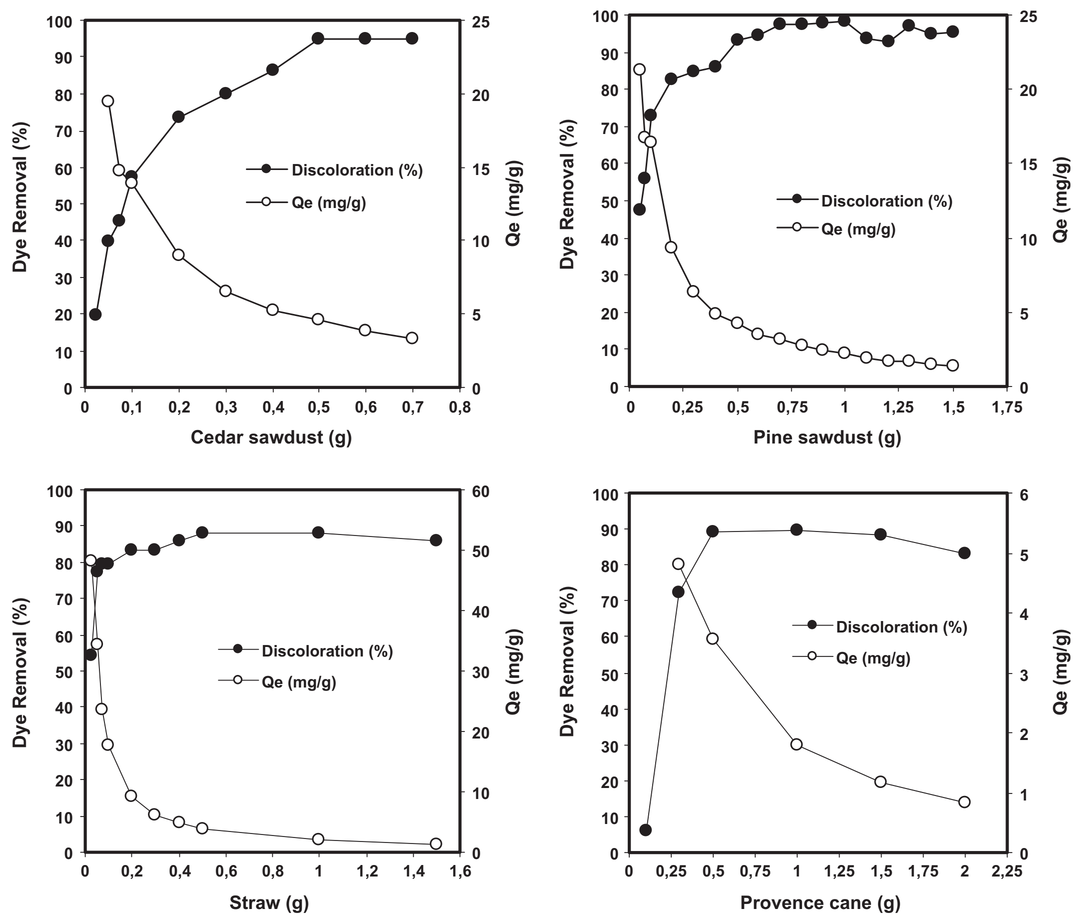

Fig. 4. Effect of adsorbent mass on the uptake of MB dye.

around MB molecules, with increased NaCl concentration, can also reduce the adsorption of MB dye.

3.5. Effect of contact time

From an economical point of view, the contact time required to reach equilibrium is an important parameter in wastewater treatment [28]. The effect of contact time on the removal of MB by cedar sawdust, pine sawdust, straw, and Provence cane at the initial concentration of 20 mg L^{-1} measured at room temperature is shown in Fig. 7. The adsorption process of MB presents generally two phases: an initial rapid phase where adsorption capacity sharply increased within the first 10 min due to the rapid surface adsorption and a second slow phase associated with the internal

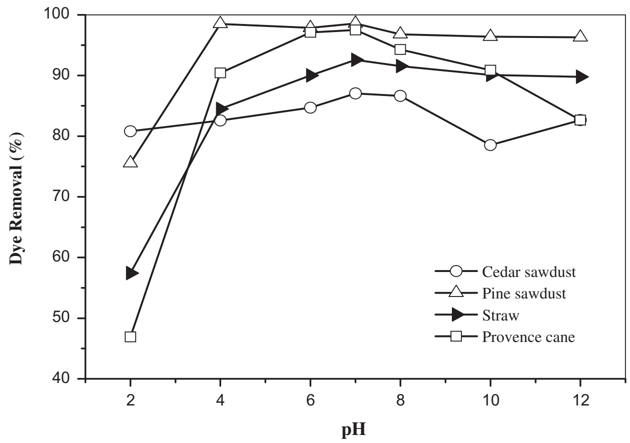

Fig. 5. Effect of the solution pH on MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane.

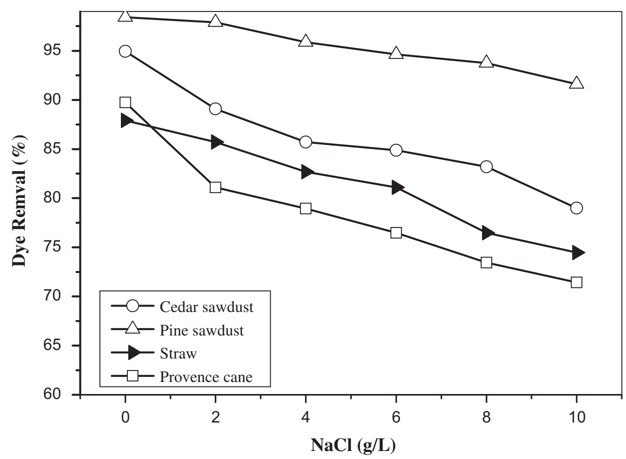

Fig. 6. Effect of ionic strength on MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane.

surface adsorption. Results obtained show that equilibrium can be reached after 20−30 min of agitation when cedar sawdust, pine sawdust, and Provence cane are used as adsorbents. However, in the case of straw, an agitation for 40 min is required. Once equilibrium has been achieved, the adsorption percentage of MB did not change with further increase in contact time because the amount of dye adsorbed reached a steady state with the amount of residual dye in the solution. A similar trend was also observed for MB adsorption onto some adsorbents, such as modified sugarcane bagasse [21] and modified rape straw [29].

3.6. Effect of dye concentration

Initial dye concentration provides an important driving force to overcome all mass transfer resistances

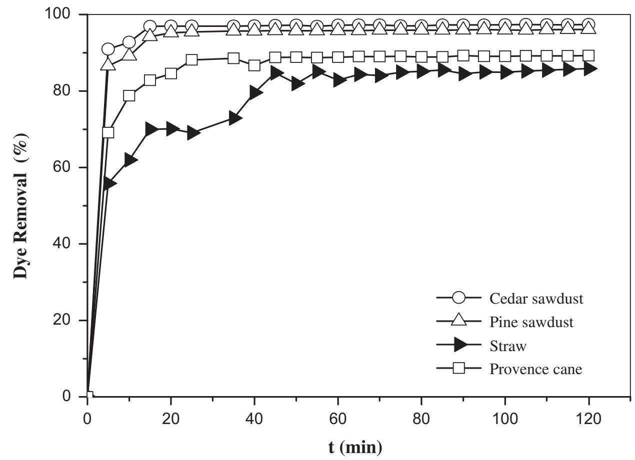

Fig. 7. Effect of contact time on MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane.

of the dye between the aqueous and solid phases. The effect of initial dye concentration on its removal by each agro-based material, tested in this work, was investigated in the concentration range from 50 till 2000 mg L^{-1}. From the obtained results shown in Fig. 8, it was found that the amount of dye adsorbed (mg g^{-1}) increases with an increase in the initial dye concentration. This is due to the increase in the driving force of the concentration gradient.

3.7. Adsorption isotherms

The adsorption isotherm represents the relationship between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. To describe the capabilities of cedar sawdust, pine sawdust, straw, and Provence cane in removing MB dye from aqueous solution, the Langmuir and Freundlich isotherm models were used.

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface [30]. The data of the equilibrium studies for the adsorption of MB onto agro-based materials may follow the following form of the Langmuir model:

$$\frac{C_e}{Q_e} = \frac{1}{K_L\, Q_{max}} + \frac{C_e}{Q_{max}} \tag{2}$$

where C_e is the equilibrium concentration (mg L^{-1}) and Q_e is the amount adsorbed per specified amount of adsorbent (mg g^{-1}), K_L is the Langmuir equilibrium constant and Q_{max} is the amount of adsorbate required to form a monolayer. The values of Q_{max} and K_L can be determined from the intercept and the slope of the

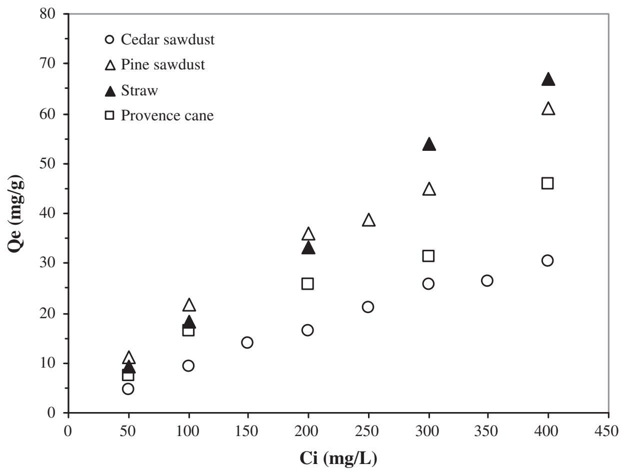

Fig. 8. Effect of initial concentration on MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane.

plot of C_e/Q_e vs. C_e from the linearized Langmuir equation (Fig. 9).

On the other hand, the Freundlich model assumes that adsorption takes place on heterogeneous surfaces. The Freundlich model [28] can be expressed as:

$$\ln Q_e = \ln K_F + \frac{\ln C_e}{n} \tag{3}$$

where K_F is Freundlich equilibrium constant, n is an empirical constant and rest of the terms have the usual significance. Thus, a plot of ln Q_e vs. ln C_e should be a straight line with a slope $1/n$ and an intercept of ln K_F (Fig. 10). This model deals with the multilayer adsorption of the considered substance on the adsorbent.

The fitness of both the Langmuir and Freundlich adsorption models on describing the equilibrium isotherms of each adsorbent/MB system was examined. The best fitted model was selected based on their determination coefficient (R^2). Data from the isotherm evaluation are summarized in Table 3. The R^2 of the Langmuir isotherm model for all adsorbents was higher than that obtained using the Freundlich model, showing that the experimental equilibrium data were better explained by the Langmuir equation. This finding supports the assumption that MB is adsorbed as a homogeneous monolayer onto the adsorbents, and has a free-energy change for all adsorption sites [31]. This result agrees with those obtained by other researchers [32,33], where the Langmuir model was used for describing the adsorption of MB onto different waste materials. The maximum adsorption capacity obtained from the Langmuir equation is about 100, 71.4, 143, and 91 mg for each gram of cedar sawdust, pine sawdust, straw, and Provence cane, respectively.

By comparing the maximum adsorption capacity of cedar sawdust, pine sawdust, straw and Provence cane found for MB adsorption to that reported for other waste-based adsorbents including Hazelnut shells [34] and cereal chaff [35], it can be concluded that these agro-based materials have a greater adsorption capacity for MB than most of the waste-based adsorbents previously reported. The favorability of MB adsorption onto the four studied agro-based materials was further analyzed using a dimensionless parameter ($R_L = 1/(1 + K_L C_0)$), derived from the Langmuir equation, where C_0 is the initial concentration of the dye. The adsorption process can be defined as irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) in terms of R_L [36]. In

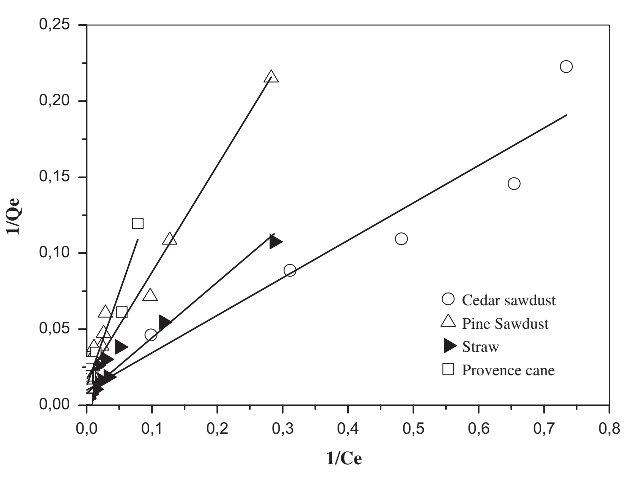

Fig. 9. Langmuir isotherm plots for MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane.

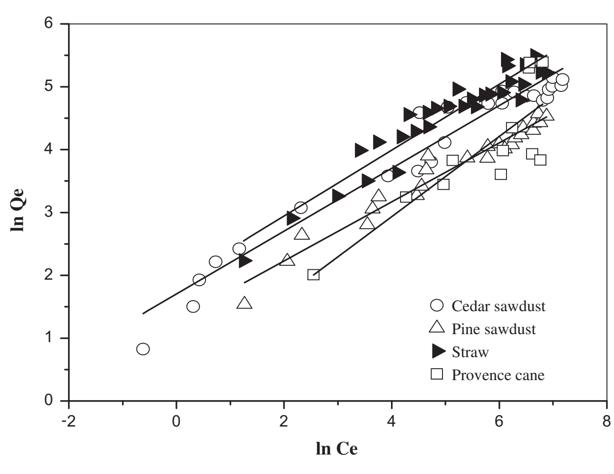

Fig. 10. Freundlich isotherm plots for MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane.

Table 3
Parameters related to the adsorption of MB onto cedar sawdust, pine sawdust, straw, and Provence cane

	Langmuir			Freundlich		
Adsorbents	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	$1/n$	K_F	R^2
Cedar sawdust	100	0.042	0.986	0.499	5.49	0.938
Pine sawdust	71.42	0.010	0.966	0.435	4.44	0.960
Wheat straw	142.85	0.021	0.951	0.524	7.38	0.909
Provence cane	91	0.008	0.923	0.638	1.64	0.685

our case, the values of R_L fall between 0 and 1; therefore, the adsorption process of MB onto each adsorbent is favorable.

The values of $1/n$ ($0.1 < 1/n < 1$) in the Freundlich model, included in Table 3, indicated a higher adsorbability of MB onto all the adsorbents; therefore cedar sawdust, pine sawdust, straw, and Provence cane can be considered as appropriate adsorbents for the removal of cationic dyes.

3.8. Adsorption kinetic

The adsorption kinetics were evaluated using the pseudo-first-order [37] and the pseudo-second-order [38] models to determine the controlling mechanism of MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane. The pseudo-first Lagergren equation is expressed as:

$$\frac{dQ_t}{dt} = K_1(Q_e - Q_t) \quad (4)$$

Pseudo-first equation is an inherently linear equation and thus, it can also be expressed as:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1 t}{2.303} \quad (5)$$

where Q_t and Q_e are the amounts of MB adsorbed (in mg g^{-1}) at time t and at the equilibrium, respectively, and K_1 being the constant rate of pseudo-first-order adsorption process (1/min). A plot of log ($Q_e - Q_t$) vs. t (Fig. 11) should give a linear relationship from which K_1 and Q_e can be determined from the slope and intercept of the plot, respectively.

Pseudo-second-order equation is expressed as:

$$\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2 \quad (6)$$

Pseudo-second-order kinetic model has four linear equation forms. The most used linearized form is expressed as [39]:

$$\frac{t}{Q_t} = \left(\frac{1}{Q_e}\right)t + \frac{1}{K_2 Q_e^2} \quad (7)$$

where K_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). The slope of the plot t/Q_t vs. t gives the value of Q_e, and from the intercept, K_2 can be calculated. The plot of t/Q_t vs. t (Fig. 12) yields very good straight lines for each adsorbent.

The results of fitting experimental data with the pseudo-first-order and pseudo-second-order models for adsorption of MB onto cedar sawdust, pine sawdust, straw, and Provence cane are indicated in Table 4. As can be seen, the second-order equation provided a better-fitting model than the first-order equation with correlation coefficients R^2 (0.998–1.000). It was found that the pseudo-second-order rate model gave perfect fittings to the experimental data. The calculated Q_e values agree very well with the experimental data. These results indicate that the adsorption system studied belongs to the second-order kinetic model. A similar result was reported for the adsorption of MB on jackfruit peel [40] and on Guava leaf powder [41].

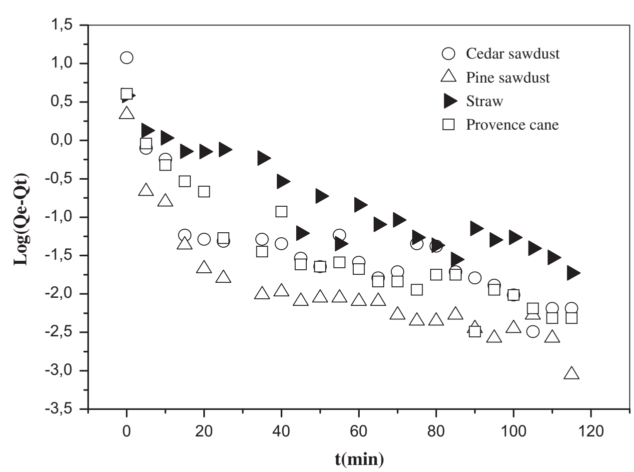

Fig. 11. Pseudo-first-order kinetic plots for MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane.

3.9. Adsorption mechanism

The pseudo-first-order and pseudo-second-order kinetic models do not identify the diffusion mechanism. The results of kinetic studies are analyzed using the intra-particle diffusion model. In this model [42,43], it is assumed that the transport of adsorbate from the solution phase to the surface of the adsorbent particles occurs in several steps: (i) transport of the adsorbate from the fluid to the external surface of the adsorbent through bulk diffusion, (ii) diffusion of adsorbate through the boundary layer surrounding the adsorbent particles (film diffusion transport), (iii) migration of adsorbate within the pores of adsorbent by intra-particle diffusion, and (iv) adsorption onto the surface of material.

The adsorption process is a diffusive mass transfer process, where the rate can be expressed in terms of the square root of time (t). The intra-particle-diffusion model is expressed as follows:

$$Q_t = K_i t^{0.5} + C \quad (8)$$

where Q_t is the fraction dye uptake (mg g^{-1}) at time t, K_i is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$), and C (mg g^{-1}) is a constant (intercept) that gives an idea about the thickness of boundary layer, that is, larger the value of C, the greater is the boundary layer effect.

The plot of Q_t vs. $t^{0.5}$ will give K_i as slope and C as intercept.

If the Weber–Morris plot of Q_t vs. $t^{0.5}$ gives a straight line, then it can be concluded that the sorption process is controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. It is assumed that the external resistance to mass transfer surrounding the particles is significant only in the early stages of adsorption. This is represented by first sharper portion. The second linear portion is the gradual adsorption stage with intra-particle diffusion dominating [44].

Fig. 13 shows the plots of Q_t vs. $t^{0.5}$ for the adsorption of MB onto agro-based materials. The data points were related by two straight lines, the first and the second straight portions represent macro-pore diffusion and micro-pore diffusion, respectively [45].

The values of K_i and C listed in Table 4 show that the constants C are not zero in any case. This showed that pore diffusion was not the rate-limiting step. So, the adsorption process may be of a complex nature consisting of both, surface adsorption and intra-particle diffusion [46]. Moreover, obtained results suggest that the adsorption of MB over cedar sawdust, pine sawdust, straw, and Provence cane may be controlled by external mass transfer followed by intra-particle diffusion mass transfer. Observably, as can be seen in Table 4, K_{i1} is larger than K_{i2}, while C_1 was smaller than C_2. The value of R^2 in first adsorption step is also larger than that in second step. This shows that the intra-particle diffusion can predict the kinetic process at different stages.

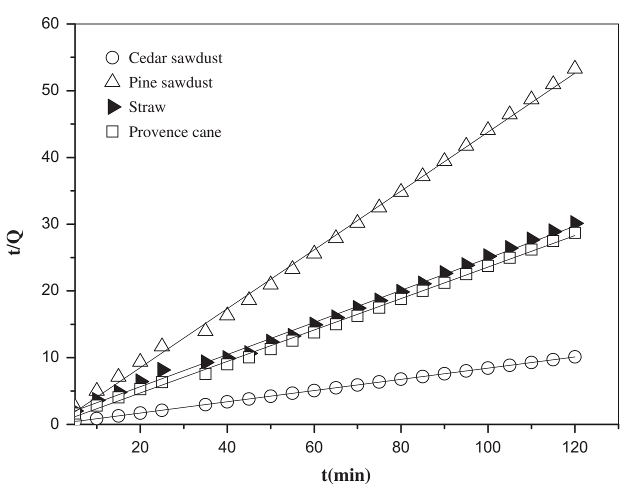

Fig. 12. Pseudo-second-order kinetic plots for MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane.

3.10. Effect of temperature and thermodynamic study

In order to understand the effect of temperature on the adsorption of MB dye onto cedar sawdust, pine sawdust, straw, and Provence cane, the adsorption studies were carried out at different temperatures 25, 30, 40, 50, and 60℃. The results obtained indicated that the adsorption decreases with the increase in solution temperature for all the adsorbents tested. Same results were obtained by various authors for the adsorption of dyes on various adsorbents [27]. This can be explained by the weakening of hydrogen bonds and van der Waals interaction at high temperatures, resulting in the weakening of physical interaction between the active sites of adsorbents and adsorbate [47].

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Thermodynamic studies reflect the feasibility and spontaneous nature of adsorption process. The parameters, such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) can be estimated from the changes in

Table 4
Pseudo-first-order, pseudo-second-order and intra-particle diffusion parameter models for the adsorption of MB onto cedar sawdust, pine sawdust, straw, and Provence cane

	Adsorbents			
Kinetic models and its parameters	Cedar sawdust	Pine sawdust	Straw	Provence cane
Pseudo-first-order kinetic				
$Q_{e,the}$ (mg g^{-1})	0.420	0.959	0.960	0.950
K_1 (min^{-1})	0.039	2.183	0.297	0.739
R	0.665	0.740	0.859	0.818
Pseudo-second-order kinetic				
$Q_{e,the}$ (mg g^{-1})	11.905	2.169	3.968	4.065
K_2 (g mg^{-1} min^{-1})	0.336	1.180	0.058	0.230
R	1	1	0.999	0.999
$Q_{e,exp}$ (mg/g)	12.875	2.16	3.826	4.013
Intra-particle diffusion				
K_{i1} (mg g^{-1} $min^{-1/2}$)	0.368	0.095	0.308	0.312
C_1	10.24	1.722	1.805	2.488
R_1^2	0.911	0.983	0.937	0.941
K_{i2} (mg g^{-1} $min^{-1/2}$)	0.008	0.002	0.045	0.006
C_2	11.78	2.137	3.345	3.941
R_2^2	0.889	0.881	0.801	0.845

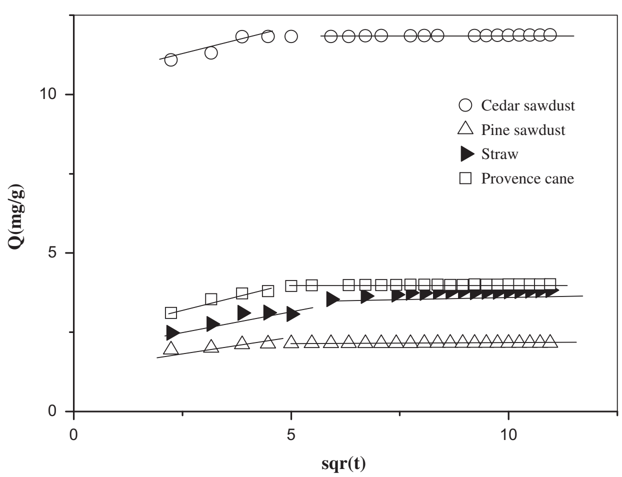

Fig. 13. Intraparticle diffusion constants for MB adsorption onto cedar sawdust, pine sawdust, straw and Provence cane.

equilibrium constants with temperature. The free energy change of adsorption reaction is given by:

$$\Delta G^\circ = -RT \ln K_C \tag{9}$$

where ΔG° is the free energy change (kJ mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), and K_C is the equilibrium constant (Q_e/C_e). The values of ΔH° and ΔS° can be calculated from Van't Hoff equation as follows:

$$\ln K_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{10}$$

When ln K_C is plotted against $1/T$ (Fig. 14), a straight line with the slope ($-\Delta H^\circ/R$) and the intercept

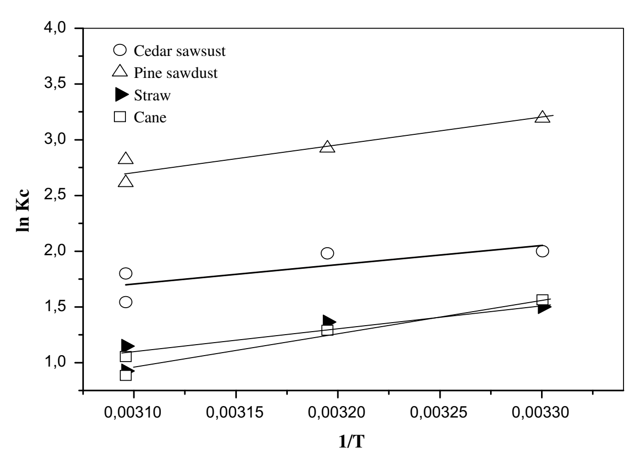

Fig. 14. Plots of ln K_C against temperature (K^{-1}).

Table 5
Values of thermodynamic parameters for MB adsorption onto cedar sawdust, pine sawdust, straw, and Provence cane

Thermodynamic parameters	Temperature (°C) 30	40	50	60
Cedar sawdust				
ΔG° (kJ mol^{-1})	−5,037.51	−5,152.12	−4,832.56	−4,141.37
ΔS° (kJ mol^{-1} K^{-1})	−0.208			
ΔH° (kJ mol^{-1})	−71.22			
Pine sawdust				
ΔG° (kJ mol^{-1})	−8,049.29	−7,607.98	−7,575.07	−7,019.05
ΔS° (kJ mol^{-1} K^{-1})	−0.028			
ΔH° (kJ mol^{-1})	−16.51			
Straw				
ΔG° (kJ mol^{-1})	−3,782.62	−3,549.12	−3,081.09	−2,482.29
ΔS° (kJ mol^{-1} K^{-1})	−0.052			
ΔH° (kJ mol^{-1})	−19.62			
Provence cane				
ΔG° (kJ mol^{-1})	−3,938.21	−3,358.99	−2,833.09	−2,374.47
ΔS° (kJ mol^{-1} K^{-1})	−0.069			
ΔH° (kJ mol^{-1})	−24.93			

($\Delta S^\circ/R$) is found. The obtained thermodynamic parameters are listed in Table 5.

Equilibrium constant values decreases with an increase in temperature. The overall ΔG° for the adsorption of MB onto the four agro-based materials studied provided negative values and increased with an increase in temperature as shown in Table 5. Since negative ΔG° indicates that the adsorption process is spontaneous, the ΔG° and its evolution in this study revealed that the adsorption of MB by cedar sawdust, pine sawdust, straw, and Provence cane is spontaneous and most favorable at a low temperature in the studied range. The negative value of ΔH° indicates that the adsorption of MB dye by all adsorbents tested is exothermic [48] and dominated by physical processes in nature. The negative value of ΔS° shows a slight decrease in randomness at the solid/solution interface with increasing temperature [49].

3.11. Characterization of supernatants

Regarding the final aspect of the MB solutions recovered after adsorption, the obtained results show that cedar sawdust treats the MB solution better than other materials. As it can be seen in Table 6, the characteristics are lower than those obtained by the use of pine sawdust, straw, and Provence cane. When cedar sawdust is used, the turbidity, conductivity, and PI are 7.4 NTU, 20.4 µs cm^{-1}, and 12.8 mg L^{-1}, respectively. The PI value reveals clearly that the solubilization of organic matter from cedar sawdust is less

Table 6
Physico-chemical characteristics of supernatants obtained after adsorption of MB onto cedar sawdust, pine sawdust, straw, and Provence cane

Material	Characteristics of supernatants pH	Turbidity (NTU)	Conductivity (µs cm^{-1})	Permanganate index (mg L^{-1})
Cedar sawdust	8.1	7.4	20.4	12.8
Pine sawdust	6.7	11.6	25.2	74.8
Straw	6.7	29.1	74.0	79.0
Provence cane	6.7	24.6	401.0	88.8

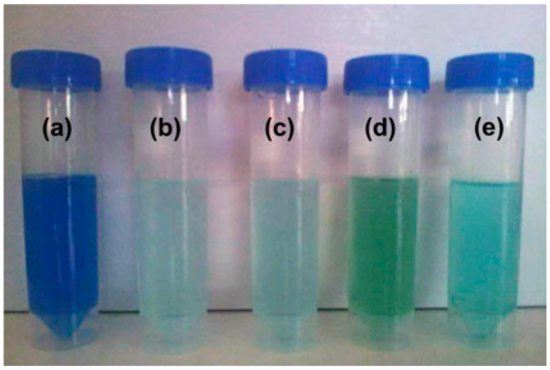

Fig. 15. Solution of MB dye before treatment (a) and after adsorption on cedar sawdust (b), pine sawdust (c), straw (d), and Provence cane (e).

important. Fig. 15 shows the aspect of MB solution before and after treatment by adsorption on tested materials.

4. Conclusion

The present study establishes the fact that cedar sawdust, pine sawdust, wheat straw, and Provence cane can be used as adsorbents for the removal of MB from aqueous solution. Adsorption experiments were carried out as function of adsorbent mass, pH, ionic strength, contact time, initial concentration of dye, and temperature. Results reveal that there is no need to change the initial pH of the MB solution and that adsorption decreases with increasing ionic strength of the dye solution. The kinetic study shows that the equilibrium was reached after 20−30 min by the use of cedar sawdust, pine sawdust, and Provence cane as adsorbents. However, a contact time of about 40 min is required in the case of straw.

Equilibrium data fitted very well with the Langmuir isotherm equation, confirming the monolayer adsorption capacity of MB onto all adsorbents tested. The maximum adsorption capacity is about 100, 71.4, 143, and 91 mg g^{-1} for cedar sawdust, pine sawdust, straw, and Provence cane, respectively. The rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation. The adsorption of MB dye decreases with the increase in solution temperature. The thermodynamic analysis revealed that the present adsorption process is exothermic and spontaneous. Adsorption of MB dye on cedar sawdust allows obtaining a supernatant with minimum values of turbidity, conductivity, and PI.

Taking into consideration the above results, it can be concluded that cedar sawdust, pine sawdust, straw, and Provence cane are able to adsorb MB dye from aqueous solution. So, they can be considered as low-cost adsorbents for dye removal, eventually, in wastewater treatment processes.

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