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Methylene Blue Adsorption from aqueous solution by low cost vine-wood biomass.

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Abstract

In this work, the sawdust of vine wood (VW) was treated with sulfuric acid and used to adsorb methylene blue (MB) from aqueous solutions via a batch adsorption process. The characteristics of the adsorbent were determined by various analytical techniques such as Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) N₂ adsorption–desorption isotherms. The effects of various experimental parameters including sulfuric acid concentration, particle size of the adsorbent, pH of the solution, contact time, initial concentration, adsorbent dosage and temperature on adsorption of MB by activating sawdust were systematically investigated. The experimental results showed that the adsorption efficiency was increased with contact time and adsorbent dosage. The maximum removal efficiency was found after 180 min of solid/liquid contact with adsorbent doses of 1 g/l for sawdust. The isotherm and kinetic experimental data for MB adsorption on VW sawdust were best-fitted by Langmuir models and Pseudo-second-order, respectively.

The calculated values of the entropy (ΔS°), enthalpy (ΔH°) and Gibbs energy (ΔG°) indicated that the adsorption process was exothermic in nature. These results suggest that the activated sawdust can be employed as a low-cost and environmentally friendly adsorbent for the treatment of wastewaters containing dyes.

Keywords: Vine wood, adsorption, methylene blue

1 Introduction

Wastewater pollution by toxic dyes is an emerging concern because of potential health impacts. They are mainly discharged into the environment through various industrial activities like textile, printing, leather, paper-making, plastics etc. their complex aromatic molecular structure makes them stable and more difficult to be removed from the effluents. Therefore, it is necessary to remove dye from wastewater before releasing them into the environment.

Methylene blue (MB) is a cationic dye used in different industries, especially in the textile and dyeing industries (Kumar et al. 2004). However, the existence of MB in the environment can cause eye and skin irritation, dyspnea, gastritis and mental confusion. Therefore, the removal of MB from polluted water is an important concern in wastewater treatment.

To date, different approaches have been applied to the removal of organic dyes from industrial wastewater, including degradation method, membrane separation method, precipitation method, biosorption, Fenton-biological treatment, and coagulation–flocculation method (Darvishmanesh et al. 2017; Konicki et al. 2017). However, most of these methods are expensive to operate and may even cause other contamination. Compared with other methods, adsorption process is widely used because of its high efficiency and low-cost. Extensive research in recent years involving extraction of dyes from effluent by adsorption has been devoted to the development of low cost adsorbent materials with high selectivity and greater adsorption capacity (Choy et al. 1999; Kanna et al. 2002). Various bioadsorbents have been reported, such as eucalyptus bark, rice husks, sawdust, and cellulose have drawn considerable attention.

Vine wood, which is composed of natural polymers such as lignin, cellulose, hemicellulose, and other extractives, is available in large quantities and is formed as waste product.

Herein, vine wood is used as raw material to prepare activated sawdust adsorbent, and the obtained material was used for the adsorption of cationic MB from aqueous solutions. The effects of adsorbent dosage, pH, contact time and initial dyes concentration (MB) were studied. Moreover, the adsorption was analyzed using isotherms, kinetic models, thermodynamics and adsorption mechanism. The results show that modified vine wood is an effective adsorbent for removal of cationic dyes from aqueous solutions.

2 Experimental

2.1 Materials

All chemicals used were analytical reagents grade and prepared in distilled water. Vine wood samples (VW) were received from a local company. The methylene blue was chosen in this study because of its known strong adsorption onto solids. A solution of 10^{-5} mol L⁻¹ methylene blue [3, 7-bis (dimethylamino) phenothiazin-5-ium ion] was prepared in distilled water as the stock solution (Fig. 1). Methylene blue (MW =319.85 g mol⁻¹ termed as MB) shows an intense absorption peak in the visible region at 664.5 nm (Fig. 2). This wavelength corresponds to the maximum absorption peak of the methylene blue monomer. The pH adjustments were carried out using dilute NaOH and HCl solutions.

Fig. 1 Chemical structure of methylene blue.

Fig. 2 Maximum absorbance wavelength $\lambda_{\max}$ (nm) of methylene blue.

A single beam Perkin-Elmer UV–Vis spectrophotometer with a 1 cm cell was used for measuring all of absorption data. A pH meter (JENWAY 3505) with a combined double junction glass electrode was used for pH measurements.

2.2 Determination of methylene blue concentration

Concentrations of methylene blue (MB) in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of the dye ($\lambda_{\text{max}}=664.5\text{nm}$) using the calibration curve shown in Fig. 3. The calibration curve of absorbance against MB concentration was obtained by using standard MB solutions at pH 6.9 (initial pH). The calibration curve shows that Beer's law ($A = \epsilon bc$) is obeyed in concentration range (2×10^{-6} - $10 \times 10^{-6} \text{ mol L}^{-1}$).

Fig. 3 Calibration curve of absorbance against concentration of methylene blue.

2.3 Preparation of vine wood biosorbent.

Vine wood samples were collected from the Ain Témouchent region (western Algeria). They were then cleaned and dried at a temperature of 105°C for 24 h. Samples were ground and sieved to particle sizes of $80 \mu\text{m}$ to 1mm . Then, they were refluxed in sulfuric acid solution of wt 10% at 100°C for 2 h to open VW surface pores. The biosorbent was washed several times with double-distilled water and dried for 24 hours after filtering.

Fig. 4 Schematic illustration of the preparation procedure for vine wood sawdust waste by H_2SO_4 .

2.4 Adsorption experiments

Factors affecting the adsorption process, which include the initial concentration of the MB dye, solution pH, vine wood dosage, particle size, chaker speed and temperature, were examined in a batch system.

50 to 300 mg of adsorbents, taken separately, were shaken in 100 ml aqueous solution of MB dye of varying concentration (10×10^{-6} - $30 \times 10^{-6} \text{ mol L}^{-1}$) at different temperatures ((20, 30, 40, and 50°C) for defined time periods. The effect of the pH on the MB removal was studied

over a pH range from 2.5 to 11. The pH of the solution has been controlled by adding 1 N of HC l and 1 N of NaOH. The effects s of the VW particle size on the removal of dyes was (80/125, 125/250 and 500/1000 µm) and shaker speed (100, 500 and 1000 rpm). The filtrates were centrifuged and analyzed for the residual (unadsorbed) concentration of methylene blue, spectrophotometrically at 664.5 nm wavelength. All experiments were carried out in triplicate with respect to each condition and mean values are used for further calculations. The following equations were used to calculate the amount of adsorbed methylene blue at equilibrium, Q_e (mmol/g) and the percentage of sorption (R %), respectively:

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 is the initial dye concentration (mol/L); C_e is the equilibrium dye concentration; m is the mass of the prepared adsorbent (g); V is the volume of the MB dye solution (L).

2.5 Biosorbent characterization

The biosorbent was characterised by Fourier Transform Infra-Red Spectroscopy (FTIR), Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM-EDX) and Brunauer-Emmett-Teller (BET) analysis. Fourier Transform Infrared Spectroscopy (FTIR, "CARY 600") was used to analysed functional groups of VW before and after activation. Scanning Electron Microscopy Energy-Dispersive X-ray (SEM-EDX, Coxem-30) was used to analyse the surface morphological of VW before and after activations. Brunauer-Emmett-Teller (BET) was used to measure the surface area and total pore volume. The pore size distribution of the sorbent was calculated based on differential pore volume of Barrett-Joyner-Halenda (BJH) adsorption-desorption and the nitrogen adsorption-desorption isotherm values were determined using an ASAP 2010-Micromeritics apparatus at 77 K. The XRD pattern of

the VW adsorbent was analyzed by X-ray diffractometer model Philips; PW 1710 with Cu α radiation, and pH was measured using a pH Meter (JENWAY 3505). The biosorbent was characterized by measuring the point of zero charge (pH pzc) by using the solid addition method.

3 Results and discussion

3.1 Biosorbent characterization

3.1.1 Fourier Transform Infrared Spectroscopy.

FT-IR analyses were carried out to identify the associated functional groups. The spectra were recorded in the range of 4000-500 cm^{-1} and are presented in Figure 5. The FTIR spectra of the raw and activated VW showed the presence of OH, aliphatic CH, carbonyl (C=O), and aromatic ring C=C functional groups by their characteristic stretching vibrations at 3280, 2919, 1730, and 1600 cm^{-1} , respectively a peak between 3337 and 3331 cm^{-1} assigned to the O-H stretching vibrations in alcohol, phenol, and carboxylic acid. The bands at 1160 cm^{-1} (SO_3^- - stretching) and 1350 cm^{-1} (O=S=O stretching in SO_3H). For the activated VW sample in the FT-IR spectrum indicates the successful activation of VW waste.

Fig. 5 FTIR spectra of the vine wood sawdust before and after chemical activation.

3.1.2 SEM /EDS Characterization

Scanning Electron Microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy(EDX) was used to assess the morphological feature and surface characteristic of VW before and after activation. Fig. 6(a) showed the SEM image in 1500x magnification for VW before sulfonation. It was characterized by the highly anisotropic character, commonly presented in the form the fibers are essentially due to spatial orientations of the natural

constituents of wood. Fig. 6(b) illustrates the SEM image of the sulfonated VW sample with well-developed pores and micro sized particles formed after the sulfonation process. The surface of the particles was rough, which could be due to the extensive sulfonation. Similar observations were made by other researchers for biosorbents from *Pinus sylvestris* (Benyoucef et al. 2015). EDS analysis of activated VW (Fig. 7(b)) showed that the activated VW sawdust contained higher contents of oxygen, which caused by oxidation process, which might be to form the oxygen-containing functional groups on VW surface. It is also observed that the reduction of contents of carbon, which is due to the degradation of hemicelluloses, lignin and the elimination of extracts, following the modification chemical of cellulosic material. This result was in good agreement with XRD.

Fig. 6 SEM Micrographs of vine wood sawdust (a) before and (b) after chemical activation.

Fig. 7 EDX image of vine wood sawdust: (a) before and (b) after chemical activation.

3.1.3 X-Ray diffraction (XRD) analysis

X-ray diffraction of untreated and treated sawdust of vine wood was performed as shown in Figure 8. Data were taken for from 2θ angles ranging from 10 to 80 degrees. It is found that the diffraction patterns of the VW untreated have low crystallinity (amorphous). The amorphous characteristic of raw VW is due to the high lignin content (amorphous compound) in its structure (Rosa et al. 2010). Significant 2θ angle peaks at 18° and 22° are observed in XRD patterns of the treated sawdust, which are associated with the crystalline cellulose structure. This is due to the partial reduction of hemicelluloses and lignin during the chemical treatment. This observation was also reported by (Alemdar and Sain (2008); Shahabi et al. 2015).

Fig. 8 X-ray diffraction (XRD) patterns of vine wood sawdust before and after treatment.

3.1.4 Characterization of the porous texture

The pore size distribution and surface area of both activated VW and unactivated VW were calculated by N₂ sorption isotherm study at 77K (BET method) (Brunauer et al. 1938) and are presented in Figures 9 & 10. For VW, the isotherms are mainly typed II (Fig. 9(a) & (b)) related to mesoporous solids. Figure 10 (a) & (b) confirms the mesoporosity of unactivated VW and activate VW, since most of the pores have the average diameter greater than 20 Å and less than 500 Å according to IUPAC classification. The BET surface area of unactivated VW and activated VW were found to be 0.5873 m²g⁻¹ and 1.6319 m²g⁻¹ respectively. The larger surface area of activated VW was attributed to the dispersion of H₂SO₄ into the pores through dissociation, thereby enhancing the pore density on its surface. The greater surface area of activated VW (Table 1) made it suitable and a favorable bio-adsorbent for the MB dye adsorption.

Table 1 Nitrogen sorption results of unactivated and activated vine wood sawdust.

Samples	BET method		BJH method		
	S _{BET} (m ² .g ⁻¹)	V _{TOTAL} (cm ³ . g ⁻¹)	S _{Meso} (m ² .g ⁻¹)	V _{meso} (cm ³ .g ⁻¹)	d _{Meso} (Å)
Unactivated vine sawdust	0.5873	0.00019	0.2911	0.00179	246.935
Activated vine sawdust	1.6319	0.00061	1.3176	0.00771	234.057

Fig. 9 Nitrogen adsorption-desorption isotherms at 77 K of (a) unactivated; (b) activated VW.

Fig. 10 BJH Pores size distribution plot of (a) unactivated; (b) activated VW.

3.1.5 Determination of point of zero charge (pH pzc)

The pH_{PZC} value is the point at which the surfaces of vine wood sawdust do not contribute to the pH of the solution (Giraldo and Moreno-Piraján 2008). When $\text{pH} < \text{pH}_{\text{pzc}}$, the sawdust surface is positively charged and thus favoring the adsorption of anionic species and negatively charged at $\text{pH} > \text{pH}_{\text{pzc}}$, which will be effective for the adsorption of cationic species (Rodriguez-Reinoso 1998). The determination of the pH_{pzc} of the sawdust of vine wood was carried out by a solid addition method of Crini and Badot (2007). 0.15 g of VWS was added to 50 ml of 0.01 M NaCl solution. The initial pH of the solutions was adjusted in the range of 1.67 to 11.2 by adding 0.1 M HCl or NaOH. The suspensions were stirred for a period of 48 h. The final pH of the solutions were measured and plotted versus the initial pH. The point of intersection of this curve with the $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$ linear plot yielded the point of zero charge (pH_{PZC}). Figure.11 shows that the pH_{PZC} of the sawdust of vine wood activated was found to be around 4.5. This value indicates the acid character of the vine wood sawdust, which was expected due to the chemical activation with sulphuric acid. Then, according to the results, the sawdust of vine wood will favor the removing of methylene Blue dye at $\text{pH} > \text{pH}_{\text{pzc}}$.

Fig. 11 The point of zero charge (pH_{pzc}) of VWS.

3.2 Effect of particle size

The effects of adsorbent particle size on the adsorption kinetics of activated VW in aqueous solution are depicted in Figure 12. It is noted that the dye adsorption capacity of the activated VW was decreased with increase in particle size. This is because bigger particle sizes have a small surface area and by consequence less active site are available for the biosorption process. However, these particles of fine sizes can cause clogging problems in the percolation systems, or may be difficult to recover (solid / liquid separation) (Fiset et al. 2001) for this reason we have chosen particles of medium size: $d = 125/250 \mu\text{m}$. Similar results were observed by (Barka et al. 2013; Gouamid et al. 2013).

Fig. 12 Effect of particle size on kinetics of MB dye adsorption.

3.3 Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of MB is shown in Figure 13. The VW dosage varied from 50 to 300 mg with 10^{-5} mol/L initial concentration of MB. The results show an increase in the adsorption efficiency of the VW sawdust with an increase in dosage. This is obviously due to an increase in the adsorbent's active sites. A maximum adsorption percentage removal of 99.85 % was achieved with 0.1 g of the sawdust. Further, escalation in the VW sawdust dosage (from 200 to 300 mg) did not change the percent removal significantly and remained nearly constant (99.5%). This is due to the saturation of adsorption sites of the VW surface. It resulted in particular interactions of dye molecules on adsorption sites, which diminished the surface area of the adsorbent. It was also found that the decrease of the amount of adsorbed dye from 19.225×10^{-3} mmol g⁻¹ to 3.317×10^{-3} mmol g⁻¹ with an increasing adsorbent dosage from 50 to 300 mg was attributed to the adsorption competition among adsorbent and the split in the concentration gradient (Kumar et al. 2010). Therefore, 100 mg was selected as the optimum dosage to study the effect of other parameters on the adsorption. A Similar results were reported and announced by other researchers (Gupta et al. 2005; Conrad et al. 2017).

Fig.13 Effect of adsorbent dose on the adsorption of MB onto VWS.

3.4 Effect of Contact Time

The effect of contact time of 0.1 g VW sawdust to remove the MB dye in particle size 125/250 μ m with agitation speed 500 rpm, 100 ml, and 10^{-5} to 30×10^{-6} mol L⁻¹ dye solution was studied from 1 – 210 min. Fig. 14 showed that the adsorption was quick during the initial 30 min and steadily reached equilibrium in 50-120 min. The maximum amount of dye adsorbed was found to be 9.88×10^{-3} - 29.95×10^{-3} mmol/g (98.88% - 99.83% removal efficiency) at 180 min, beyond which saturation was seen suggesting the adsorption-

desorption equilibrium. Furthermore the adsorption of MB became difficult due to the repulsion of solutes between solid (saturation of the active sites) and bulk phase (Malik, 2003).

Fig. 14 Effect of contact time on the adsorption of the BM onto VWS with various concentrations.

3.5 Effect of the initial concentration of dye BM

To observe the effect of the MB dye concentration in the adsorption process, the solution of MB dye with different initial concentrations (10^{-5} M to 310^{-5} M) was prepared and treated with a 100 mg dosage for 180 min with 500 rpm agitation speed. Fig. 15 indicated that increasing the initial concentration of MB dye could be an increased biosorption capacity of VW sawdust to MB dye without reaching the equilibrium point. which indicates that with the increase in the initial concentration of the MB, the driving force became stronger and the interaction between dye and adsorbent was enhanced (Tan et al. 2008). The sawdust of vine wood can be used as an efficient adsorbent for the removal of methylene blue at a wide concentration range. The same results were announced by (Merzoug et al. 2016; Fayoud et al. 2015).

Fig. 15 Effect of initial dye concentration on the adsorption of MB onto VWS.

3.6 Effect of solution pH

The effect of the solution pH was examined in the range of pH 2.5 to 11 at a fixed adsorbent dosage of 100 mg, and 10^{-5} mol/L of MB concentration. As clearly indicated in Figure 16, as the solution pH increases, the dye adsorption increases due to the increasing electrostatic force of attraction between positive charged adsorbate and negatively charge adsorbent surface ($\text{pH} > \text{pH}_{\text{pzc}}$) in alkaline condition due to the ionization of VW. While in acidic pH, the adsorbent surface is positively charged ($\text{pH} < \text{pH}_{\text{pzc}}$), the dye adsorption is lower, this is mainly due to the presence of higher concentration of H^+ ions on the VW sawdust

surface hindered the adsorption of cationic MB dye. Nevertheless, it was also observed that the despite surface of activated VWS being positive, the adsorption of MB remains high (84.50 to 89.15%), when pH was within the range of 2.5 to 4, suggesting that not only electrostatic mechanism but rather also by chemical reaction between the adsorbent and dye molecules. Therefore, the normal pH of MB solution was selected to be the best for further studies. This is in concord with the results of (Han X et al. 2011).

Fig. 16 Effect of the pH on the adsorption of MB onto VWS.

3.7 Effect of Temperature

The temperature-dependent adsorptions were performed using 0.1g of the adsorbent in 100 mL of the MB solution (10^{-5} mol/l) at 20, 30, 40 and 50°C (Fig. 17). It was found that with rising the temperature, the percent removal decreased (from 99.85% to 97.71 %.). This may be due to the decreased surface activity, suggesting that adsorption between MB and VWS was an exothermic process. This phenomenon is in agreement with the Arrhenius rule. Similar types of results for the MB adsorption have been reported by several researchers (Sen et al. 2011; Boumchita et al. 2016; Sakr et al. 2015).

Fig. 17 Effect of the temperature on the adsorption of MB onto VWS.

3.8 Effect of shaker speed

The shaker speed is also a very significant factor to interfere the adsorption efficiency. Its effect on the removal rate of dye by disrupting the film resistance surrounding the adsorbent particles (Al-Chouti et al. 2009). The effect of shaker speed was studied at different speed from 100 to 1000 rpm and fixing the all experimental parameters. Fig. 18 shows that the removal efficiency increases from 98.40% to 99.64% as the shaker speed is increased from 100 to 1000 rpm. As the speed increased, the time required to achieve equilibrium was reduced, so the available biomass surface area increases due to the deficiency of aggregation of the biosorbent that finally leads to rapid adsorption of MB) Maurya et al. 2014).

Fig. 18 Effect of shaker speed on the adsorption of MB onto VWS.

3.9 Kinetic study of adsorption of the BM on the sawdust of vine wood.

The kinetics modelling was conducted using 100 mL of 10^{-5} - 3.10^{-5} mol L⁻¹ of dye solution with an initial pH (pH= 6.9), then contacted with 100 mg VW sawdust and shell agitated at 500 rpm for 180 min. This kinetics were analyzed by kinetic rate equations, ie pseudo-first order, pseudo-second order, and intra-particle diffusion models. The model parameters of all the three models were estimated by plotting graphs $\ln(Q_e - Q_t)$ versus t , t/Q_t versus t and Q_t versus $t^{0.5}$, for pseudo-first order, pseudo-second order, and intra-particle respectively, and fitted linearly. The results of linear fitting experimental data of the different models are presented in Figs. 19, 20, 21, 22.

3.9.1 Pseudo-first-order kinetic model (Lagergren model)

The adsorption kinetics data were evaluated using Lagergren's pseudo-first order (Lagergren 1898), it is the first speed equation established to describe the adsorption kinetics in a system (solid-liquid). This model is introduced by the following relation:

$$\frac{dQ}{dt} = K_1(Q_e - Q_t) \quad (3)$$

The integration form of the equation (3) applying the initial conditions $t = 0$ to $t = t$ and $Q = 0$ to $Q = Q_t$ becomes:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (4)$$

Where Q_e and Q_t are the amount of dye adsorbed at equilibrium and at contact time t , respectively (mmol / g); t is the time of contact (min); K_1 is the equilibrium rate constant of pseudo-first-order kinetics (min⁻¹). The values of K_1 and Q_e were obtained from the slope and intercept respectively of plots of $\ln(Q_e - Q_t)$ versus t (Fig. 19). Values of K_1 , Q_e (experimental and calculated) and correlation coefficient (R^2) subsequently given in Table 2.

Fig. 19 Pseudo-first-order kinetics plots for the adsorption of the MB on VWS.

According to the plots $\ln (Q_e - Q_t)$ vs t , as shown in Fig. 19, the obtained graph are not linear, the calculated capacities of adsorption ($Q_{e \text{ cal}}$) did not agree with experimental Q_e values, which indicates that the adsorption of MB onto VWS did not follow pseudo-first-order equation. This was comparable with results reported by other researchers (Fayoud et al. 2015; Ncibi et al. 2007).

3.9.2 Pseudo-second-order kinetic model (Blanchard model)

The experimental results of the adsorption kinetics obtained for various initial concentrations are expressed by using Blanchard's pseudo-second-order model equation (Ho and McKay 2000):

$$\frac{dQ}{dt} = K_2 (Q_e - Q_t)^2 \quad (5)$$

Integrating the equation (5) and applying the boundary conditions $t=0$ to $t=t$ and $Q = 0$ to $Q = Q_t$ we get the equation of the linearized form which is shown as follows:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \quad (6)$$

Where K_2 is the second order rate constant ($\text{g. mmol}^{-1} \cdot \text{min}^{-1}$). The values of Q_e and K_2 have been calculated from the slope and intercept of the linear graph of a plot of t/q_t versus t , as shown in Fig. 20 and summarized in Table 2. The constant k_2 is used to calculate the initial sorption rate h , at $t \rightarrow 0$, as follows:

$$h = K_2 Q_e^2 \quad (7)$$

The verification of the models proposed to describe the adsorption kinetics and adsorption isotherms is based on the correlation coefficients (R^2) and "average relative error, ARE" was calculated from eq. (8) (Banerjee et al. 2017):

$$ARE\% = \frac{100}{n} \sum_{i=1}^n \left| \frac{Q_{e \text{ exp}} - Q_{e \text{ cal}}}{Q_{e \text{ exp}}} \right| \quad (8)$$

With, $Q_{e \text{ exp}}$ is the experimental value of the amount adsorbed at equilibrium, $Q_{e \text{ cal}}$ is the theoretical value calculated by the model of the amount adsorbed at equilibrium and n is the

number of the experimental data.

Lower value of ARE indicates good fit between experimental and calculated data.

Fig. 20 Pseudo-second-order kinetics plots for the adsorption of the MB on VWS.

The fit of the experimental data to a pseudo-second-order kinetic model at different initial concentration present in Fig.20 shows a linear relationship with, intercept very close to zero with the excellent high correlation coefficient values (between 0.9996 and 0.9999). From the table 2, the theoretical values calculated by pseudo-second-order model ($Q_{e\text{ cal}}$) are very close to that of experimental values ($Q_{e\text{ exp}}$). These results indicate that the adsorption of MB onto vine wood sawdust obey the pseudo-second-order kinetics model. We also notice from the Table 2, that the values of the second order rate constant (K_2) decrease with the increase in the initial concentration of BM and the initial rate of adsorption (h) increase with increasing the initial MB concentration, which would be expected due to the increase in driving force at higher concentration. Similar results were found for the adsorption of MB on various adsorbents by (Abdallah et al. 2016; Belaid et Kacha. 2011; B.H. Hameed et al. 2008).

3.9.3 intra-particle diffusion model (IPD)

The application of the equation (9) of the intra-particle diffusion model proposed by Weber and Morris (1963) to the experimental data was applied to examine the adsorption mechanism of the adsorption system. The linear form of the intraparticle equation is shown as follows:

$$Q_t = K_i t^{1/2} + C \quad (9)$$

Where K_i is the intra-particle diffusion rate constant ($\text{mmol} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$); C is the constant that gives an idea about the thickness of the boundary layer (mmol /g) and Q_t is the amount of dye adsorbed at time t (mmol /g) .

The slope of the graph Q_t versus $t^{1/2}$ makes it possible to evaluate the intra-particle diffusion rate constant (K_i) and correlation coefficient (R^2) indicate the fitness of this model . The

values of intercept inform about the thickness of the boundary layer (C). If the plots of Q_t versus $t^{1/2}$ yield straight lines do not passing through the origin, then the adsorption process is not the only limiting mechanism of the adsorption kinetics and this is confirm the imply of some other mechanisms (Weber and Morris 1963). The obtained results, for the various initial concentrations are represented in Fig. 21 & 22 and are summarized in Table 2.

Fig. 21 Intra-particle diffusion kinetics plots for the adsorption of the MB on VWS

Fig.22 Linear representation of the right sections of the intra-particle diffusion model for the adsorption of the MB on VWS.

According to the Fig. 21, the intra-particle diffusion are equipped with successive three linearity's, indicating that three steps in the adsorption process of MB. The first sharp section is related to the adsorption on the external surface of the sawdust of vine wood with a very high speed of adsorption. The second region is a stage of diffusion of the molecules of MB through the pores of the adsorbent, it is the longest stage. The parameters K_i and C is given on the basis data corresponding to this stage and finally the third horizontal linear stage is attributed to the gradual adsorption stage, where's the equilibrium is reached and intra-particle diffusion is rate controlled when the molecules of dye occupy all the active sites of the adsorbent. From the Fig .22 and the Table 2, the R^2 values of this diffusion model were closer to 1 (0.94.95-0.9954) and the linear lines of the second stage at each concentration did not pass through the origin. These indicate that the intra-particle kinetics of diffusion into the pores is implied in the mechanism of adsorption process but is not the only rate controlling step. The increases in the initial concentration of the MB entrain an increase in the constant C which is proportional to the thickness of the boundary layer.

Table 2 Kinetic models parameters for the adsorption of MB onto VWS at different initial MB concentrations.

Kinetic models and its parameters	Initial concentrations ($C_0 \cdot 10^{-6}$ mol/L)				
	18	10	20	22	30
$Q_{e \text{ exp}} \times 10^{-3}$ (mmol/g)	9.746	17.536	19.428	21.386	29.288
Pseudo-first-order kinetic					
$Q_{e \text{ cal}} \times 10^{-3}$ (mmol/g)	4.483	13.592	16.569	11.496	20.845
K_1 (min^{-1})	0.0863	0.0829	0.0889	0.0750	0.0833
R^2	0.9820	0.7167	0.5865	0.9916	0.7664
ARE%	54	22.49	14.71	46.66	28.83
Pseudo-second-order kinetic					
$Q_{e \text{ cal}} \times 10^{-3}$ (mmol/g)	10.010	18.087	20.220	22.295	30.387
K_2 ($\text{g mmol}^{-1} \text{ min}^{-1}$)	45.823	18.598	15.178	15.045	11.263
h ($\text{mmol g}^{-1} \text{ min}^{-1}$)	0.0046	0.0061	0.0062	0.0075	0.0104
R^2	0.9999	0.9998	0.9996	0.9998	0.9998
ARE %	2.79	3.14	4.08	3.9	3.75
Intraparticle diffusion					
K_{id} ($\text{min}^{1/2}$)	0.116	0.463	0.513	0.253	0.426
C	8.730	13.476	14.810	19.243	25.358
R^2	0.9475	0.9511	0.9954	0.9542	0.9672
ARE %	0.55	1.89	9.48	9.60	0.74

3.10 Adsorption Isotherms of MB Adsorption of VW Adsorbent

The adsorption process was fitted using the Langmuir (eq 11), Freundlich (eq 14), and Temkin (eq 16) models for the different initial dye concentration from 10^{-5} mol/L to $30 \cdot 10^{-6}$ mol/L after 180 min in the presence of 100 mg of VWS at room temperature.

3.10.1 Langmuir Adsorption Isotherm

It is the model more used. Langmuir supposes that adsorption is done into monolayer surface, identical and well defined of adsorption sites, also without interaction among of the adsorbed dye molecules, the non linear form of Langmuir equation is illustrated by the following equation (Langmuir 1918):

$$\frac{Q_e}{Q_{max}} = \frac{K_L C_e}{1 + K_L C_e} \quad (10)$$

Where:

C_e: equilibrium concentration of solution dyes (mol/L);

Q_e: the amount of dye adsorbed (mmol/g) ;

Q_m: theoretical maximum adsorption capacity (mmol/g);

K_L: the equilibrium constant (L/mg).

However, The Langmuir equation is represented by five linear expressions which used different equations for calculating the constant K_L and Q_m.

The linear form of this model is given by the following equation:

$$\frac{1}{C_e} = K_L Q_m \frac{1}{Q_e} - K_L \quad (11)$$

Where C_e is the equilibrium concentration of solution dyes (mol/L), Q_e is the amount of dye adsorbed at equilibrium (mmol/g), Q_m is the maximum adsorption capacity (mmol/g), K_L is the Langmuir equilibrium constant related to the affinity of the binding sites or the free energy of adsorption (L/mol).

The values of the constant Q_m and K_L can be determined from the intercept and the slope of the linear plot of 1/C_e versus 1/Q_e (Fig. 23) and are presented in Table 3.

The essential characteristics of the Langmuir isotherm was expressed in terms of dimensionless constant separation factor R_L of Hall (without dimension) is given by the following equation (Hall et al. 1966).

$$R_L = \frac{1}{1 + K_L C_0} \quad (12)$$

Where C₀ is the initial concentration of dye (mol/L), K_L is the Langmuir constant (L/mol).

The parameter R_L indicates the type of the isotherm and whether it is favorable (0 < R_L < 1), unfavorable (R_L > 1), linear (R_L = 1), Irreversible (R_L = 0).

3.10.2 Freundlich Adsorption Isotherm

Freundlich adsorption isotherm supposes that adsorption occurs on a heterogeneous surface by multilayer adsorption with interactions between the adsorbed molecules and the heat of adsorption decreases exponentially with the rate of surface saturation of the solid. Freundlich model is an empirical equation as follows (Freundlich 1906):

$$Q_e = K_F C_e^{1/n} \quad (13)$$

The linear form of this model is given by the following equation:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (14)$$

Where K_F is Freundlich equilibrium constant related to the adsorption capacity of adsorbent ($\text{mmol/g(L/mol)}^{1/n}$), n is the adsorption intensity of adsorbent, C_e is the equilibrium concentration of solution dyes (mol/L), Q_e is the amount of dye adsorbed (mmol/g).

From the slope and intercept obtained by plotting $\ln(Q_e)$ versus $\ln(C_e)$ (Fig. 24), the values of n and K_F were calculated. The Freundlich parameter $1/n$ relates to the surface heterogeneity gives us the intensity of adsorption and the shape of the isotherm.

.When $0 < 1/n < 1$, the adsorption is favorable; $1/n = 1$, the adsorption is homogeneous and there is no interaction among the adsorbed species; $1/n > 1$, the adsorption is unfavorable. (Rauf et al. 2008)

When $1/n = 1$ the isotherm is linear type C; $1/n > 1$ the isotherm is S-type convex; $1/n < 1$ the isotherm is type L concave; $1/n \ll 1$ the isotherm is type H.

3.10.3 Temkin Adsorption Isotherm

The Temkin isotherm model rest on the assumption that, during adsorption in gas phase, the heat of adsorption of all molecules in the layer decrease linearly with the increase surface coverage due to the account the effects of indirect adsorbate / adsorbate interactions (Ringot et al. 2007).

The isotherm of Temkin is represented by the following relation (Temkin and Pyzhev 1940):

$$\frac{Q_e}{Q_{max}} = \frac{RT}{\Delta Q} \ln(K_T \times C_e) \quad (15)$$

The linearized form of the equation is given as:

$$Q_e = B_T \ln K_T + B_T \ln C_e \quad (16)$$

With:

$$B_T = \frac{RT}{b_T} \quad (17)$$

Where B_T is the Temkin Constant related to the heat of adsorption (J / mol), T is the absolute Temperature (K), R is the universal gas constant (8. 314 J. mol⁻¹. K⁻¹), K_T is empirical Temkin r isotherm constant (L.mg⁻¹) related to the equilibrium binding constant, ΔQ is the variation of energy of adsorption (J.mol⁻¹) . Both B_T and K_T can be calculated from the slope and intercepts of the plot of Q_e versus $\ln (C_e)$ (Fig. 25) and are presented in Table 3.

Table 3 Langmuir, Freundlich and Temkin isotherms parameters for adsorption of MB onto VWS.

Adsorption isotherms and its constants	Parameter values
Langmuir adsorption isotherm constants	
Q_m (mmol/g)	0.4579
K_L (L/mol)	8.44E+04
R_L	0.542–0.283
R^2	0.9846
ARE%	5.44
Freundlich adsorption isotherm constants	
K_F (mmol/g(L/mol) ^{1/n})	3.037
n	1.020
$1/n$	0.984
R^2	0.9496

ARE%	5.66
Temkin adsorption isotherm constants	
K_T (L/mol)	1.064
B_T (J/mol)	0.2571
R^2	0.8495
ARE%	121.8

Fig. 23 The linear plot of Langmuir isotherm (Version 1 and 5) for adsorption of MB onto VWS.

Fig. 24 The linear plot of the Freundlich isotherm for adsorption of MB onto VWS.

Fig. 25 The linear plot of the Temkin isotherm for adsorption of MB onto VWS.

By comparing the results of fitting experimental data, the Langmuir isotherm showed the best fit confirmed by giving the highest correlation coefficient adsorption of MB value closer to unity ($R^2 = 0.9846$) and lower value of average relative error, suggesting that a mainly monolayer adsorption behavior on the prepared biosorbent. It is obvious from Table 3 and Fig. 26 that the R_L values are greater than 0 and less than 1 and decreased with the increasing initial concentration; therefore, the adsorption process of the MB onto the sawdust of vine wood is favorable. The Freundlich model showed that the value of n was greater than 1 which represents favourable adsorption of both dyes at experimental condition and $1/n$ less than 1 indicated that the adsorption of MB onto VW follows the L-type Langmuir isotherm.. The maximum monolayer adsorption capacity of MB on vine wood sawdust 0.4579 mmol/g (correspond 146.46 mg/g) has been compared with other adsorbents reported in the literature which is listed in Table 4.

Fig. 26 Plot of separation factor R_L of Langmuir model against initial MB concentration on VWS.

Table 4 Comparison of maximum adsorption capacities of various adsorbents for removal of MB dye.

Adsorbent	Maximum adsorption capacity, Q_m (mg/g)	Reference
Posidonia oceanica (L.) fibres	5,56	Ncibi et al 2006
Datte Stones	6,7010	Khelifi et al. 2016
Palm Kernel Shell	16,20	Benjamen Niran et al.2018
Andrographis paniculata Leaves	16,6666	Nirmala et al. 2016
Jack Fruit Leaf	20,41	Banerjee S et al. 2017
Cane Bark Powder	23,49	Enenebeaku C K et al. 2016
Tea Residue	41,841	Truong et al.2019
Activated Carbon Coated With Fe_2O_3	50,51	Imam and Abdullahi 2017
Pine apple peel powder	78.125	Lutpi et al. 2011
Pine Apple Stem	109,89	Sen et al. 2011
Pine Cone Biomass	119.05	Hameed et al. 2009
meranti sawdust	120.48	Ahmada et al.2009
vine-wood Sawdust	146,46	This study
Eucalyptus Sheathiana Biomass	204,08	Afrozea et al.2015
lotus leaf	241,4	Xiuli Han et al. 2018
Banana Peel	256,666	Kayaalp et al. 2017
Sawdust biochar	333,333	Ghani et al. 2013

3.11 Thermodynamic analysis

To explore the thermodynamic characteristics of the VW sawdust adsorbent, the adsorption process was examined at different temperatures (293, 303, 313, and 323 K) (Fig. 27). The thermodynamic parameters such as free energy change (ΔG^0), enthalpy change (ΔH^0), entropy change (ΔS^0), etc. for adsorption were calculated via the Gibbs free energy and the Van't Hoff equation (Eqs. 19 & 20).

The change in free energy is related to the equilibrium constant by the following relationship:

$$\Delta G^0 = -R \times T \ln K_d \quad (18)$$

According to the Gibbs' free energy equation:

$$\Delta G^0 = \Delta H^0 - T \times \Delta S^0 \quad (19)$$

Combining equation 18 and 19, we get:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (20)$$

where T is the absolute temperature (Kelvin), R is universal gas constant (8.314 Jmol⁻¹ K⁻¹), K_d is the distribution coefficient for adsorption. The ΔH⁰ and ΔS⁰ values obtained from the slope and intercept of Van't Hoff plots are given in Table 5.

Fig. 27 Vant Hoff plot for adsorption of MB on VWS.

In Table 5, the negative value of enthalpy ΔH⁰ shows that the adsorption of MB dye to VW sawdust is exothermic in nature, while the positive value of ΔS⁰ indicated that the randomness at the solid/solution interface decreased during the adsorption process. In general, the change of standard free energy for physisorption is in a range of -20 to 0 kJmol⁻¹, and the chemisorption varies between -80 and -400 kJmol⁻¹ (Vimonses et al. 2009). The negative ΔG⁰ values from -9.77 to -7.77 kJ mol⁻¹ at the temperature range studied indicated the spontaneity and feasibility of the adsorption process and physical nature of the adsorption. The increase in ΔG⁰ with increase in temperature indicates high efficient adsorption at lower temperature. A similar observation has been reported by (Boumchita et al. 2016; Fayoud et al. 2015).

Table 5 Thermodynamic parameters for adsorption of MB dye at different temperatures

Temperature (K)	K _d (L/g)	ΔG ⁰ (KJ. mol ⁻¹)	ΔH ⁰ (KJ. mol ⁻¹)	ΔS ⁰ (KJ. mol ⁻¹ .K ⁻¹)	R ²
293	135.635	- 9.769			0.994
303	33.333	- 9.104	-29.325	- 0.0665	
313	25.882	- 8.439			
323	19.080	- 7.774			

4 Conclusions

This work demonstrated the successful preparation of a low-cost biomass adsorbent based on vine wood sawdust with sulfuric acid treatment for methylene blue dye removal. The

optimum adsorption condition was achieved by analyzing the influencing parameters such as adsorbent dose, initial dye concentration, pH, temperature, contact time, agitation speed and particle size. The maximum adsorption of MB was found at the normal pH of the MB solution, temperature 20°C, and after 3 h of equilibration time. The kinetic experimental data conformed to the pseudo-second-order model, with a high correlation coefficient of 0.999. The adsorption of MB followed the Langmuir isotherm model with maximum adsorption performance of 0.4579 mmol / g (146.46 mg g⁻¹). This study provided a practical method for preparing an economical, efficient bioadsorbent from a wide variety of biomass.

Declarations

- **Ethics approval and consent to participate**

Not applicable

- **Consent for publication**

Not applicable

- **Availability of data and materials**

Not applicable

- **Competing interests**

We have no competing interests

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- **Authors' contributions**

Rachida Souidi: analysis, interpretation of data and a major contributor in writing the manuscript.

Yasmina Khane: interpretation of data and help for writing the manuscript.

Lahcen Belarbi: have drafted the work

Smain Bousalem: revised the work

All authors read and approved the final manuscript

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Figures captions

Fig. 1

Fig. 2

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Fig. 22

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Figures

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Chemical structure of methylene blue.

Figure 2

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Figure 3

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Figure 4

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Figure 20

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Figure 21

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Figure 23

The linear plot of Langmuir isotherm (Version 1 and 5) for adsorption of MB onto VWS.

Figure 24

The linear plot of the Freundlich isotherm for adsorption of MB onto VWS.

Figure 25

The linear plot of the Temkin isotherm for adsorption of MB onto VWS.

Figure 26

Plot of separation factor R_L of Langmuir model against initial MB concentration on VWS.

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