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# Application of walnut tree sawdust modified with $KMnO_4$ for removal of methylene blue from aqueous solution in batch system: Isotherm, kinetic and thermodynamic studies

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In this study, the adsorption of methylene blue from aqueous solution by modifying sawdust with $KMnO_4$ has been studied as an effective adsorbent. The surface and characteristics of the composite are studied by Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The result demonstrate, that by increasing *p*H, the amount of methylene blue adsorption also increases, and the amount of optimum removal of this dye (96.36%) was obtained at methylene blue dye *p*H aqueous solution equal to 6 with initial concentration 100 mg $L^{-1}$. The studies have shown that the kinetics of the adsorption process follows the pseudo-second-order model with a correlation coefficient $R^2$>0.999, and equilibrium data conform the Langmuir isotherm model with $R^2$>0.9982 and a maximum capacity of single layer adsorption $q_e$ equal to 100 $mgg^{-1}$. Thermodynamically, the reaction is endothermic and spontaneous. Consequently, the result has shown, that the modified sawdust can be used as a quick, inexpensive and effective adsorbent in order for removal of methylene blue dye from aqueous solution.

**Keywords:** Modified sawdust, Methylene blue, Adsorption, Isotherm, Batch system

Methylene blue dye is one widely used materials in the industry that is used for staining cotton and silk. Methylene blue (MB) (3, 7-bis (dimethyl amino)-phenothiazine-5-iumchloride) is a thiazine cationic dye with the heterocyclic aromatic chemical compound. A heterocyclic compound or ring structure is a cyclic compound that has atoms of at least two different elements as members of its ring(s)[1]. This dye is produced from an initial simple material N, N-dimethyl aniline by several chemical steps[2]. Methylene blue is not very dangerous, but long-term continuous contact with it can make harmful effects on the body, such as increased heart rate, vomiting, shock, cyanosis, jaundice, mild bladder irritation, dizziness, and headache; or increased sweating. Separation and removal of dyes from water sources are done by three methods such as chemical, physical and biological methods. In physical/chemical methods, we can mention coagulation, reverse osmosis, precipitation, adsorption, membrane filtration[3], electrochemical techniques[4], ozonation[5], ion-exchange[6] and bio-sorption.[7] Nowadays, among above methods, the adsorption with introduction different biological species and agricultural wastes as an adsorbent, have a lot of advantages such as economic efficiency, the ease performance, adjustable with the environment, and it is as a suitable method for refining sources and wastewaters[8].

Potassium permanganate ($KMnO_4$) is a strong oxidizing agent and often used for disinfection by-products formation control[9], taste and odor control[10], algae removal[11], organic chemicals degradation[12] and the adsorption of heavy metals, humic acid, and anions during water treatment. Permanganate may oxidize organic compounds through different reaction pathways primarily including electron abstraction, hydrogen atom abstraction, hydride ion abstraction and oxygen donation[13]. It is commonly accepted that the initial step of the reactions between alkenes and permanganate is the formation of a (2+3) cyclic hypomanganate ester intermediate[14]. Next reaction involves a competition between permanganate and hydroxyl ions for the initial intermediate. The reaction may yield carbonyl compounds, ketones, glycols, and carboxylic acid, strongly depending on the reaction conditions (e.g., *p*H and oxidant concentration). Also, it has been applied to the oxidation of some organic compounds, such as trichloroethylene (TCE) and

toluene[15]. $KMnO_4$ contributes to the degradation and transformation of organic species. In strong acid conditions, $KMnO_4$ exhibits high oxidative reactivity with the oxidation potential ($E_0$) of +1.51 V[10].

In the current study, sawdust (SD) as a modified cellulose source with potassium permanganate ($KMnO_4$) as chemical oxidant has been used for removing methylene blue dye (MB) from aqueous solution. According to previous reports, untreated sawdust has not exhibited good efficiency in removal of methylene blue dye[16-18]. Methylene blue was selected as a test probe for evaluating the sorption efficiency of oxidative chemically modified sawdust compared to untreated sawdust, and also with those reported by other researches. For determining the optimal conditions of the adsorption, the influence of the effective parameters has been investigated. Furthermore, for recognition of the adsorbent, the methods of Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) has been used.

## Experimental Section

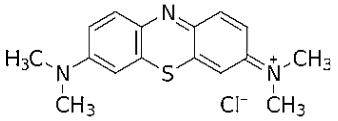
### Materials

All chemicals used has been purchased from Merck Company, such as potassium permanganate ($KMnO_4$), sulfuric acid ($H_2SO_4$), and methylene blue dye (MB). The sample of dicer sawdust has been obtained from a local carpentry workshop, and it has been sifted through a 297-500 µm sieve. Also, entire chemicals used were prepared in distilled water. The chemical structure of methylene blue has been presented in Table 1.

### Analytical methods

A Metrohm *p*H meter (model 827) with a combined double junction glass electrode, calibrated against two standard buffer solutions at *p*H 4.0 and 7.0, was used for *p*H measurements. A single beam UV-Vis spectrophotometer (model JENWAY 7315) with a 1cm cell was used for measuring all the adsorption data. MB concentration was measured by UV-visible spectrophotometer at 660 nm wavelength of maximum absorption[19].

Table 1 — The structure and characteristics of methylene blue.

| | |
|---|---|
| Color index name | Methylene blue |
| Systematic (IUPAC) name | 3,7-bis(dimethyl amino)-phenothiazin-5-ium chloride |
| Molecular formula | $C_{16}H_{18}C_lN_3S$ |
| Molecular mass | 319.85 g $mol^{-1}$ |
| $\lambda_{max}$ | 660 nm |
| Chemical structure |  |

### Preparation of sawdust modified with $KMnO_4$

Suggest adsorbent used in this study, $KMnO_4$/sawdust composite was prepared by the co-precipitation method. 200 mL of 0.4 mg $L^{-1}$ potassium permanganate in sulfuric acid solution was prepared. Then 20 g of sawdust was poured into the solution, and this solution has been continuously stirred with a magnetic stirrer for about one hour. Then, this product was dried in the oven and under the temperature of 60 °C. Finally, in this way, the modified sawdust was gained.

### Adsorption batch study

This study was conducted in batch mode. Some adsorption experiments to study adsorption efficiency for MB dye solution removal were carried out for $Ag_2O$ nanoparticles alone and both adsorbents (unmodified and modified SD). The *p*H of the MB solution was adjusted by using either 0.10–0.01 mg $L^{-1}$ of HCl or 0.10–0.01 mg $L^{-1}$ of NaOH solutions. The effect of different parameters such as *p*H (2-10), contact time (5 to 60 min), the initial concentration of MB (25.0–250.0 mg $L^{-1}$), adsorbent dosage (2.0-12.0 mg $L^{-1}$) and the temperature have been investigated. In this work, 25 mL of sample with a certain *p*H and the amount of adsorbent was mixed by a stirrer at the 150 rpm. After shaking at a certain time, the solution was separated from the adsorbent using centrifuged and dye concentration was determined. Measurement of unadsorbed MB dye was carried out according to the standard method[19].

The removal percentage and adsorption capacity of methylene blue dye can be calculated by the following equation[20]:

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad \ldots(1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad \ldots(2)$$

## Result and Discussion

### Characterization

After treatment of sawdust with $KMnO_4$ under acidic conditions, a hybrid material with a complex structure might be formed. $KMnO_4$ under acidic media can take part in chemical reactions resembling

oxidation-reduction of the lignin and hemicellulose components.

**Morphology of sawdust modified with $KMnO_4$**

The morphology of the sawdust modified with $KMnO_4$ was determined by scanning electron microscopy. In order to see the surfaces of particles, SEM images were obtained for the untreated and modified adsorbents in Fig. 1. As shown in the Fig. 1, the sawdust has a smooth, laminated surface with no porosity (Fig. 1a). Contrarily, the surface of sawdust after modifications has tiny particles in different sizes that causes the adsorption capacity of the adsorbent increase and has more pores (Fig. 1b).

**Fourier transform infrared spectroscopy**

The FTIR spectra of the $KMnO_4$/SD composite has been shown in (Fig. 2). The observed broad vibration band at 1062 and 1110 $cm^{-1}$ could be assigned as $MnO_4^-$stretching vibrations bond and stretching frequency of modified sawdust with potassium permanganate respectively[21]. The sawdust has a fibre structure, and its main component is cellulose $(C_6H_{10}O_5)_n$, which has a straight chain structure and very large molecule mass (1700 000–2400 000 unit Carbon). The C=C stretching vibrations at 1602 $cm^{-1}$ indicates the aromatic functional groups. The peak at 2937 $cm^{-1}$ corresponds to the C-H stretching vibration of alkanes. C=O stretching of hemicelluloses and lignin aromatic groups is seen at 1620 $cm^{-1}$. Sawdust modified by $KMnO_4$ showed peaks around 1422, 1380, 1319, 1270, and 1163 $cm^{-1}$, which corresponds to C-H deformation in lignin, C-H deformation in cellulose and hemicellulose, C-H vibration in cellulose, C=O stretch in lignin, and C-O-C vibration in cellulose,respectively[22].

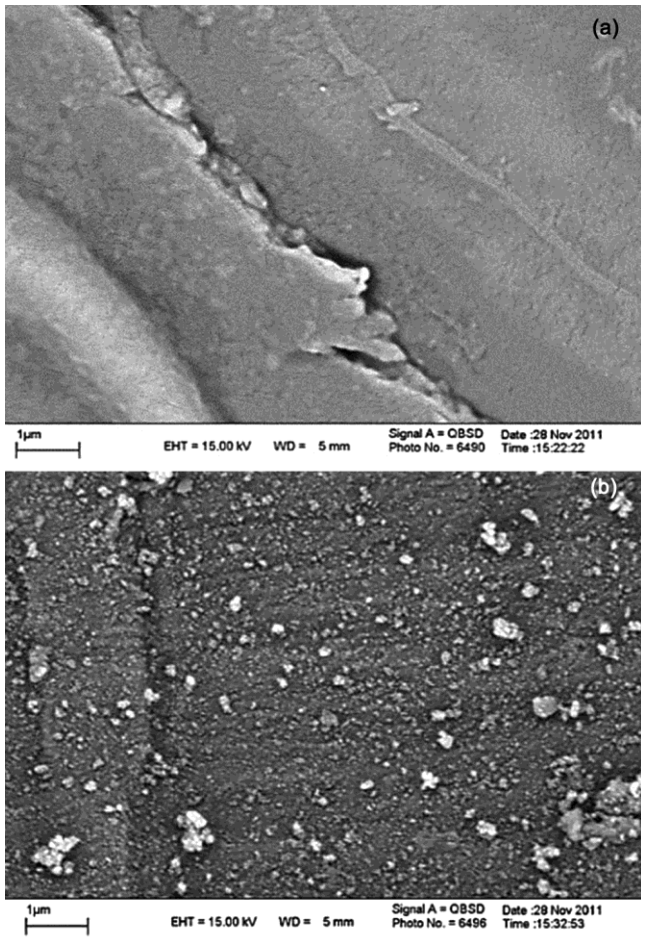



Fig. 1 — Scanning electron microscopy (SEM) (a) untreated sawdust (b) modified sawdust with $KMnO_4$

**X-ray diffraction analysis (XRD)**

The XRD patterns of untreated sawdust and sawdust modified $KMnO_4$ are shown in Fig. 3. The XRD pattern of sawdust modified with $KMnO_4$ ($KMnO_4$/SD) indicates the absence of any crystalline form of $KMnO_4$ such as α-$MnO_2$[23]. Thus, the possibility of formation of a new hybrid material is offered after chemical treatment. However, the formation of some anionic groups (e.g. carboxylic) during modifying of sawdust with the use of $KMnO_4$ as a chemical oxidant, which improves sorption or

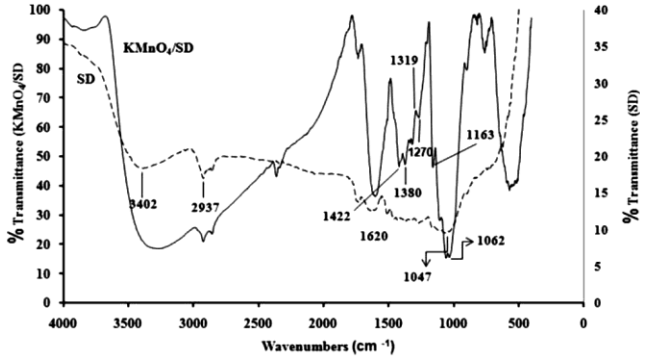



Fig. 2 — FT-IR spectrum of sawdust and sawdust modified with $KMnO_4$ ($KMnO_4$/SD).

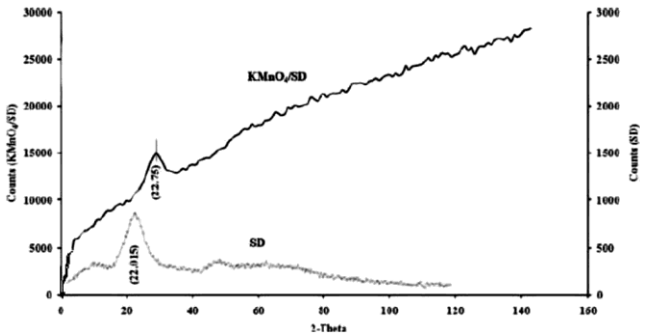



Fig. 3 — XRD pattern of untreated sawdust and sawdust modified with $KMnO_4$ ($KMnO_4$/SD).

binding of MB dyes in basic conditions, can be proposed.

**Effects of *p*H**

One of the factors that significantly influence the adsorption process is the *p*H of the solution. In the present work, the effect of *p*H has been examined by varying the *p*H of the solution in the range of 2.0–10.0 using MB dye initial concentration of 100 mg $L^{-1}$ (Fig. 4). The *p*H at the point of zero charge ($pH_{pzc}$) for the modified adsorbent (sawdust modified with $KMnO_4$) obtained from experiments conducted at the laboratory and the *p*H amount was equal to 7. At *p*H values higher than $pH_{pzc}$, the surface of adsorbent became negatively charged and the adsorption of positively charged MB was enhanced through electrostatic force attraction[24]. According to Fig. 4, the new negative sites resulting from the chemical oxidative treatment of SD or the formation of a hybrid material it can be supposed to the main reason for the increasing removal efficiency. The electrostatic force attraction might not fully explain the approximately constant adsorption density (mg of adsorbate per g of adsorbent) from *p*H 2 to 10; it is possible that ion exchange was involved in the adsorption process[17]. Also, because untreated sawdust has a lower removal efficiency of methylene blue dye ,sawdust modified was used as an adsorbent for removal of MB dye from aqueous solution. Since there isn't any significant difference in the removal efficiency of methylene blue in the *p*H = 6 and *p*H = 10, the *p*H of dye solution was selected as an optimum *p*H equal to 6.

**Effect of contact time on the removal efficiency**

The contact time between adsorbent and adsorbate is one of the important parameters in the adsorption process that we can find out the adsorption kinetic[25]. The effect of contact time on methylene blue removal with the 100 mg $L^{-1}$initial concentration of dye is shown in (Fig. 5). The results of this diagram show that the adsorption process was very fast, and the main adsorption has occurred in the first five minutes. By increasing the contact time, the empty sites in the adsorbent were filled and so the adsorption efficiency increased from 83.75% to 89.93%, and after 30 minutes, there were any remarkable changes. As a result, 30 minutes time was chosen as an optimum time.

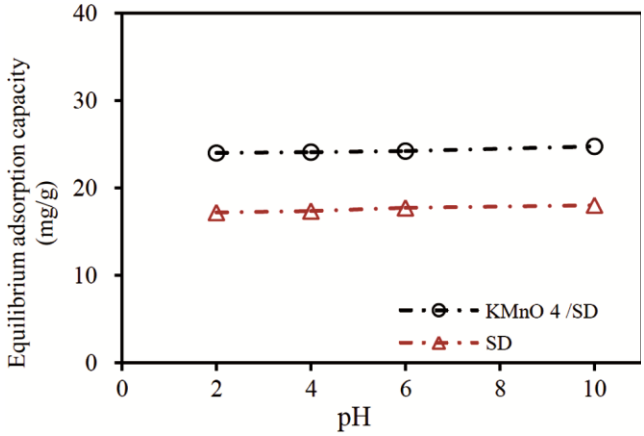



Fig. 4 — Effect of solution *p*H on the adsorption of MB. (Time = 30 min, $C_0$ = 100 mg $L^{-1}$ and adsorbent dosage = 4 mg $L^{-1}$).

**Effect of the initial dye concentration on the removal efficiency**

Initial solute concentration is the other parameter that can influence the adsorption efficiency. The effect of the initial concentration of methylene blue dye on the removal efficiency was shown in Fig. 6. According to Fig. 5, by increasing the concentration of methylene blue, the removal efficiency decreased; and the capacity the adsorbent adsorption also

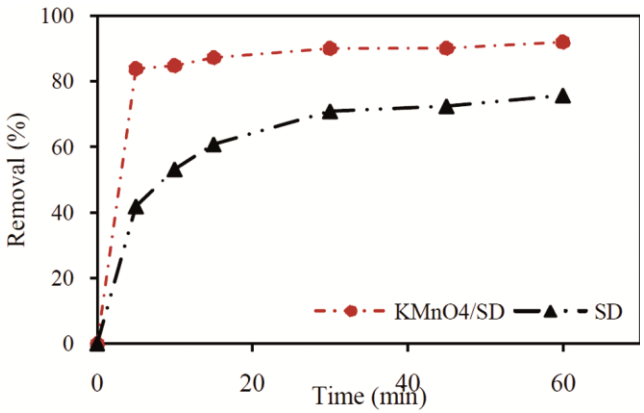



Fig. 5 — Effect of contact time on the adsorption of methylene blue by $KMnO_4$/SD ($C_0$= 100 mg $L^{-1}$, m= 4 mg $L^{-1}$, *p*H = 6).

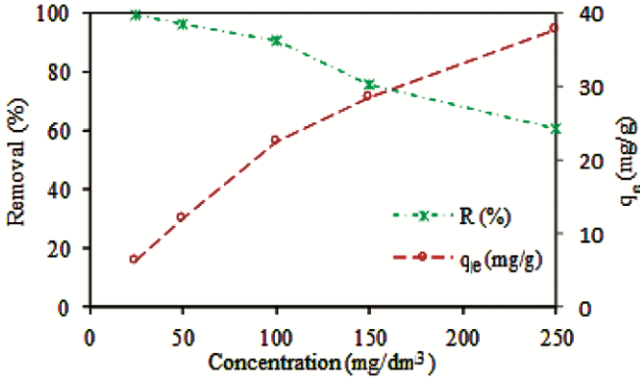



Fig. 6 — Effect of initial concentration on the adsorption of methylene blue on modified sawdust (Adsorbent dosage = 4 mg $L^{-1}$, time = 30 min, *p*H = 6).

increased. This phenomenon can be described in two ways: 1) by decreasing of the available sites for adsorption on the surface of the adsorbent. 2) by increasing the adsorbed concentration[1].

**Kinetic of an adsorption process**

The adsorption kinetic provides us some useful information about the mechanism of the adsorption, the reaction mechanism, and also a description about the rate of the dye adsorption in aqueous solutions[22]. The equation (3) and (4) were used for the pseudo-first-order kinetic model of Lagergren and pseudo-second-order kinetic model of Hu and Mackay for the evaluation of the results, respectively.[26]

$$\log(q_e - q_t) = \log q_{e1} - \frac{k_1}{2.303} \quad \ldots (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{1}{q_{e2}} t \quad \ldots (4)$$

The results of this investigation are given in the Fig. 7 and Table 2.

According to these results, the correlation coefficient of the second-order-kinetic model is higher. The value of $q_{e2}$ in this model was more correlated with the experimental values of $q_{e(exp)}$ for the adsorbent. So, it can be concluded that the adsorption process follows the second-order kinetic model, and the adsorption mechanism is chemical adsorption[27, 28]. In addition, the major adsorption of methylene blue on the surface of the modified sawdust with $KMnO_4$ happens through chemical reaction and ion exchange. In the sawdust modified with $KMnO_4$, some anionic groups (e.g. carboxylic) was formed that participated in ion exchange reaction and improve sorption or binding of MB dyes in basic conditions. The $R^2$ above 0.99 confirms that the removal of MB onto sawdust modified with $KMnO_4$ followed second-order kinetics (Fig. 8b) that second-order kinetics model indicating chemisorption (adsorption in which the adsorbed substance is held by chemical bonds) was the rate-limiting step in the adsorption process.

**Equilibrium isotherms studies**

For obtaining the adsorption isotherm of methylene blue dye, were used Langmuir and Freundlich isotherms.[24]The linear form of the Langmuir model (Eq.5) is as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \frac{1}{C_e} \quad \ldots (5)$$

It was said that the desirable adsorption based onthe Langmuir isotherms can be expressed with a constant without unit, which is called the separation factor or equilibrium parameter $R_L$.

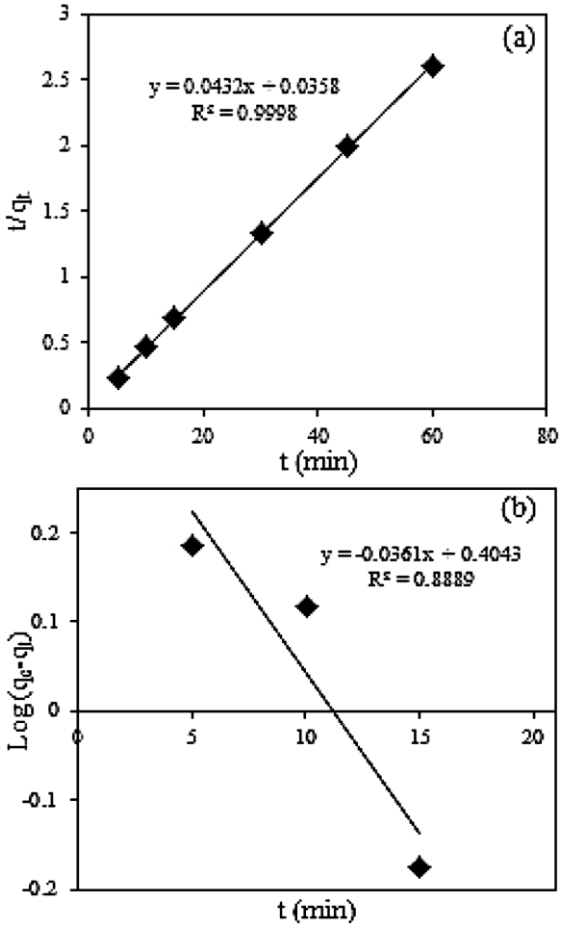



Fig. 7 — Kinetic equations (a) first order kinetic (b) second order kinetic ($C_0$: 100 mg $L^{-1}$, m= 4 mg $L^{-1}$, *p*H = 6)

Table 2 — Parameters of pseudo-first-order kinetic and pseudo-second-order kinetic

| | Pseudo-first-order model | | | | Pseudo-second-order model | | |
|---|---|---|---|---|---|---|---|
| $C_e$ (mg $dm^{-3}$) | $q_e$(exp)(mg $g^{-1}$) | $K_1$($min^{-1}$) | $q_{e1}$(mg $g^{-1}$) | $R^2$ | $K_2$ (g $mg^{-1}min^{-1}$) | $q_{e2}$(mg $g^{-1}$) | $R^2$ |
| 25 | 6.24 | 0.09 | 0.077 | 0.9954 | 6.25 | 6.25 | 1 |
| 50 | 12.04 | 0.28 | 1.43 | 0.8834 | 0.65 | 12.09 | 0.9999 |
| 100 | 22.48 | 0.083 | 2.48 | 0.8889 | 0.052 | 23.15 | 0.9998 |
| 150 | 28.48 | 0.119 | 14.94 | 0.9892 | 0.014 | 30.12 | 0.9997 |
| 200 | 30.92 | 0.146 | 14.69 | 0.9773 | 0.014 | 33.33 | 0.9999 |

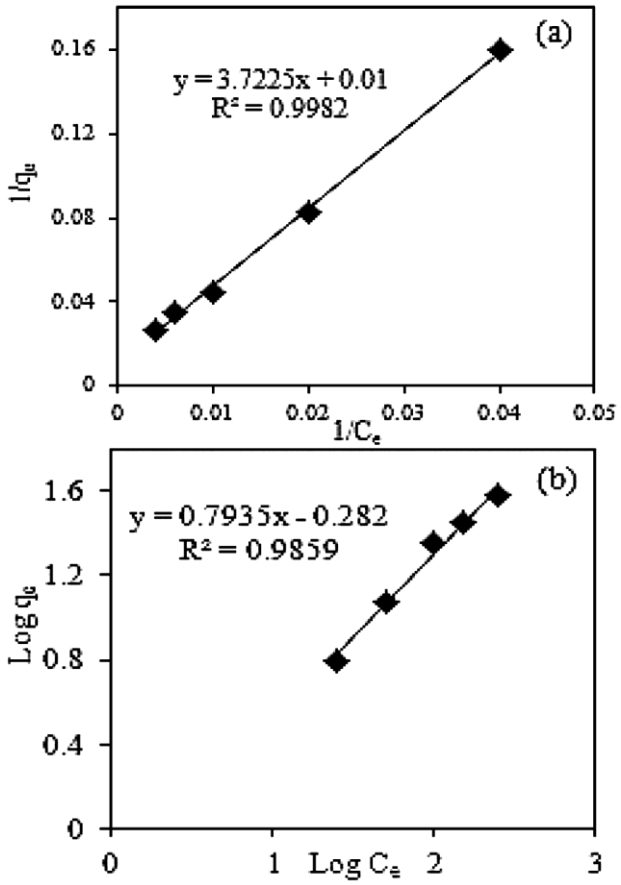



Fig. 8 — Adsorption isotherms for the adsorption of methylene blue by $KMnO_4$ /SD, a) Langmuir isotherm and b) Freundlich isotherm ($C_0$: 25-250 mg $L^{-1}$, adsorbent dosage: 4 mg $L^{-1}$, time = 30 min, *p*H = 6).

$$R_L = \frac{1}{1 + K_L C_i} \quad \ldots (6)$$

Where $C_i$ is the maximum of the initial concentration of methylene blue dye ($mgdm^{-3}$). Basically, the values of $R_L$ indicate the type of isotherm to be favorable ($0 < R_L < 1$), irreversible ($R_L = 0$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) and the value of separation for adsorbent is found to be less than oneness, confirming thereby the favorable adsorption process[29].

The form of Freundlich linear equation (Eq. 7) is as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \ldots (7)$$

Where $K_F$ ($dm^3mg^{-1}$) and n are the Freundlich constants that are related to the multilayer adsorption capacity and adsorption intensity. The value of n ($1<n<10$) indicated favorable adsorption and significant adsorption onto the adsorbent[19]. Figure 8 (a), (b) show the linear diagram of Langmuir and Freundlich isotherms for the methylene blue adsorption, respectively. Furthermore, the constant parameters of these models with correlation coefficient are presented in the Table. 3.

Table 3 — Langmuir and Freundlich isotherms constant

| Freundlich constant | | | Langmuir constant | | | |
|---|---|---|---|---|---|---|
| $K_F(dm^3\ mg^{-1})$ | $n$ | $R^2$ | $q_m$ (mg $g^{-1}$) | $K_L$ (mg $L^{-1}$) | $R_L$ | $R^2$ |
| 0.522 | 1.26 | 0.9859 | 100 | 0.003 | 0.93 | 0.9982 |

Table 4 — Maximum adsorption capacity for the removal of methylene blue using various modified adsorbents

| Adsorbents | $q_m$ (mg $g^{-1}$) | *p*H | Reference |
|---|---|---|---|
| Treated sawdust of Indian Rosewood | 10 | 3.0 | (Garg *et al*., 2004) |
| Treated sawdust (Gmelina arb oria) | 236.16 | 7.0 | (Bello *et al*., 2010) |
| Palladium nanoparticles loaded on activated carbon | 75.4 | 7.0 | (Ghaedi *et al*., 2012) |
| Kaolin | 50 | 6.0 | (Mouni *et al*., 2018 |
| Tartaric acid modified rice hull | 25.0 | 6.0 | (Lee *et al*., 2010) |
| Treated shoreadasyphylla sawdust | 24.39 | 2.0 | (Hanafiah *et al*., 2012) |
| Neem sawdust | 4.354 | 7.0 | (Khattri *et al*., 2009) |
| $Fe_3O_4$@$SiO_2$-CR | 31.44 | 11.0 | (Yimin *et al*., 2018) |
| Walnut tree sawdust modified | 100 | 6.0 | This study |

According to the diagrams and Table 3, the isotherm model fitted the equilibrium Langmuir data for MB adsorption significantly better than the isotherm Freundlich model. The plots of $1/C_e$ versus $1/q_e$ in the inset of Fig. 8 present straight lines with correlation coefficients for MB of 0.9982. The monolayer adsorption capacity ($q_m$) was obtained as 100 mg/g for $KMnO_4$/SD composite. It seems that increased adsorption capacity, due to the new negative sites resulting from the chemical oxidative modification of SD or the formation of a hybrid material. So, the adsorption of methylene blue dye on the surface of adsorbent takes place in the form of homogeneous and single layers. The values of $R_L$ and n for this study are 0.93 and 1.26, respectively, which indicates the adsorption process was favorable. The comparison of the adsorbent capacity of different low-cost adsorbents is shown in Table 4. When compared with other adsorbents, the results of this study indicate, that sawdust modified with $KMnO_4$, has a better adsorption capacity in almost all cases and proves to be a cost-effective

adsorbent that can be used for the removal of MB from aqueous solution.

**Effect of the dosage of sawdust modified with $KMnO_4$on adsorption efficiency**

The influence of the amount of adsorbent in the range of 2 to 12 mg $L^{-1}$on its removal percentage and amount of adsorbed dye was investigated and results are shown in Fig. 9.

The results indicated that by increasing the amount of adsorbent (from 2 to 12mg $L^{-1}$), the percentage removal of MB rapidly increased (from 69.0% to 99.0%). But at the same conditions, the amount of methylene blue adsorbed per unit mass of adsorbent decreases with increasing the amount of absorption (Fig. 9). There are two main reasons for this phenomenon: 1) the increasing of the contact surface area,2) the available sites in the adsorption process[30, 31]. At last, the amount of 6mg/$dm^3$ modified sawdust with $KMnO_4$ was selected as an optimum dosage.

**Effect of temperature and thermodynamic parameters**

Temperature is one of the important parameters in the adsorption process, that by means of it, we can realize the enthalpy and the entropy of reaction. By using temperature, we can determine the rate of spontaneous reaction. Thermodynamic parameters such as the equilibrium constant of the adsorption ($K_c$), Gibbs-free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were given by using the following equations[32]:

$$K_C = \frac{C_{Ae}}{C_e} \quad \ldots (8)$$

$$\Delta G^0 = -RT \ln K_C \quad \ldots (9)$$

For this purpose, an amount of 6mg $L^{-1}$modified sawdust was contacted in the *p*H = 6 and 100 mg $L^{-1}$of methylene blue dyeconcentration at the temperature of 5 – 65°C for 30 min. So, according to obtained result, the $LnK_c$ diagram was drawn versus 1/T diagram (Fig. 10), and Gibbs activation energy, enthalpy and entropy were calculated, then they were put in Table 5.

According to Table 5, the negative values of the Gibbs-free energy show that the process is spontaneous. Favorable entropy causes that the adsorption is more favorable at high temperature because in the MB adsorption process, standard enthalpy acts as an unfavorable factor[33]. In such cases, the adsorptive forces are strong enough to cross over the potential barrier. The positive values of standard enthalpy change suggest the endothermic nature of the process. According to the

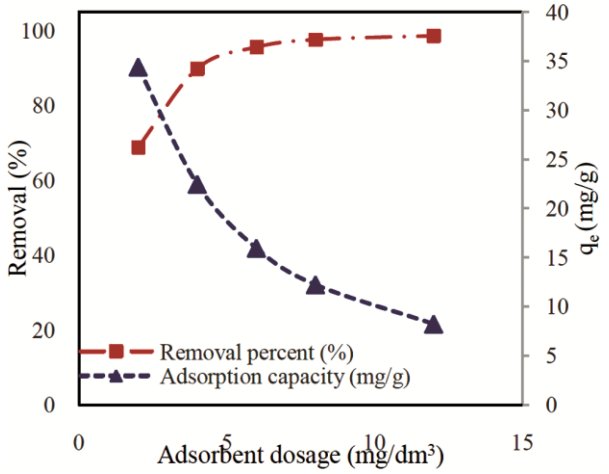



Fig. 9 — Effect of adsorbent dosage on the MB removal performance (time = 30 min, $C_0$ = 100 mg $L^{-1}$, *p*H = 6).

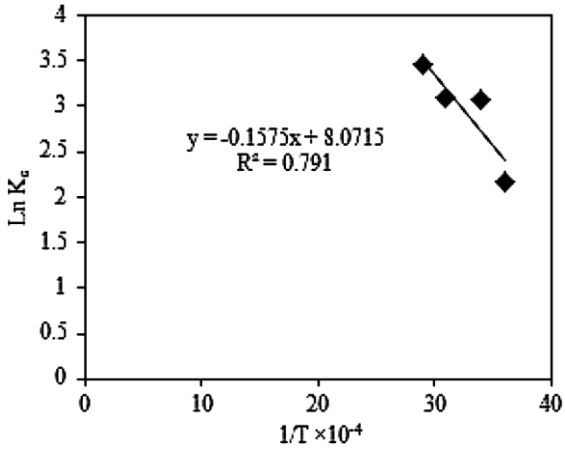



Fig. 10 — Diagram of $LnK_c$ versus 1/T for methylene blue adsorption ($C_0$ = 100 mg $L^{-1}$, m= 6 mg $L^{-1}$, temperature: 278-338 K, t = 30 min, *p*H = 6).

Table 5 — Thermodynamic parameters for methylene blue adsorption

| *T* (K) | $K_c$ | $\Delta G^\circ$ (kJ $mol^{-1}$) | $\Delta H^\circ$ (kJ $mol^{-1}$) | $\Delta S^\circ$ (J $mol^{-1}$ $K^{-1}$) |
|---|---|---|---|---|
| 278 | 2.17 | -5.02 | | |
| 298 | 3.07 | -7.62 | +1.31 | +67.11 |
| 318 | 3.09 | -8.18 | | |
| 338 | 3.47 | -9.75 | | |

obtained values in Table5, the rise of temperature is suitable for adsorption of this dye, and the adsorption process is spontaneous in higher temperature[34-36].

## Conclusion

The modified sawdust with potassium permanganate was synthesized by a simple chemical process and shows a high capability in the rapid and efficient removal of the methylene blue dye. According to the results of theimportant efficient parameters inthe

adsorption process,The results of removal percent and adsorption capacity of MB dye in pH= 10 were almost similar to the results in *p*H=6. As a results, the amount of absorption at *p*H=6 were studied. The results of these adsorption data were matched with Langmuir isotherms with 100 $mgg^{-1}$ adsorption capacity and pseudo-second-order models. Thermodynamic studies showed that the adsorption process is spontaneous and endothermic, and entropy is a favorable factor in this reaction. Therefore, we can use this adsorbent as a simple, inexpensive and efficient adsorbent for removal of cationic dyes from aqueous solutions.

## Nomenclature

| Symbol | Concept |
|---|---|
| $\mathbf{C_0}$ | Initial MB dye concentration (mg $L^{-1}$) |
| $\mathbf{C_e}$ | Equilibrium concentration of residual dye (mg $L^{-1}$) |
| $\mathbf{C_{Ae}}$ | Concentration of MB dye on the adsorbents at adsorption–desorption equilibrium solution (mg $L^{-1}$) |
| $\mathbf{C_i}$ | Maximum initial concentration of methylene blue dye (mg $L^{-1}$) |
| $\mathbf{q_e}$ | Equilibrium adsorption capacity (mg $L^{-1}$) |
| $\mathbf{q_t}$ | Amount of solute adsorbed at any time (mg $g^{-1}$) |
| $\mathbf{q_{e1}}$ | Amount of solute adsorbed at equilibrium per unit mass of adsorbent for pseudo-first-order kinetic (mg $g^{-1}$) |
| $\mathbf{q_{e2}}$ | Amount of solute adsorbed at equilibrium per unit mass of adsorbent for pseudo-second-order kinetic (mg $g^{-1}$) |
| $\mathbf{q_m}$ | Maximum amount of dye adsorbed per unit mass of the adsorbent reflected a complete monolayer (mg $g^{-1}$) in Langmuir isotherm model |
| $\mathbf{q_{e,exp}}$ | Experimental data of the equilibrium capacity (mg $g^{-1}$) |
| **M** | Mass of adsorbent (g) |
| V | Volume of solution ($dm^3$) |
| $k_1$ | Rate constant of pseudo-first-order adsorption ($min^{-1}$) |
| $k_2$ | Second-order rate constant of adsorption (g $mg^{-1}$ $min^{-1}$) |
| $K_L$ | Langmuir constant or adsorption equilibrium constant ($dm^3$ $mg^{-1}$) |
| $K_F$ | Multilayer adsorption capacity ($dm^3$ $mg^{-1}$) |
| $K_c$ | Equilibrium constant of the adsorption |
| N | Freundlich constants |
| $R_L$ | Separation factor |
| $R^2$ | Correlation coefficient |
| T | Time of adsorption (min) |
| T | Absolute temperature in Kelvin |
| ΔG | Gibbs-free energy of the adsorption |
| ΔH | Enthalpy of the adsorption |
| ΔS | Entropy of the adsorption |

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