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Adsorptive removal of new methylene blue from water by treated *Malus domestica* sawdust as a low cost biosorbent – equilibrium, kinetics and thermodynamic studies

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ABSTRACT

In this study the adsorption of New Methylene blue (Basic blue 24) on sawdust of *Malus domestica* was investigated. The sawdust was chemically treated to enhance the adsorption capacity. Adsorption experiments were performed at different temperatures ranging from 20–40°C on both raw and treated sawdust samples. The residual concentration of the dye was determined by UV-Vis spectrophotometric technique. Effect of various reaction parameters like temperature, initial dye concentration, equilibration time and pH was studied. Sawdust was characterized by BET, FTIR, Scanning electron microscopy (SEM), and Energy dispersive spectroscopy (EDS) techniques. Adsorption kinetics was interpreted using intra particle diffusion and Bangham models and both models were found to best describe the sorption of New Methylene blue onto *M. domestica*. Thermodynamic parameters like ΔE°, ΔH°, ΔS° and ΔG° were calculated from the adsorption kinetics data. The data show that the adsorption is an endothermic process. The negative value of entropy shows that the dye molecules take an oriented position on the adsorbent surface. Adsorption data fitted well with Langmuir, Freundlich and Temkin adsorption isotherms. All results clarify that *M. domestica* sawdust is a useful cheap adsorbent for removing basic dyes.

Keywords: New Methylene blue; Sawdust; *Malus domestica*; Adsorption; Kinetics; Isotherms; Adsorption; Thermodynamics

1. Introduction

With the advent of the synthetic dyes, dyeing industry has changed remarkably attributed to the cheap production and widespread application in different industries including paper, printing, leather, food, cosmetics, fabrics and plastic etc. [1]. Though highly useful and applicable on domestic as well as industrial scales, these dyes are toxic, carcinogenic and are considered as major group of pollutants in aquatic ecosystems [2,3]. Due to their ubiquitous use in the aforementioned industries, it is likely that they make their way through industrial effluents, to the water bodies initiating an eco-toxic process and bioaccumulation. Dyes have complex molecular structures containing aromatic rings, which are stable and resistant to biodegradation. Basic dyes are utilized in the textile industry due to their bright color, high solubility in water, cost effective production and good performance upon application to fabric [3,4,5]. New Methylene blue (Basic blue 24) is a cationic basic dye causing serious health hazards to human and animal's eyes and in some cases could lead to mental confusion [6–9]. Attributed to these risks, it is mandatory to remediate New methylene blue before they enter water bodies. Many approaches have been used for this purpose including membrane filtration,

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ion exchange, biological degradation, photo-catalytical degradation, reverse osmosis, adsorption [10,11]. The adsorption has proved to be an effective technique for removal of dyes by adsorption onto agricultural residues has attracted significant attention [12,13]. Activated carbon is the most commonly used adsorbent; the steps of activation and regeneration are delicate and too costly, limiting its use. The importance of finding renewable, inexpensive, abundant and easy to handle adsorbents is necessary. Several adsorption studies of dyes on bioadsorbents have been carried out such as the wood sawdust [11], orange tree sawdust [14,15], raw Algerian kaolin [16]. As to the author's knowledge, no reports on sawdust of *M. domestica* as a low-cost adsorbent for basic dye removal can be found. The approach is worth studying attributed to the fact that this sawdust is cost effective, abundantly available involving easy and environment friendly treatment. Thus, this study highlights the use of sawdust of *M. domestica*, an agricultural waste, for effective removal of New methylene blue from aqueous solution *via* batch experimental set up.

2. Experimental

2.1. Materials

New Methylene blue supplied by BioM Laboratories, Cerritos USA (Chemical Division Malaysia) was used as adsorbate. New Methylene blue (C.I. 52030) having molecular formula $C_{18}H_{22}ClN_3S$ and molecular Weight 416.05 g possesses λ_{max} of 630 nm and is water soluble. All chemicals used in this study were of analytical grade purchased from Sinopharm Chemical Reagent Co., Ltd., China. A stock solution of methylene blue was prepared and different working solutions were prepared in order to draw calibration curve.

2.2. Sawdust treatment

M. domestica sawdust was treated with excess of standardized 0.5 mol/L NaOH solution for 24 h to remove the color elements. The sample was thoroughly washed with distilled water and neutralized with 0.5 mol/L HCl solution. The sample was again washed with double distilled water to neutral pH and was dried in an oven at 105 ± 2°C till complete dryness. For comparison purpose, equal amount of sawdust was used without such treatment.

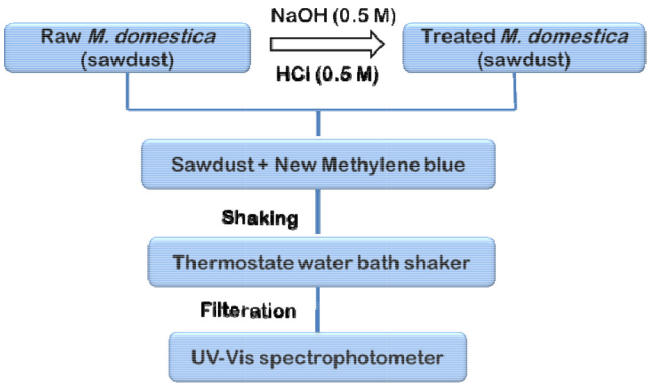


Fig. 1. Flow sheet diagram for adsorption of New Methylene blue on *M. domestica*.

2.3. Characterization of adsorbent

Specific surface area of the adsorbent was determined using Brunner Emmett and Teller (BET) method. Scanning electron microscopy (SEM) was used to investigate surface morphology of *M. domestica* while elemental composition was determined by Energy dispersive spectroscopy (EDS). FTIR was used to find out the functional groups and chemical constituent of the sawdust.

2.4. Adsorption studies

2.4.1. Equilibrium time

Equilibrium time studies were carried out with two different initial dye concentrations. 0.2 g of treated sawdust and 20 cm^3 of New Methylene blue solutions were shaken in thermostat water bath shakers at 25°C for time period of 0.5, 1, 2, 4, 6 and 8 h. pH was noted before and after experiment. The change in dye concentration was determined with UV-visible spectrophotometer. All the experiments were carried out in triplicate. The quantity of dye adsorbed (D_Φ $mol{\cdot}g^{-1}$) was calculated with the help of Eq. (1).

$$D_\Phi = \frac{D_o - D_\sigma}{W} \quad (1)$$

where D_o and D_σ are initial and equilibrium concentration ($mol{\cdot}dm^{-3}$) of dye respectively.

2.4.2. Adsorption kinetic experiments

A mixture of 0.2 g *M. domestica* and 20 cm^3 of New Methylene blue solution was shaken at 20°C, 30°C and 40°C, for 5–30 min. The slurry was filtered and the filtrate was examined for change in concentration by UV-vis spectrophotometer. The pH was noted before and after filtration with digital pH meter. The dye adsorbed (D_Φ $mol{\cdot}g^{-1}$) was then computed by using Eq. (1) mentioned above.

2.4.3. Adsorption isotherms

Adsorption isotherm studies were carried out at dye concentrations (1×10^{-5}, 2×10^{-5}, 3×10^{-5} $mol{\cdot}dm^{-3}$ etc.) over a fixed duration of 1 h equilibrium time. 0.2 g of *M. domestica* and 20 cm^3 of New Methylene blue solutions were shaken in thermostate water bath shaker at 20°C, 30°C and 40°C. Clear filtrate was received by filtering the reaction mixture and the remaining dye concentration was determined by UV-Vis spectro photometer.

2.4.4. Desorption experiments

The MB loaded *M. domestica* was mixed with 3% NaOH desorption solution, methanol and distilled water in an Erlenmeyer flask, shaken at 25°C for 1 h. The resulting suspension was filtrated, washed by deionized water to remove unadsorbed New Methylene blue, and dried to get regenerated *M. domestica* sawdust. The adsorption capa-

bility of regenerated *M. domestica* was investigated in 20 cm^3 New Methylene blue with 0.2 g *M. domestica* sawdust at 40°C for 1 h. The MB concentrations before and after adsorption were measured on a UV-Vis spectrophotometer at wavelength of 630 nm. The amount adsorbed was calculated by using Eq. (1).

2.4.5. Procedure for UV-Vis spectrophotometric analysis

0.01 M stock solution of dye was prepared. From this stock solution, various working solutions were prepared by using dilution formula. All the standard solutions were analyzed in visible range on UV-Vis spectrophotometer (Model: UV-1800 240 V). Concentration vs. adsorption was plotted to get working curve. All the observations were noted against blank distilled water.

3. Results and discussion

3.1. Characterization of adsorbent

3.1.1. BET analysis

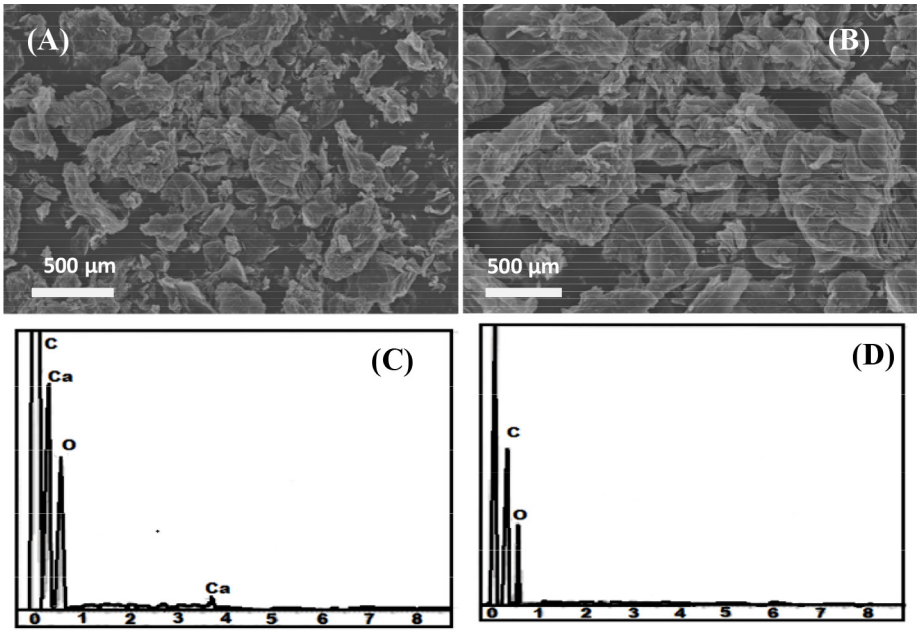
Surface area of *M. domestica* sawdust was calculated using BET method [12]. This process makes use of multilayer adsorption of nitrogen gas on adsorbent for surface area determination. Surface area was found to increase from 150 $m^2 \cdot g^{-1}$ (raw) to 355 $m^2 \cdot g^{-1}$ (treated) sawdust attributed to treatment with NaOH and HCl. The surface became clean and foreign constituents were removed which exposed the adsorbent surface for more dye molecules to be adsorbed. Another reason for increase in surface area could be the presence of non-polar sawdust surface particles at high temperature [13].

3.1.2. SEM/EDS analysis

SEM was used to identify the characteristic morphologies of *M. domestica*. The SEM images confirm that the surface of adsorbent have pores of different size and shapes (Fig. 2). The EDS spectra of raw and treated *M. domestica* indicate that the surface of both the samples has excess carbon, some oxygen. Some amount of calcium was detected in raw sample which is absent in treated *M. domestica*.

3.1.3. FTIR studies

FTIR spectra of raw and treated *M. domestica* sawdust are given in Fig. 3. Absorption in region from 3500 cm^{-1} to 3000 cm^{-1} are due to the presence of hydroxyl group (-OH) stretching [17,18]. The OH-stretching bands in raw and treated *M. domestica* are in regions of 3346 cm^{-1} and 3334 cm^{-1} respectively. The bands at 2908 cm^{-1} and 2902 cm^{-1} are characterized to aliphatic -CH_3, and -CH_2 stretching, mainly due to -CH_2 groups [19,20]. Peaks at 1732 cm^{-1} in raw *M. domes-*



(E)

Element	Raw *M. domestica* Weight(%)	Treated *M. domestica* Weight(%)
C	46.07	52.18
O	49.53	47.82
Ca	4.39	0

Fig. 2. SEM (X 200) images of (A) raw and (B) treated *M. domestica* sawdust sample, EDS spectra of (C) raw and (D) treated *M. domestica*. (E) weight (%) of elemental composition of *M. domestica* sawdust.

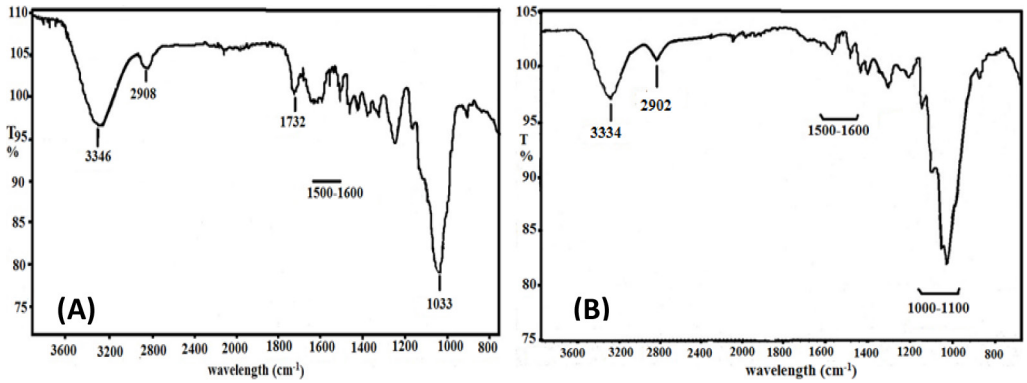


Fig. 3. FTIR spectra of (A) raw and (B) treated *M. domestica* sawdust sample.

tica is due to C=O or C=C double bonds [21] where a weaker peak for C=O stretching might be due the presence of trace amounts of ketonic functionalities. Such bands are absent in treated *M. domestica*. The peaks in the region 1500–1600 cm^{-1} are mainly due to C=C stretching bonds in benzene rings [19,22,23]. Absorption bands at 1240 cm^{-1} in raw *M. domestica*, 1228 cm^{-1} in treated *M. domestica* indicate the presence of C-O bond [19,24,25]. Sharp bands in the region 1000–1100 cm^{-1} indicate the presence of minerals in the sample.

3.2. Adsorption studies

3.2.1. Equilibration time and adsorption kinetics

Equilibrium time for sorption experiments were studied for a period of 0.5, 1, 2, 4, 6 and 8 h at 25°C, which show that equilibrium was attained in less than 1 h time (Fig. 4). Optimum time for complete surface coverage is approximately 1 h (Fig. 4). Adsorption kinetics of New Methylene blue were studied at 20–40°C on raw and treated *M. domestica* samples. Rate of adsorption in first fifteen minutes was fast and then slows down onward due to the maximum diffusion into pores of adsorbent (sawdust). Also with temperature rise sorption of dyes on sawdust increases which indicate an endothermic process [26].

3.2.2. Adsorption kinetic linear equations

The rate constant for sorption of New Methylene blue on dust of *M. domestica* was determined by first order rate equation.

$$\ln D_\sigma = \ln D_o - k_{ad} \cdot t \tag{2}$$

D_o and D_σ are initial and equilibrium concentration of dye (mol·dm^{-3}) respectively. k_{ad} stands for the rate constant and was calculated from the straight line plots of ln D_σ vs. t at 20–40°C (Table 1). The values for rate constant increased with rising temperature. The R^2 value for first order equation (0.8–0.99) shows good agreement of the data with rate equation. Activation energy for sorption was determined by using Arrhenius equation [27] in the following form:

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \tag{3}$$

E_a shows activation energy while k_1 and k_2 are rate constants. The activation energies for New Methylene blue adsorbed on dust are given in Table 1. The data illustrate that treated samples show enhanced activation energy as compared to raw samples attributed to better contact between sawdust surface molecules and dye leading to enhanced adsorption. From activation energies the thermodynamic parameters like ΔH° and ΔS° were also illustrated (Table 1) using following equations [27].

$$\Delta H^\circ = \Delta E^\circ - RT \tag{4}$$

$$\Delta S^\circ = R\left[\ln\frac{Kh}{K_B T} + \frac{\Delta H^\circ}{RT}\right] \tag{5}$$

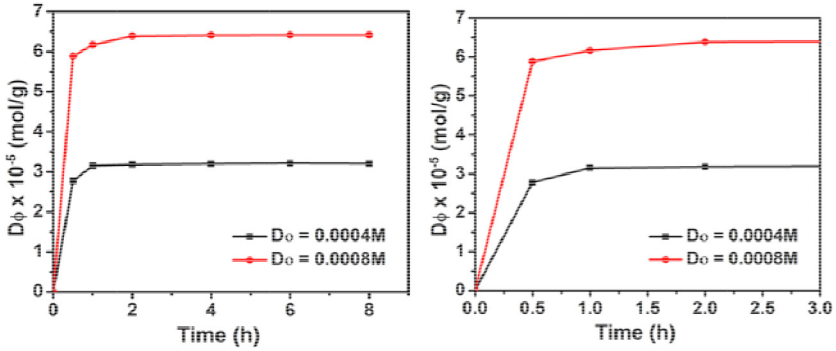


Fig. 4. Equilibrium time plot for New Methylene blue adsorption on treated *M. domestica* sawdust.

Table 1
Thermodynamic constants for sorption of New Methylene blue onto *M. domestica* sawdust

Sample	k (min^{-1})			ΔE°($kJ·mol^{-1}$)	ΔH° ($kJ·mol^{-1}$)			ΔS° ($J·mol^{-1}K^{-1}$)		
	20°C	30°C	40°C		20°C	30°C	40°C	20°C	30°C	40°C
Raw	0.942	0.967	0.988	1.661	1.495	1.412	1.328	–7.114	–4.067	–1.105
Treated	0.925	0.968	0.981	2.182	2.016	1.933	1.849	–3.750	–3.721	–1.833

where k, k_B and h are rate constant, Boltzmann constant and Plank constant, respectively. Thermodynamic parameters indicated that the adsorption process was feasible, spontaneous and endothermic under studied conditions [28,29]. The negative values of the entropy of activation (ΔS°) showed that randomness or entropy decreased with rise in adsorption temperature which means that dye molecules attains a stable position (i,e. dye get adsorbed) onto dust surface.

4.2.3. Bangham equation

The Bangham equation in linear form is presented as Eq. (6) [30].

$$\log\cdot\log\frac{D_o}{D_o - D_\sigma W} = \log\frac{k_o W}{2.303V} + \alpha\log t \tag{6}$$

Here, D is the initial concentration of dye, D_σ is adsorbed amount after time (t). Using the intercepts and slopes of linear plots (Fig. 5) k_o and α are calculated (Table 2). The plot was found to be linear with good correlation co-efficient ($R^2 > 0.9$) indicating the uniform distribution of dye into pores of dust and is a pore diffusion controlled process [31].

3.2.5. Parabolic diffusion model (Intra particle diffusion)

Intra particle diffusion implies multi-linearity which clarifies the different steps involved in adsorption process [32]. According to Morris and Weber parabolic diffusion is defined by Eq. (7) below:

$$D_\Phi = k_{id}t^{1/2} + B \tag{7}$$

The plot of D_Φ vs. $t^{1/2}$ gives a straight line indicating that adsorption of a solute is controlled by the intra particle diffusion process. As none of plot passes through the origin (Fig. 6) indicating that the intra particle diffusion is not the only rate controlling step and suggests some degree of boundary layer control [33]. The intra particle diffusion coefficient (k_{id}) is given in Table 2 where the R^2 (0.999) is close to 1 which indicates that this equation is best fitted for the New Methylene blue adsorption onto sawdust. It is

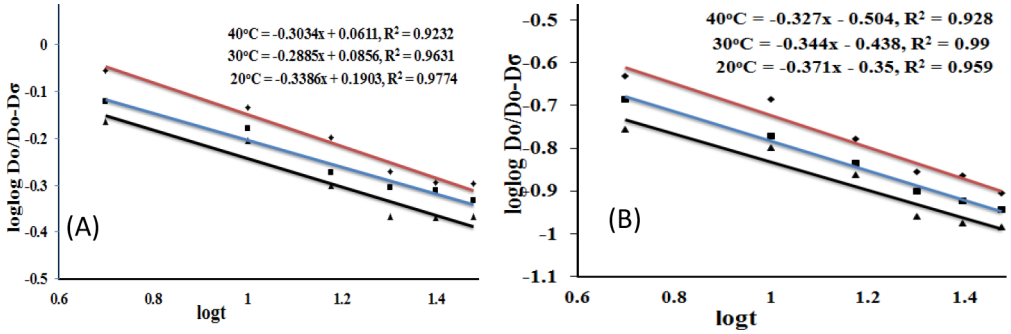


Fig. 5. Banghum plots of New Methylene blue on (A) raw and (B) treated *M. domestica* sawdust.

Table 2
Kinetic parameters for adsorption of New Methylene blue on raw and treated *M. domestica* sawdust

Kinetic model	Parameter	Raw *M. domestica*			Treated *M. domestica*		
		20°C	30°C	40°C	20°C	30°C	40°C
Intra particle diffusion	C (mg/g)	–0.014	0.237	0.297	1.843	2.108	2.289
	K_{dif} ($mg/gmin^{1/2}$)	0.245	0.217	0.2366	0.219	0.1863	0.166
	R^2	0.96	0.95	0.91	0.97	0.97	0.95
Bangham	α	–0.339	–0.288	–0.303	–0.372	–0.344	–0.33
	K_O	2.74	1.574	1.384	0.156	0.098	0.069
	R^2	0.97	0.96	0.92	0.95	0.99	0.93

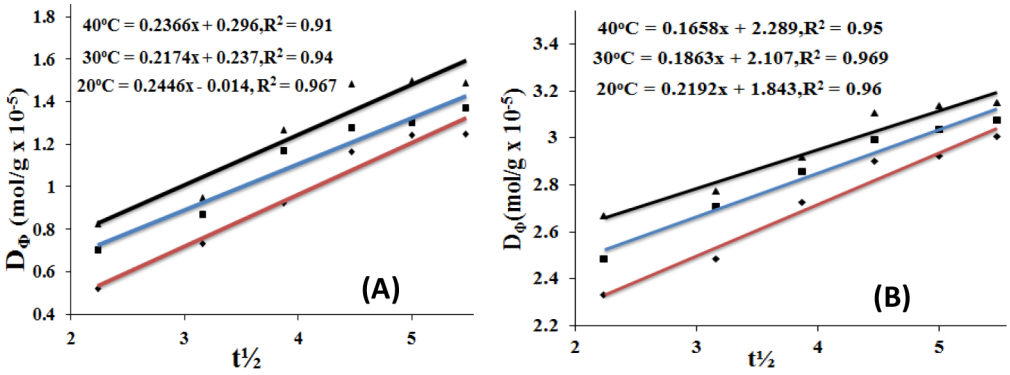


Fig. 6. Intra particle diffusion plots for new Methylene blue on (A) raw and (B) treated *M. domestica*.

because of the immediate action of most effortlessly adsorption sites on sawdust surface. It is further believed that the process is controlled by external mass transfer combined with intra particle diffusion though the later dominates the control of adsorption process [29,34].

3.3. Adsorption isotherm studies

Adsorption isotherms studies over sawdust of *M. domestica* clarify the distribution of dye molecules in between the liquid-solid interface [35]. In order to reveal the distribution behavior of adsorbent and adsorbate molecules, adsorption isotherm models, the Langmuir, Freundlich, Temkin and Harkins-jura isotherms were applied. Isotherm constants for various adsorption parameters are given in Table 4. Results indicate that dye uptake by sawdust particles increased with rise of temperature [36] while dye uptake by treated sample was greater as compared to raw sample. The sensitivity of the adsorption process towards temperature indicated that overall procedure is endothermic and adsorbent with greater surface area, open pores and high interaction for dye molecules demonstrated greater uptake [37].

3.3.1. Freundlich isotherm

This isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface [38]. By applying Freundlich Isotherm [Eq. (8)] to the adsorption data linear plots were obtained as shown in Fig. 7.

$$\ln D_{\Phi} = \ln K + \frac{1}{n}\ln D_{\sigma} \tag{8}$$

Values of the parameters n and K were calculated from the plots (Fig. 7) and are displayed in Table 4. Constant n provides information about surface morphology, heterogeneity and its ability to adsorb solute [39]. Large value of $1/n$ represents the efficiency of the adsorbent toward adsorbate. $1/n > 1.0$ demonstrates the solute concentration adsorbed is greater than that present in the solution [40]. The values of constant, K ($mol{\cdot}g^{-1}$) show adsorption capacity of sawdust samples. The sorption ability of sawdust increased with increasing temperature. It is also indicative of the heterogeneous surface of the sawdust.

3.3.2. Langmuir isotherm

The Langmuir isotherm describes quantitatively the formation of a mono layer on the outer surface of the adsorbent, and after that no further adsorption takes place. The linear form of Langmuir isotherm shown in Eq. (9), was applied to adsorption isotherms data and the plots are shown in Fig. 8.

$$\frac{D_{\sigma}}{D_{\Phi}} = \frac{1}{b\,K_L} + \frac{D_{\sigma}}{b} \tag{9}$$

b is the amount adsorbed (mol/g) consequent to a whole mono layer coverage, k_l (L/g) is binding energy constants and is ($0 < k_l < 1$) which confirms that the used adsorbent is favorable for New Methylene blue dye uptake [41]. The

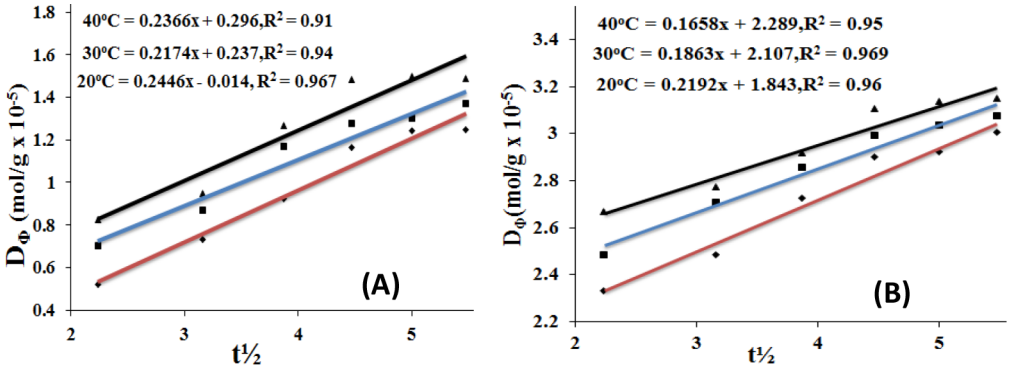


Fig. 7. Freundlich isotherm plots for New Methylene blue on (A) raw and (B) treated *M. domestica*.

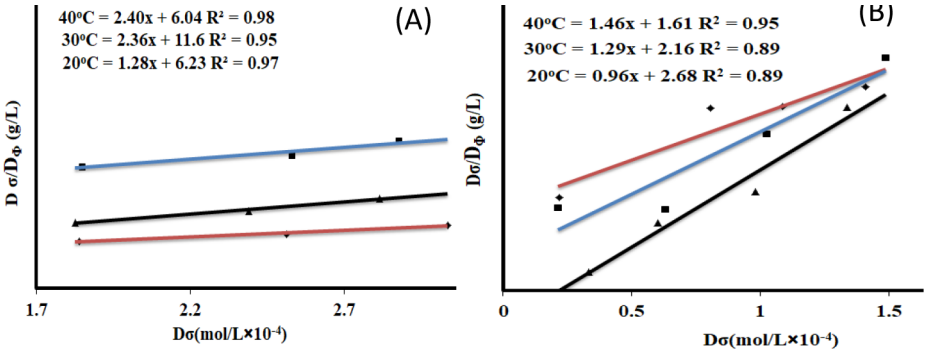


Fig. 8. Langmuir plots for New Methylene blue on (A) raw and (B) treated *M. domestica* sawdust.

linear plots of D_σ/D_Φ (g dm^{-3}) against D_σ (mol dm^{-3}) give the values of K_l and b (Table 4).

The plot in Fig. 8 demonstrates that the Langmuir equation provides description of the experimental data which is confirmed by the high values of correlation coefficients (Table 4). The driving force for such a tendency is represented by the Gibbs free energy (ΔG°) [42]. Negative values of free energy (ΔG°) for the systems indicate spontaneity of the adsorption process. Gibbs free energy was calculated as suggested by Yu Lin [43] using Eqs. (10) and (11).

$$K_T \approx bM_A \tag{10}$$

$$\Delta G^o = -RT \ln K_T \tag{11}$$

where b (mol·g^{-1}) is Langmuir mono layer adsorption capacity and M_A is molecular weight of the dye. The data in Table 3 show that ΔG° values decrease with increase in temperature, which reveals spontaneous nature and direct relation between adsorption uptake and temperature [13,44].

Table 3
Thermodynamic parameter ΔG for New Methylene blue onto *M. domestica* sawdust

Sample	ΔG × 10^3 (kJ/mol)		
	20°C	30°C	40°C
Raw *M. domestica*	–12.56	–13.03	–15.04
Treated *M. domestica*	–13.76	–14.54	–15.79

3.3.3. Temkin isotherm

The linear type of Temkin isotherm is given by Eq. (12) below [42]

$$D_c = \beta \ln \alpha + \beta \ln D_\sigma \tag{12}$$

By plotting D against ln D_σ, straight curves are obtained with slope β and intercept β *ln* α (Fig. 9). The values of '*B*' increase with increase in temperature from 20 to 40°C (Table 4) indicating enhanced adsorption at higher temperature. Close to 1 values of R^2 suggest the best fitting of Temkin isotherm for uptake of New Methylene blue by sawdust [43,44].

3.3.4. Harkin-jura isotherm

The Harkin-jura adsorption isotherm is represented by Eq. (13) [45]:

$$\frac{1}{(D_\delta)^2} = \left(\frac{B}{A}\right) - \frac{1}{A \cdot \log D_\sigma} \tag{13}$$

Harkins-Jura explains multilayer adsorption of dyes on heterogeneous pore distribution on the sawdust surface [46], where D_Φ is the amount adsorbed and D_σ is equilibrium concentration. By plotting $1/(D_\Phi)^2$ against log D_σ, we

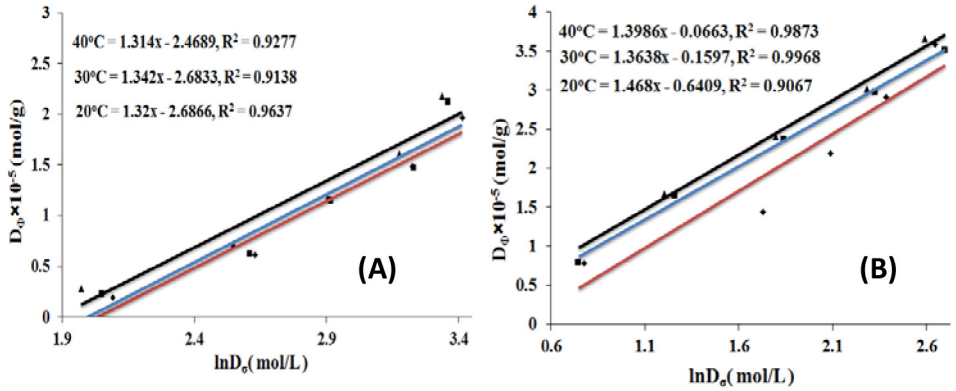


Fig. 9. Temkin plots for New Methylene blue on (A) raw and (B) treated *M. domestica* sawdust.

Table 4
Isotherm constants for New Methylene blue onto *M. domestica* sawdust

Isotherm	Parameters	Raw *M. domestica*			Treated *M. domestica*		
		20°C	30°C	40°C	20°C	30°C	40°C
Freundlich	$1/n$	1.759	1.666	1.469	0.828	0.727	0.589
	K_F (mg/g)	0.055	0.078	0.16	3.89	5.52	8.17
	R^2	0.97	0.98	0.99	0.98	0.934	0.99
Langmuir	K_L (L/mg)	0.125	0.037	0.069	0.387	0.357	0.426
	R^2	0.97	0.94	0.98	0.89	0.89	0.954
	α (dm^3/g)	0.131	0.136	0.153	0.646	0.8896	0.954
Temkin	β (mg/dm^3)	1.32	1.342	1.314	1.468	1.3638	1.3986
	B	1845	1877	1980	1659	1847	1860
	R^2	0.963	0.914	0.927	0.907	0.996	0.987
	A	0.167	0.148	0.202	0.987	2.195	2.14
Harkins-jura	B	1.506	1.467	1.464	1.18	1.288	1.24
	R^2	0.778	0.858	0.93	0.898	0.92	0.942

obtained a straight line with a negative slope (Fig. 10) and there was a direct relation between B and temperature.

The sorption of New Methylene blue is assumed to be a little complex process due to the formation of multi layers on sawdust surface. The difference of sorption activity is expected with different surface coverage [47]. The data obtained were well fitted with Freundlich model under different concentrations studied indicating that heterogeneous surface conditions exist under the current experimental conditions.

3.4. Effect of sawdust dosage and solution pH

The influence of the pH on the adsorptive behaviour of dyes onto various adsorbent was considered previously [5,14,33,52–54]. pH is an important parameter influencing the adsorption capacity of adsorbent, since it affects the surface charges of adsorbent and the ionization degree of dye molecule. It was noted that when adsorption of MB was performed below pH 4 and pH 3, the pH somewhat raised after adsorption. Therefore, basic cations on the surface of adsorbent would exchange with proton in the solution under strong acidic conditions by suppressing exchange of MB cation [53]. While above pH 5 and pH 4, the pH of solution decreased after adsorption, which indicated that proton on the surface of adsorbent should exchange with MB cation under weakly acidic and nearly neutral conditions [52]. In our experiment the pH values were not adjusted. The pH was observed before and after adsorption process. The pH noted before adsorption was 7.42, owing to the higher cation exchange capability of New Methylene blue with proton of the *M. domestica* sawdust results in decrease of solution pH to 6.43 when noted after adsorption.

Futher, the adsorption rate of dye increased with adsorbent dosage, as more adsorption sites were available [14,52]. New Methylene blue absorption onto *M. domestica* sawdust increases with increasing sawdust dosage (Fig. 11). In addition, treated *M. domestica* generally exhibited higher adsorption efficiency than raw *M. domestica* using the same sawdust dosage.

3.6. Possible mechanism

The FTIR analysis of raw and treated *M. domestica* sawdust declared the surface has oxygen containing functional

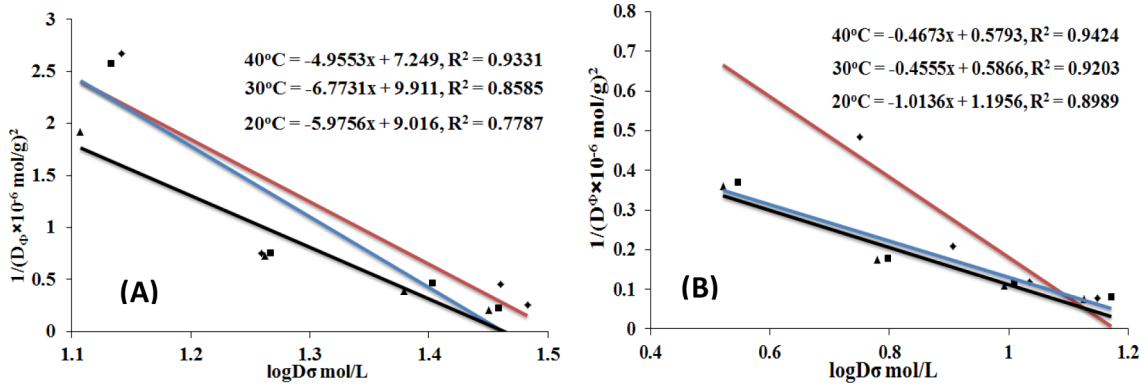


Fig. 10. Harkins-jura plots of New Methylene blue on (A) raw and (B) treated *M. domestica* dust.

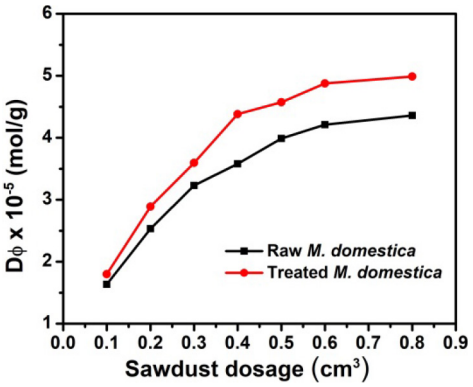


Fig. 11. Effect of sawdust dosage on adsorption efficiency. (20 cm^3 New Methylene blue solution (4 x 10^{-5} mol/L), pH = 7, 1 h.)

groups, dominantly hydroxyl groups. The oxygen-functional groups participate in adsorption of cationic dyes by hydrogen bonding and ion exchange [54]. The H-bond interaction of New Methylene blue with the sawdust should contribute to the adsorption. As New Methylene blue existed as cation in aqueous solution and the sawdust surfaces was negatively charged, electrostatic interactions should be involved in the adsorption process. The cation exchange of New Methylene blue with proton of the sawdust occurred at pH 7, demonstrated by a decrease of pH after adsorption.

The investigation of the kinetics and mechanism of basic dye, New Methylene blue onto *M. domestica* wood sawdust was further analyzed by applying pseudo-first order kinetic model, Bangham model and intra particle diffusion model. The kinetics of sorption processes is concerned with forces between sawdust sites and dye molecules, and this forms an important area of surface chemistry. The experimental data was found to follow the pseudo-first order kinetics with relatively high correlation co-efficient. The plot for Banghum model was found to be linear with good correlation co-efficient ($R^2 > 0.9$) indicating the uniform distribution of New Methylene blue into pores of sawdust and suggesting a pore diffusion controlled process on *M. domestica* surface. Similarly, parabolic diffusion model indicating that adsorption is controlled by the intra particle diffusion process but intra particle diffusion is not the only rate controlling step involving some degree of boundary layer control process. Besides, the type of adsorption (physisorption or chemisorption) can also be determined by the magnitude of ΔH^o, whereby low magnitudes of ΔH^o are characteristic of physisorption. Therefore, the new Methylene blue adsorption onto *M. domestica* is a physisorption process owing the low magnitude of ΔH^o (Table 1). The comparison of adsorptive removal of basic dyes on various bioserbents is also listed in Table 5.

3.5. Re-usability/regeneration of sawdust (desorption experiment)

According to the resource and economic standpoint, the adsorbents re-usability is a crucial factor that needs to be considered during the selection of adsorbent. The adsorp-

Table 5
Comparison of various wood sawdust biosorbent for adsorptive removal of basic dyes

Adsorbent	Dye	Adsorption kinetics	Adsorption isotherms	Reaction nature	pH	Year [Ref]
Red wood & beech wood sawdust	MB	Pseudo second order kinetics	Nil	Nil	2.0	2017, [10]
White pine sawdust	MB	Nil	Redlich-Petersen isotherm	Endothermic	3–10	2016, [37]
Treated wood sawdust, commer-activ-carbon	MB	Nil	Langmuir isotherm monolayer adsorption	Nil	5.0	2014, [51]
Fugas sawdust	GRL	Nil	Langmuir isotherm	Endothermic & spontaneous	6.7	2014, [48]
Wood sawdust	Tartrazine	Second order kinetics, Film diffusion process	Dubinin radushkevich model	Endothermic & spontaneous	3.0	2017, [49]
Activated carbon (sawdust)	MB	Nil	Langmuir isotherm	Nil	7.8	2012, [50]
Raw & treated *Malus domestica* sawdust	New MB (BB-24)	First order equation, diffusion-control process	Freundlich isotherm, multilayered adsorption	Endothermic & spontaneous	7.0	Present work

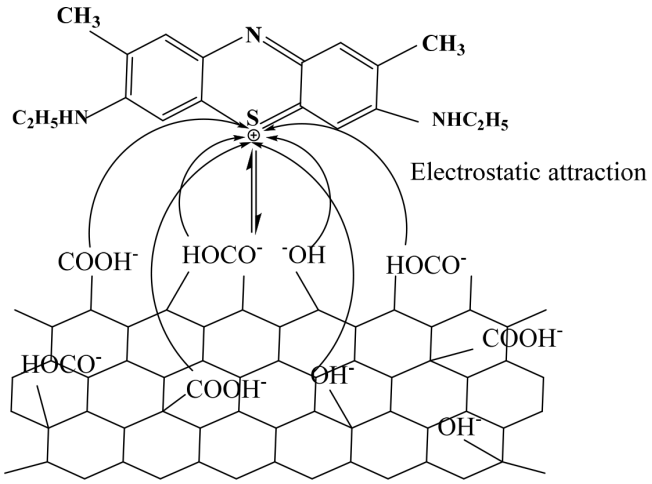


Fig. 12. Electrostatic interaction of cationic dye and sawdust surface.

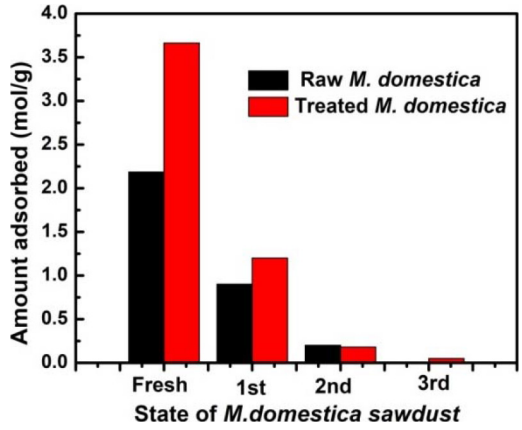


Fig. 13. Regeneration of New Methylene blue adsorbed raw and treated *M. domestica* sawdust.

tion capability of regenerated *M. domestica* was investigated in 20 cm^{-3} (4×10^5 $mol.L^{-1}$) New methylene blue with 0.2 g *M. domestica* adsorbent at pH 7 40°C for 60 min with three adsorption cycles, in which in every adsorption cycle, the sawdust was filtered and oven-dried completely at 80°C before reused. The MB concentrations before and after adsorption were measured on a UV-vis spectrophotometer at wavelength of 630 nm. The adsorbed amount of dye onto *M. domestica* sawdust was calculated by using Eq. (1). As shown in Fig. 11, the efficacy of the *M. domestica* towards New Methylene blue removal was decreased to about half in first cycle and almost ceases in second cycle.

4. Conclusions

In the present study raw and treated *M. domestica* sawdust was used as low cost adsorbent for adsorptive uptake of New Methylene blue. The obtained results show that sorption of basic dye onto raw and treated *M. domestica* sawdust increased with increase in initial dye concentration, adsorbent dose and experimental temperature at neutral pH. Surface area of raw sawdust was increased from 150 to 355 $m^2 \cdot g^{-1}$ on treatment with NaOH and HCl. The kinetic analyses show that sorption of New Methylene blue onto dust particles follows linear equations and the process is controlled by diffusion. Freundlich and Tempkin equations were best fitted to adsorption data while thermodynamic studies reveal the endothermic nature of the process. Attributed to the cost-effectiveness, easy and abundant availability and environment friendly nature of adsorbent (*M. domestica*), It can therefore be concluded that saw dust offers promise as an economically viable alternative for sequestering of the dye from the aqueous solution. The work can be extended for the removal of dyes from effluents as well.

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