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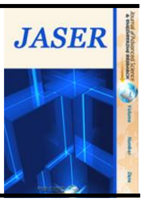

Adsorption of Basic Dye From Aqueous Solution Using Mixture of Agricultural Solid Wastes (Maw): Isotherm, Kinetic Studies and Process Design

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ABSTRACT

The aim of this study is to evaluate the adsorption capability of mixture of agricultural solid wastes, which is a mixture of agricultural solid wastes (Empty coconut bunch, banana stalk, coconut frond, oil palm frond and bamboo leaf). Low doses of these rejected wastes (0.1 g each) mixed together to be used as adsorbent in order to investigate its ability for methylene blue dye (MB) removal. Batch adsorption system was studied at 30 °C with respect to the initial dye concentration (50 - 300 mg/L), contact time and pH of solution (2-10). The maximum removal was obtained at pH 8. The equilibrium data were analyzed using the Langmuir (3 forms), Freundlich and Temkin isotherm models. The adsorption isotherm followed the order Langmuir form 1> Freundlich isotherm > Temkin isotherm > Langmuir form 2> Langmuir form 3. The adsorption isotherm data were fitted well to form 1 of Langmuir isotherm and the adsorption capacity was found to be 93.458 mg/g. The adsorption kinetic was well described by the pseudo-second-order model. The intraparticle diffusion was not the only rate controlling step of adsorption process. Single stage batch adsorber was designed using Langmuir isotherm to predict the minimum amount of adsorbent need to achieve a specific percentage of dye removal. The adsorption capacity obtained for the adsorption of MB onto MAW was good compare with other reported values.

Keywords: **Wastes mixture, Methylene blue, Isotherm, Kinetic, Process design**

1. Introduction

The industrial development in recent years has left its impression on the environmental society. Many industries discharge wastewaters such as textile, chemical, refineries, plastic and food- processing plants (Mohan et al., 2007). Textile industry represents an important sector to Malaysian economic, where the colored textiles grow continuously day by day according to the growth of population providing a new dimension to Malaysian economic.

The wastewaters discharge from textile industries includes residual dyes; these dyes are not bio-degradable therefore they may cause water pollution and serious threat to the environment

(Kumar et al., 2005). That is why the Interim National Water Quality Standards for Malaysia (2006) considered the maximum contaminant level for color is 15 color units. Methylene blue (MB) a cationic dye is very popular for dyeing process in many industries. Acute exposure to methylene blue (MB) may cause some harmful effect, where it may cause increased heart rate, shock, vomiting, jaundice, heinz body formation, cyanosis, quadriplegia and tissue necrosis in human (Vadivelan & Kumar, 2005). Therefore it is important to remove such dye from effluents with respect to both environmental and aesthetical views.

Many methods used to remove dyes from wastewaters such as coagulation and membrane separation process, electrochemical, chemical oxidation, reverse osmosis and aerobic and anaerobic microbial degradation, but these methods have many restrictions, and therefore not successful for removing the color completely from wastewater (Sulak et al., 2007). With compare to other conventional physico-chemical methods for dye removal, adsorption has proved to be more efficient, versatile, ease of operation and low cost of application (Senthilkumaar et al., 2006; Eren & Afsin, 2007). Activated carbon is widely used as adsorbent, but it is expensive and therefore not economical for wastewater treatment (Chandra et al., 2007), thus it is worthwhile to find low-cost, available and renewal adsorbents such as agricultural solid wastes.

Agricultural solid wastes used as adsorbents to remove many types of pollutants, such as cotton fiber for adsorption of acid violet 17 and direct red 80 dyes (Saleem et al., 2007), Lemon peel for adsorption of malachite green (Kumar, 2007), sugarcane bagasse for adsorption of Cu(II), Cd(II) and Pb(II) (Gurgel & Gil, 2009), palm seed for adsorption of phenol (Rengaraj et al., 2002) and Avacado peel for adsorption of COD and BOD (Devi et al., 2008).

Many researchers studied the feasibility of adsorption of methylene blue dye onto agricultural solid wastes and they proved that these wastes have good adsorption capacities, such as tea waste (Uddin et al., 2009), coir pith (Kavitha & Namasivayam, 2007), indian rose wood (Garg et al., 2004), jute processing waste (Banerjee & Dastidar, 2005), waste apricot (Önal, 2006), castor seed shell (Oladoja et al., 2008), wood sawdust (Ofomaja, 2008), pomelo peel (Hameed et al., 2008), wheat straw (Han et al., 2010) and hazelnut shell (Doğan et al., 2009).

The agricultural sector in Malaysia represents an important sector of its economy where there is a diversity of the agricultural products such as palm oil, Coconut (Cocos nucifera), Banana (Musa cavendishii) and bamboo. According to the Malaysian Palm Oil Council (2010), Malaysia currently accounts for 39 % of world palm oil production, while coconut palm (Cocos nucifera) is one of the most familiar tropical fruits in Malaysia where 142,000 hectares of planted land of coconut available (Azam et al., 2009). Banana (Musa cavendishii) is grown in most of the Malaysian states and considers one of the most important fruit crop there. Bamboo is natural renewable resource in Malaysia, where the Food and Agriculture Organization of the United Nations (2005) reported that there are about 421,719 hectares of bamboo are available of forest reserves in west Malaysia (peninsular Malaysia). Production of these agricultural products will accompany with a lot of wastes and most of these wastes are burned directly such as oil palm fronds and coconut fronds. Oil palm fronds and coconut fronds used as wood fuels can be estimated about 48 (ton/km^2/year) and 234 (ton/km^2/year) respectively (Koopmans, 2005). Some wastes accumulate without any industrial or commercial uses such as empty coconut bunch, banana stalk and bamboo leaf, as a result poses serious environmental problems to the community. A survey of literature showed that no study has been done so far on utilization of mixture of different wastes as adsorbent.

In this study a mixture of oil palm frond, empty coconut bunch, coconut frond, banana stalk and bamboo leaf was used as an adsorbent to remove methylene blue (MB).

2. Materials and methods

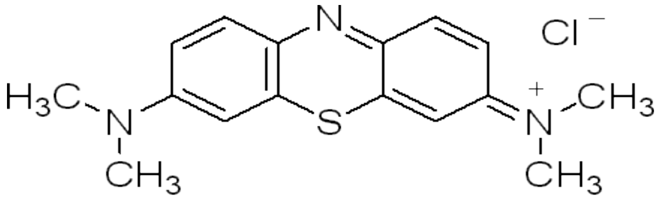
2.1 Preparation and of adsorbent

Empty coconut bunch, banana stalk, coconut frond, oil palm frond and bamboo leaf were collected locally. The collected materials were sun dried, ground, soaked in hot distilled water for 24h, washed several times with distilled water, dried in a hot air oven at 60°C for 48 h then sieved separately. Mixture of agricultural wastes (MAW) prepared by mixing 0.1g of each material to prepare 0.5 g of adsorbent then stored in plastic bottle for further use. No other chemical or physical treatments were used prior to adsorption experiments.

2.2 Dye solution preparation

The properties of methylene blue dye (MB) presented in Table 1. MB dye was made up in stock solution of concentration 1000 mg/L and was diluted to the required concentrations (50-300 mg/L).

Table 1: Properties of MB dye

Properties	
Dye name	Methylene blue
Molecular formula	$C_{16}H_{18}N_3SCl$
Molecular weight, g/mol	373.90
λ max. (nm)	668
●(measured)	
Chemical structure	

2.3 Analyses and Measurement

A calibration curve for MB dye was prepared by plotting the diluted solutions concentrations versus corresponding absorbance values. The samples were agitated in shaking incubator (VS-8480 SRN, Korea) and the concentrations of dye solutions were analyzed using UV-Vis

Spectrophotometer (Spectronic Helios Alpha, Thermo Electron Corporation, UK). The pH measurement was conducted using pH meter (Jenway -3305, UK).

2.4 Batch equilibrium studies

Batch adsorption experiments were conducted with varying pH, contact time and initial dye concentration. The effect of pH solution on the adsorption process was conducted by adding 0.5 g of MAW to 200 ml dye solution of 100 mg/L initial concentration at different pH values (2.0–10.0). The pH was adjusted by adding 1M of Sodium hydroxide (NaOH) or 1M of Hydrochloric acid (HCl) solutions. The samples were agitated at 30 °C for 300 min at a constant agitation speed of 150 rpm. The experiments were carried out by adding a fixed amount of (MAW) (0.5 g) into 250 ml Erlenmeyer flasks containing 200 ml of different initial concentrations (50–300 mg/L) of dye solution at temperature 30˚C. Agitation was provided at 150 rpm for 300 min. The initial and equilibrium dye concentrations were determined by absorbance measurement using double beam UV–Vis spectrophotometer (Spectronic Helios Alpha, Thermo Electron Corporation, UK) at 668 nm. It was then computed to dye concentration using standard calibration curve.

The amount of sorption at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{M} \tag{1}$$

Where C_t (mg/L) is the liquid-phase concentration of dye at any time, the amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{M} \tag{2}$$

The percentage of dye removal can be calculated as follows:

$$\%C = \frac{(C_o - C_e)}{C_o} \times 100 \tag{3}$$

Where C_o and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively, V (L) is the volume of the solution and M (g) is the mass of dry sorbent used.

3. Results and discussion

3.1 Effect of initial dye concentration and contact time

To study the effect of the initial concentration of MB on the rate of dye adsorption onto MAW, the experiments were carried out at a fixed adsorbent dose (0.5 g) and at different initial dye concentrations of methylene blue (50, 100, 200 and 300 mg/L) for different time intervals (15, 30, 45, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280 and 300 min) at 30 ˚C as shown in Fig.1.

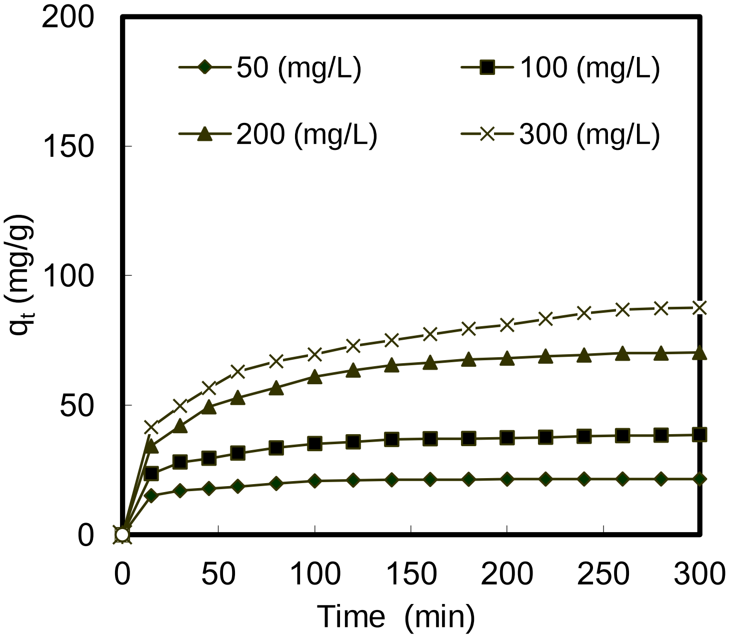


Fig.1. Effect of initial dye concentration and contact time on the uptake of MB onto MAW (C_o =50-300 mg/L, MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5).

It was obvious from Fig.1 that the amount of MB adsorbed increase with the increase in the initial MB concentration. For MB dye adsorption onto MAW at 30˚C it was observed that the amount of MB adsorbed increased from 21.49 mg/g to 87.55 mg/g with increasing dye concentration from 50 mg/L to 300 mg/L. The initial MB concentration provides an important driving force to overcome all mass transfer resistance. Hence a higher initial concentration of dye will enhance the adsorption process.

Fig.2 shows that the percentage removal of MB adsorbed decreased from 98.029 to 71.196 % as the initial concentration was increased from 50 to 300 mg/L. This due to the saturation of the adsorption sites at higher MB concentrations (Özer et al., 2007).

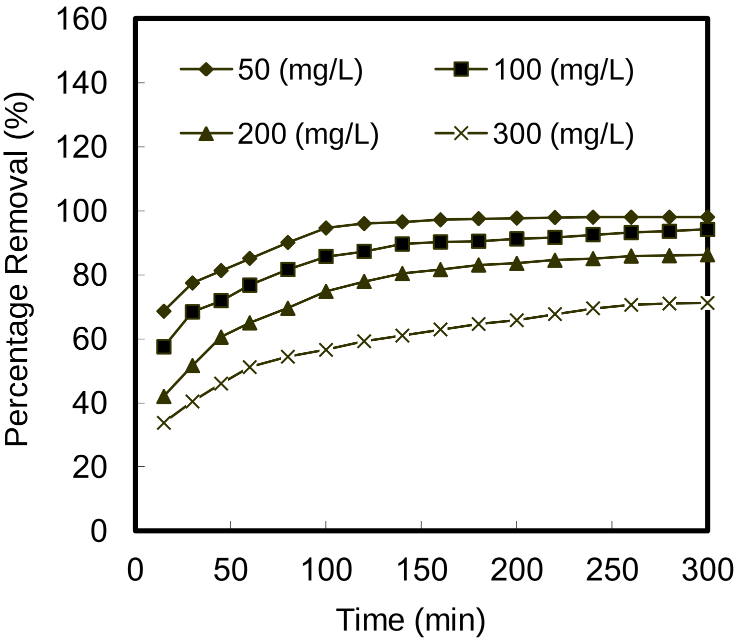


Fig.2. Effect of initial dye concentration and contact time on percentage removal of equilibrium for MB adsorption onto MAW (C_o =50-300 mg/L, MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5).

The equilibrium conditions were reached within 260 min for low concentrations (50-100 mg/L) while the rate of adsorption was slower (280 min) for concentrations ranging from 200 to 300 mg/L. In the initial stages the adsorption process was rapid and gradually decreased with the progress of adsorption and finally attained saturation when adsorption reached equilibrium.

3.2 Effect of solution pH on dye adsorption

The pH factor is very important at adsorption process especially for dye adsorption. The pH of medium will control the magnitude of electrostatic charges which imparted by ionized dye molecules. As a result the rate of adsorption will vary with pH of aqueous medium (Önal et al., 2006).

The effect of pH on the removal of MB by MAW is shown in Fig.3 and it was observed that the adsorption was clearly depending on pH factor where the percentage removal of MB was 29% at pH 2 and increased to 93% with pH up to 8, then decrease at pH higher than 8. The lower adsorption of MB at low pH is because the adsorbent surface may get positively charged due to the presence of H^+ ions excess as a result competing with the cation groups on the dye for adsorption sites, while at higher solution pH, the adsorbent surface may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction.

At pH higher than 8, the dye percentage removal decreased and this may be due to hydrolysis of adsorbents surfaces, which create positively charged sites (Hamdaoui, 2006).

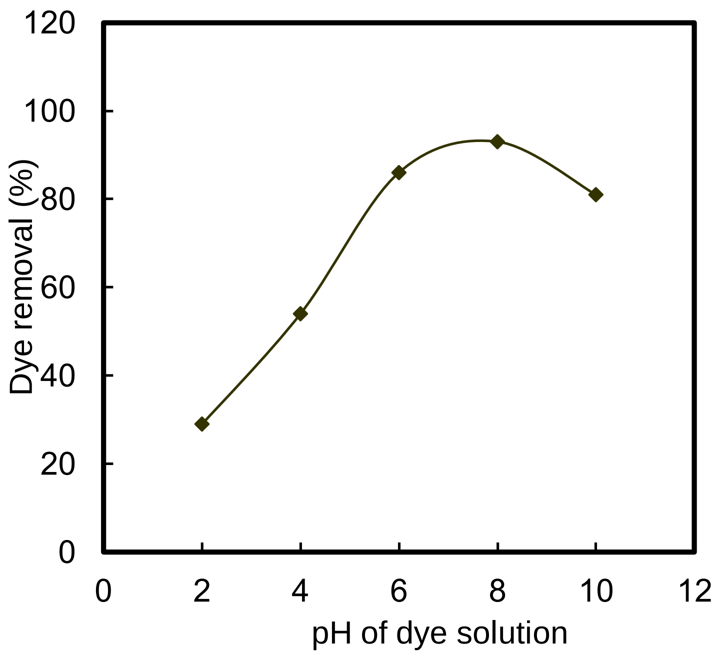


Fig.3. Effect of pH solution on percentage removal of equilibrium for MB adsorption onto MAW (C_o =100 mg/L, MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150).

3.3 Adsorption isotherms

The adsorption isotherm is representing the relationship between the mass of adsorbate adsorbed per unit weight of adsorbent and the liquid-phase equilibrium concentration of adsorbate (Hamdaoui & Naffrechoux, 2007). The isotherm results were analyzed using three forms of Langmuir, Freundlich and Temkin isotherm. The Langmuir isotherm model (Langmuir, 1918) assumes that the adsorption occur at homogeneous sites at adsorbent surface, and saturation happen when the dye molecule fill the site where no more adsorption can occur at that site. Langmuir isotherm can represent by the following equation:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{4}$$

q_e	Amount of adsorbate adsorbed at equilibrium (mg/g)
q_{max}	Maximum monolayer adsorption capacity of the adsorbent (mg/g)
C_e	Equilibrium concentration of adsorbate (mg/L)
K_L	Langmuir adsorption constant related to the free energy adsorption (L/m)

Since the estimation of the adsorption isotherms parameters interference by the method of linearization (Hamdaoui, 2006), therefore three forms of Langmuir isotherm equations used to determine the constants K_L and q_{max}. Equation 4 can be linearized in to these three forms of Langmuir isotherm equations (Hamdaoui & Naffrechoux, 2007):

Form (1)
$$\frac{Ce}{q_e} = \frac{1}{q_{\max} K_L} + \frac{Ce}{q_{\max}} \tag{5}$$

Form (2)
$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{K_L q_{\max} Ce} \tag{6}$$

Form (3)
$$q_e = -\frac{q_e}{K_L Ce} + q_{\max} \tag{7}$$

The constants values can be evaluated from the intercept and the slop of the linear plot of experimental data of (C_e/q_e) versus C_e or ($1/q_e$) versus ($1/C_e$) or q_e versus (q_e / C_e).

Langmuir equation (form1) is the most popular form for analyzing adsorption equilibrium data. Lata et al., (2007); Kannan & Sundaram (2001); Gupta et al., (2003); Amin, (2008) applied Langmuir equation (form1) in order to analyze the adsorption equilibrium data in their studies, while Ahmad et al., (2007) and Mittal et al., (2008) used Langmuir equation (form 2) in order to analyze the adsorption equilibrium data in their studies.

The essential feature of the Langmuir isotherm can be expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter R_L is calculated using the following equation (Hall et al., 1966):

$$R_L = \frac{1}{1 + K_L C_o} \tag{8}$$

K_L Langmuir adsorption constant related to the free energy adsorption (L/mg)
C_o The highest initial adsorbate concentration (mg/L)

The value of separation factor R_L indicates the adsorption process as given:

- Unfavorable ($R_L > 1$)
- Linear ($R_L = 1$)
- Favorable ($0 < R_L < 1$)
- Irreversible ($R_L = 0$)

The Freundlich isotherm can be used for adsorption that involves heterogeneous surface energy systems (Malik, 2004). The Freundlich model (Freundlich, 1906) equation is expressed as:

$$q_e = K_F C_e^{\ 1/n} \tag{9}$$

Where K_F and n are Freundlich constants, K_F (mg/g (L/mg)$^{1/n}$) is the adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. If the value of exponent n was greater than 1 (n >1) then the adsorption represent favorable adsorption condition (Namasivayam et al., 1994).

The constants K_F and n can be determined from the linear form of Freundlich isotherm equation from the graph of ln q_e against ln C_e as expressed from the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{10}$$

In general, as the K_F value increases the adsorption capacity of adsorbent will also increase (Malik, 2004).

The heat of adsorption and the adsorbate-adsorbent interaction on adsorption isotherms were studied by Temkin and Pyzhev, who assumed that because of the adsorbate-adsorbent interactions, the energy of the molecules adsorption will decrease linearly with coverage (Sekar et al., 2004). The Temkin isotherm (Temkin, 1940) has been generally applied in the following form:

$$q_e = (\frac{RT}{b_t}) \ln(A_t C_e) \tag{11}$$

and can be linearized as:

$$q_e = \mathrm{B} \ln \mathrm{A_t} + \mathrm{B} \ln C_e \tag{12}$$

Where B = RT/b_t. B is the Temkin constant related to heat of sorption (J/mol); A_t is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (K). Therefore, by plotting q_e versus ln C_e enables one to determine the constants A_t and B.

The isotherm plots of Langmuir (form 1), Langmuir (form 2), Langmuir (form 3), Freundlich and Temkin models presented in Figures. 4, 5, 6, 7 and 8, respectively and the parameters for all isotherms are listed in Table 2.

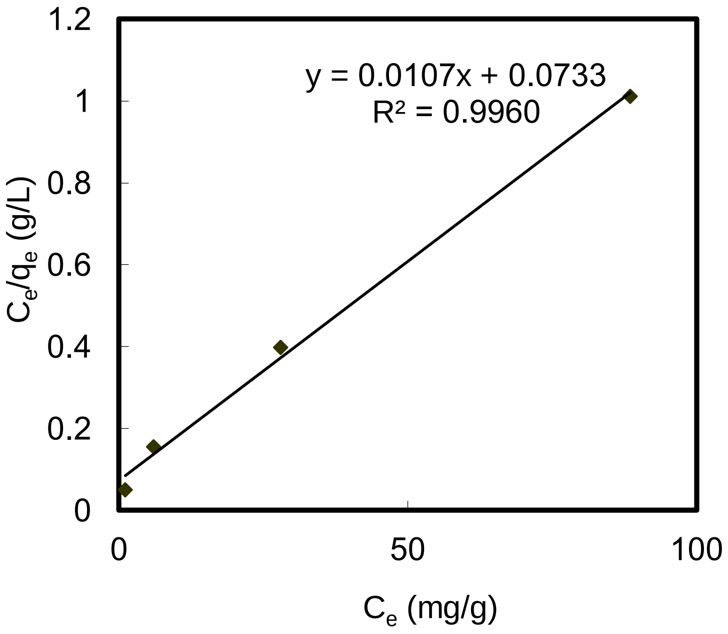


Fig.4. Langmuir isotherm (form 1) for the sorption of MB onto MAW (MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5).

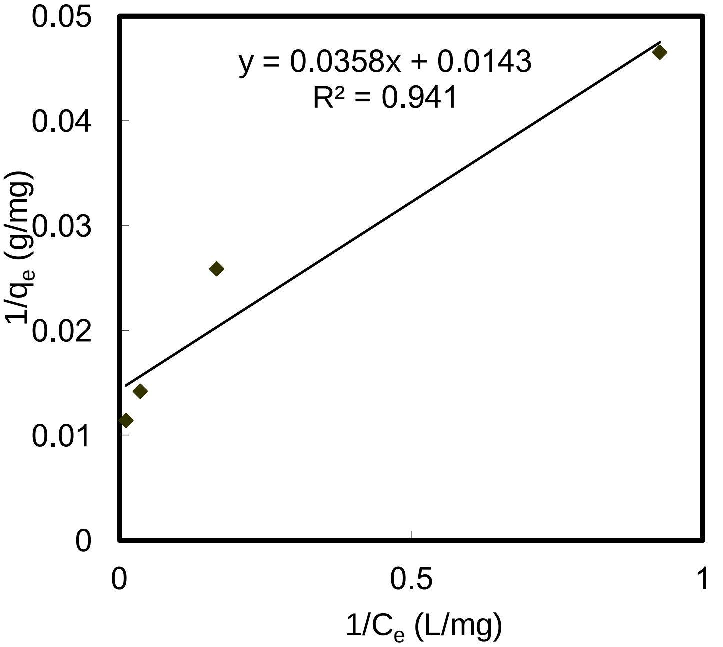


Fig.5. Langmuir isotherm (form 2) for the sorption of MB onto MAW (MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5).

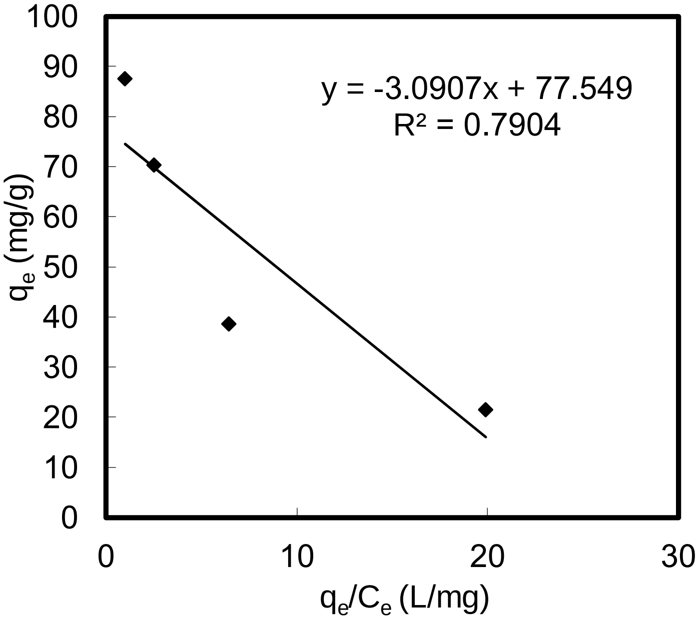


Fig.6. Langmuir isotherm (form 3) for the sorption of MB onto MAW (MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5).

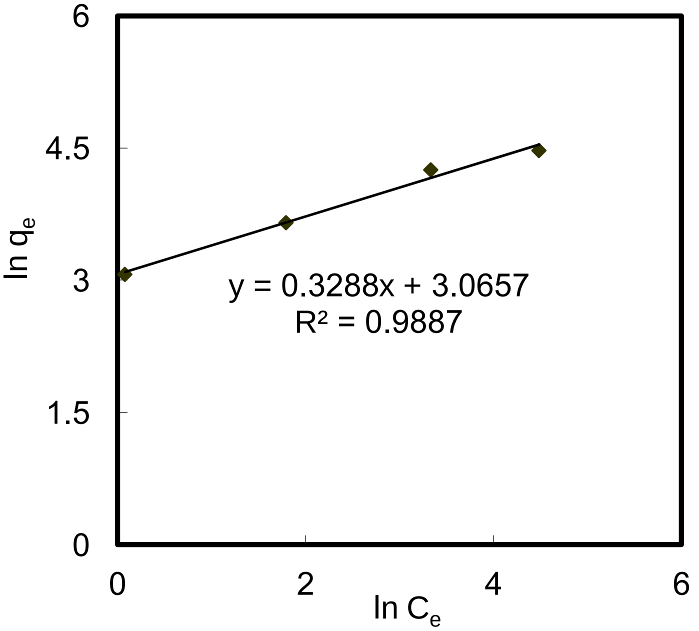


Fig.7. Freundlich isotherm for the sorption of MB onto MAW (MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5).

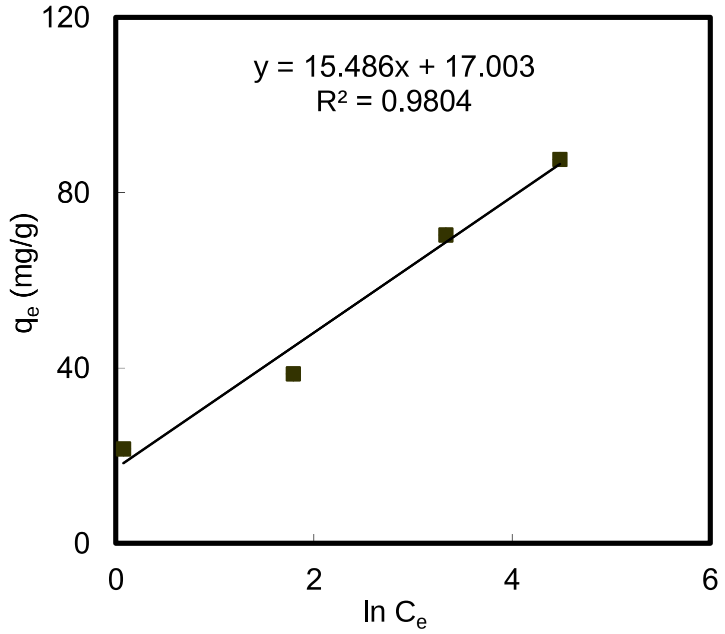


Fig.8. Temkin isotherm for the sorption of MB onto MAW (MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5).

Table 2: Langmuir (3 forms), Freundlich and Temkin models constants and correlation coefficients for sorption of MB onto MAW at 30˚C

Isotherm	Constants	Values
Langmuir form-1-	Q_o (mg/g) K_L (L/mg) R^2 R_L	93.458 0.146 0.996 0.022
Langmuir form-2-	Q_o (mg/g) K_L (L/mg) R^2 R_L	71.429 0.400 0.941 0.008
Langmuir form-3-	Q_o (mg/g) K_L (L/mg) R^2 R_L	77.540 0.324 0.790 0.010
Fruendlich	K_F n R^2	21.434 3.049 0.988
Temkin	A_t (L/g) B R^2	2.999 15.480 0.980

The values of the correlation coefficient (R^2) indicate that the experimental data were more suitable to the Langmuir isotherm (form 1) than other models and this indicating the homogeneous nature of MAW. Table 2 shows that the values of R_L were in the range of 0-1, which confirms the favorable uptake of the MB dye. Freundlich model shows that the value of n was greater than 1 which represents a favorable adsorption condition. A comparison of the maximum monolayer adsorption of MB dye onto other different adsorbents is shown in Table 3.

Table 3: Comparison of the maximum monolayer adsorption of MB dye onto other different adsorbents

Adsorbent	Dye	Temp. °C	q_{max}. (mg/g)	References
MAW	MB	30	93.458	Present study
Pomelo (Citrus grandis) peel	MB	30	344.830	Hameed et al., (2008)
Peanut hull treated with sulphuric acid	MB	30	123.500	Özer et al., (2007)
Walnut sawdust	MB	20	59.170	Ferrero, (2007)
Oak sawdust	MB	20	29.940	Ferrero, (2007)
Gulmohar (Delonix regia) plant leaf powder	MB	30	186.220	Ponnusami et al., (2009)
Rice bran	MB	20	54.993	Wang et al., (2008)
Yellow passion fruit waste	MB	25	44.700	Pavan et al., (2008)
Wheat shells	MB	30	16.560	Bulut & Aydın, (2006)
Brazil nut shells	MB	30	7.810	de Oliveira Brito et al., (2010)
Posidonia oceanic (L.) fibres	MB	30± 2	5.560	Ncibi et al., (2007)
Glass wool	MB	35	2.244	Chakrabarti & Dutta, (2005)
Glass wool	MB	35	2.244	Chakrabarti & Dutta, (2005)

Based on Table 3, it could be seen that the adsorption capacity obtained for the adsorption of MB onto MAW is good compare with other reported values.

3.4 Adsorption kinetics

In order to analyze the sorption kinetics of MB onto MAW, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied to the experimental data. The linear form of pseudo-first-order model was described by Lagergren (Lagergren, 1898) as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{13}$$

Where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the pseudo-first-order rate constant (min^{-1}).

Integrating Eq.13 for the initial and end conditions t = 0 to t = t and q_t = 0 to q_t = q_t, and after some rearrangement, a linear plot is obtained:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{14}$$

Values of k_1 and q_e were obtained from the slope and intercept respectively of plots of log (q_e − q_t) versus t (Fig.9).

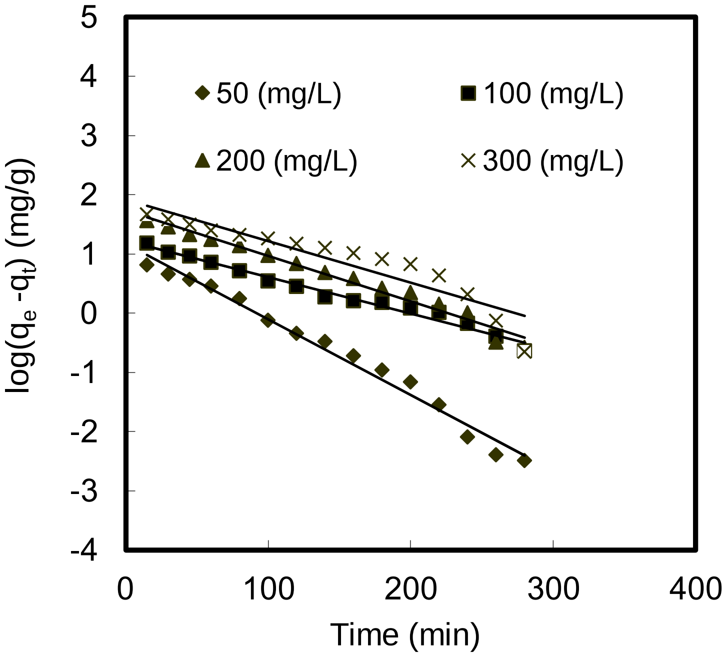


Fig.9. Pseudo-first-order kinetics for sorption of MB onto MAW (MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5). The pseudo-second-order model can express as (Ho & McKay, 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{2}} + \frac{1}{q_e}t \tag{15}$$

Where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mg/g), respectively, and k_2 (g/mg min) is the rate constant of second-order adsorption. Values of k_2 and q_e can be determined experimentally from the slope and intercept of plot t/q_t versus t (Fig.10).

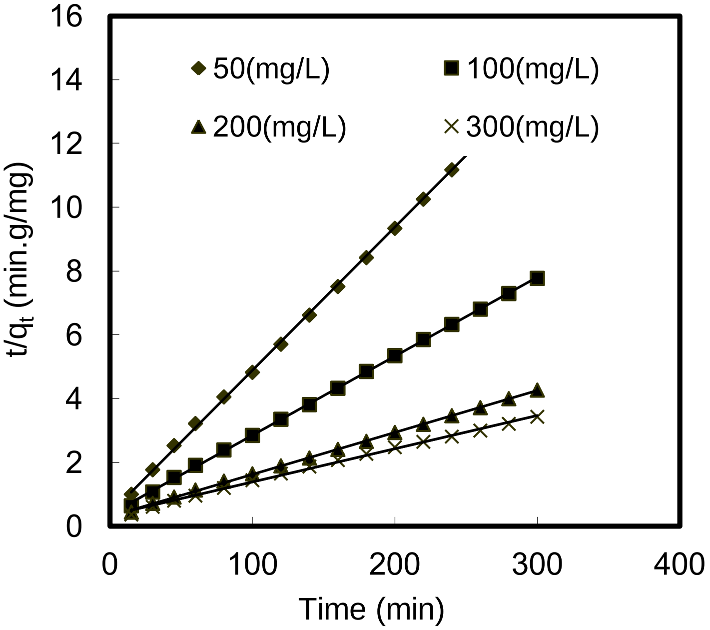


Fig.10. Pseudo-second-order kinetics for sorption of MB onto MAW (MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5).

Table 4: Comparison of the pseudo-first-order, pseudo-second-order for different initial MB concentrations at 30 °C

Initial dye concentration mg/L	$q_{e\ exp.}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		$q_{e\ cal.}$ (mg/g)	k_1 (1/min)	R^2	$q_{e\ cal.}$ (mg/g)	k_2 (min g/mg)	R^2
50	21.490	14.962	0.028	0.98	22.727	0.0008	0.999
100	38.620	16.520	0.014	0.98	41.667	0.0002	0.999
200	70.324	53.333	0.016	0.97	76.923	0.0001	0.999
300	87.550	83.176	0.028	0.86	100.00	0.0001	0.996

According to Table.4, the calculated q_e values did not agree with experimental q_e values thus the pseudo-first-order model did not fit well. The correlation coefficients R^2 for the linear plots of pseudo-second-order model arranged between 0.996-0.999 which higher than correlation coefficients R^2 for pseudo-first-order.

This indicates that the adsorption kinetic is better represented by the pseudo-second-order model. Similar phenomenon was observed for the adsorption of MB onto bamboo-based activated carbon (Liu et al., 2010) and the adsorption of MB onto hazelnut shells and wood sawdust (Ferrero, 2007).

The intraparticle diffusion model was proposed to identify the adsorption mechanism and to predict the rate controlling step, where intraparticle equation can be expressed as (Kannan & Sundaram, 2001):

$$q_t = k_{diff.} t^{1/2} + C \tag{16}$$

Where C is the intercept and $k_{diff.}$ (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant which can be evaluated from intercept and slope of the plot of q_t versus $t^{1/2}$. The large intercept can reflect the great of boundary layer effect. If the plot of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the rate-controlling step. Fig.11 shows that the linear plot of all concentrations did not pass through the origin which indicates that the intraparticle diffusion was not only the rate controlling step. The values of C and k_{diff} are given in Table.5. The values of intercept C increased with an increase in initial dye concentration (50 to 300 mg/L) which indicate increasing of boundary layer effect.

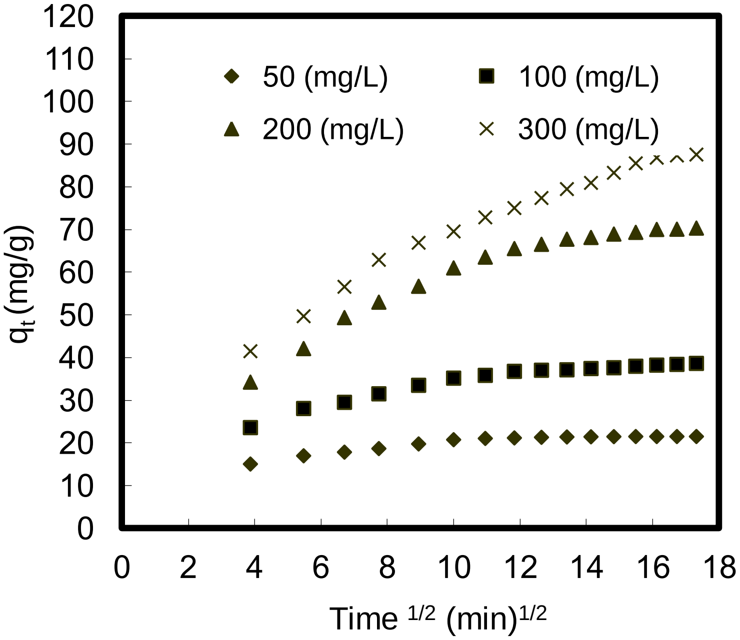


Fig.11. Plot of intraparticle diffusion model for adsorption of MB onto MAW (MAW dosage= 0.5 g, temperature= 30 °C, t= 300 min, rpm =150, pH= 7.5).

Table 5 Intraparticle diffusion model parameters for the adsorption of MB dye adsorption onto MAW

Initial dye concentration mg/L	C	$k_{diff.}$ (mg/g min$^{1/2}$)	R^2
50	15.171	0.429	0.811
100	23.220	0.991	0.883
200	31.871	2.503	0.898
300	34.220	3.304	0.968

3.5 Design of batch adsorber from isotherm data

To predict the adsorber size and performance, a common empirical design procedure based on sorption equilibrium conditions can be used (Prasad & Srivastava, 2009).

Fig.12 shows a schematic diagram for the batch sorption process where the effluent contains V (L) of solution and the initial MB concentration C_o reduced to C_1 in the adsorption process. In the treatment stage, a mass of fresh adsorbent M (g) is added to solution and the solute loading changes from q_o to q_1.

At t=0, q_o=0 and the mass balance for the dye in the single stage can be written as:

$$V(C_o - C_1) = M(q_o - q_1) = Mq_1 \tag{17}$$

Under equilibrium conditions,

$$C_1 \rightarrow C_e \text{ and } q_1 \rightarrow q_e \tag{18}$$

Since the sorption isotherm studies confirm that the equilibrium data for MB onto adsorbent fitted well to Langmuir isotherm (form 1), a Langmuir isotherm equation can be used for q_1 in the equation of batch adsorber design. Equation (18) can be rearranged as (Kumar & Porkodi, 2007):

$$\frac{M}{V} = \frac{C_o - C_1}{q_1} = \frac{C_o - C_1}{q_e} = \frac{C_o - C_e}{q_{\max} K_L C_e /(1 + K_L C_o)} \tag{19}$$

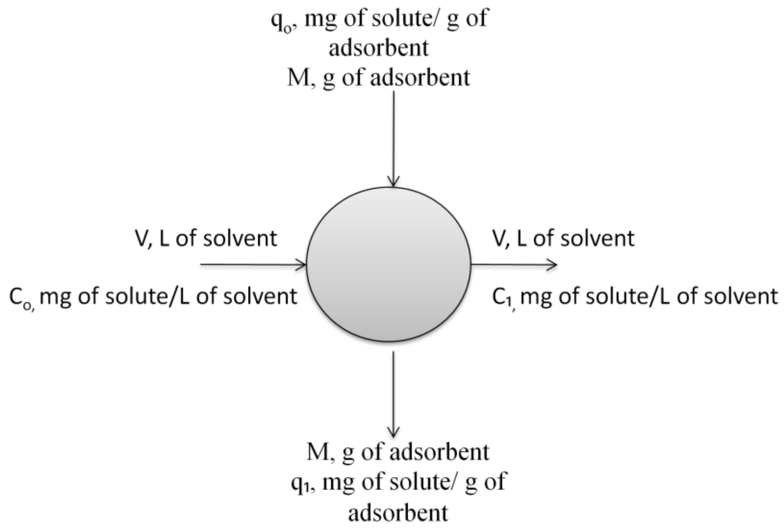


Fig.12. Single-stage- batch-adsorber design

Fig.13 shows a series of plots derived from Equation (19). At initial MB dye concentration of 50 mg/L, Fig.13 shows the required amount of MAW to remove of dye content 60- 90% at different solution volumes.

At initial dye concentration 50 mg/L, the amount of MAW required to remove 90% of MB solution was 2.375, 4.749, 7.124, 9.499, 11.874, 14.248, 16.623 and 18.998 g at MB solution volumes of 2, 4, 6, 8, 10, 12, 14 and 16 L, respectively.

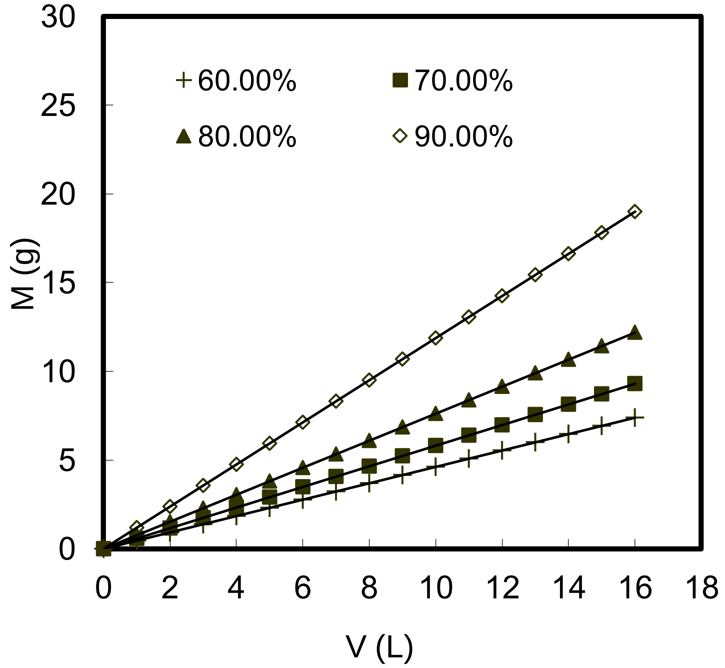


Fig.13. Mass (M) of MAW against volume of solution treated (V) for different percentage of dye removal at 50 mg/L of initial MB concentration.

4 Conclusions

This study shows that the MAW is effective adsorbent for methylene blue dye (MB) removal from aqueous solutions. The adsorption was found to be dependent on the pH solution, initial dye concentration and contact time. The maximum removal was obtained at pH 8. The amount of MB dye adsorbed increased with the increase in the initial concentration of dye, while the percentage of MB dye removal decreased with the increase in the initial concentration of dye. The equilibrium adsorption data was best represented by the Langmuir isotherm (form 1), indicating monolayer adsorption on a homogenous surface and the adsorption capacity was found to be 93.458 mg/g. Adsorption kinetic was described well by pseudo-second-order, while the intraparticle diffusion was not the only rate controlling step of adsorption process. From the design of a single-batch adsorber it was predicted that at MB dye concentration 50 mg/L, the amount of MAW required to remove 90% of MB solution was 18.998 g at solution volume 16 L.

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