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Kinetic and Isotherm Studies of Methylene Blue Removal from Aqueous Solution by Adsorption on Activated Charcoal prepared from Wood apple fruit shell, an agricultural waste

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ABSTRACT

The aim of this study is to use Activated charcoal prepared from wood apple shell (Limonia acidissima L.) by chemical and microwave activation method as an adsorbent for the removal of methylene blue (MB) dye. The kinetics and equilibrium adsorption of methylene blue dye on this adsorbent were then examined at 299.4K. The adsorption isotherm of the methylene blue on the adsorbent was determined and correlated with common Langmuir and Freundlich adsorption isotherm equations. The Langmuir isotherm exhibited a better fit for the adsorption data than the Freundlich isotherm with maximum monolayer adsorption capacity of 48.31 mg g^{-1}*. The kinetics of methylene blue adsorption on the treated adsorbent has also been studied by fitting the data in various kinetic models. It was observed that the removal of methylene blue over the activated adsorbent undergoes the pseudo-second order kinetic. The kinetic parameters of this best-fit model were calculated and discussed.*

Key words: adsorbent; dye; Equilibrium; Microwave; wood apple shell.

INTRODUCTION

Dyes and pigments are widely used in the textiles, paper, plastics, leather, food and cosmetic industry to color products. One of the major problems concerning these dyes and pigments industries is colored effluent. These colored effluent wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organisms [1]. Organic dyes are an integral part of many industrial effluents and demand an appropriate method to dispose them off. Most commercial dyes are chemically stable and are difficult to be removed from wastewater [2]. The release of colored wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man through the food chain. Methylene blue (MB) dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturition, and methemoglobinemia [3, 4]. Therefore the treatment of effluent containing such dye is of interest due to its esthetic impacts on receiving waters. Adsorption processes using activated carbons are widely used to remove pollutants from wastewaters. However, commercially available activated carbon is expensive. In the last decade, special emphasis on the preparation of activated carbons from several agricultural by-products has been given due to the growing interest in low cost activated carbons from renewable, copious, especially for application concerning treatment of wastewater. Researchers have studied the production of activated carbon from palm-tree cobs [4], plum kernels [5], cassava peel [6], bagasse [7], wood apple shell [8, 9], jute fiber [10], rice husks [11], olive stones [12], date pits [13], fruit stones and nutshells [14]. The advantage of using agricultural by-products as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to manufacture. Plant biomass is a natural renewable resource that can be converted into useful materials and energy [15]. The adsorption process can be either physical or chemical in nature, and frequently involves both. Physical adsorption involves the attraction by electrical charge differences between adsorbent and the adsorbate. Chemical adsorption is the product of a reaction between the adsorbent and the adsorbate.

In the present work, the activated charcoal was prepared by chemical and microwave activation method from wood apple shell (*Limonia acidissima* L.). Study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid–solution interface. The common Langmuir and Freundlich adsorption isotherm and kinetics of methylene blue adsorption on the prepared activated were analyzed. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (r^2, values close or equal to 1). A relatively high r^2 value indicates that the model successfully describes the isotherms and kinetics of adsorption.

MATERIAL AND METHODS

2.1. Preparation of adsorbent

The activated carbon was prepared from the wood apple shell. The shells were cut into smaller pieces and soaked in concentrated H_2SO_4 (98%) at 1:1 ratio (weight of raw material/volume of acid) for 24 h and activated in commercial microwave oven at power level 450 watt for 5 minutes and at power level 300 watt for 5 minute, cooled at room temperature. The activated carbon was repeatedly washed with distilled water until the pH of the wash water became the pH of the distilled water (nearly 7). The carbon obtained was dried at 373 ± 1K for nearly 2 hours to remove the moisture and stored in desiccators. The prepared charcoal was called as WASAC.

2.2. Preparation of adsorbate solutions

Stock solution of methylene blue (MB) was prepared (1000 mg L^{-1}) by dissolving the desired quantity A. R. Grade MB in distilled water. The test solutions were prepared by diluting the stock solution to the desired concentrations.

2.3. Adsorption experiments

In batch pH studies, 0.2 g WASAC and 50 mL MB solutions (100 mg L^{-1}) with a range of pH values from 1.0 to 10.0 were transferred in a conical flask, and shaken on a thermo-stated magnetic stirrer for 120 min (the time required for equilibrium to be reached). The pH of the solutions was adjusted with 0.1 M HCl or 0.1 M NaOH solution by using a pH-meter. Removal efficiency of MB (P) was determined as:

$$\%\ \text{MB removal(P)} = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

Where C_o (mg L^{-1}) and C_e (mg L^{-1}) are initial and equilibrium concentrations of MB in the liquid-phase respectively.

In the determination of equilibrium adsorption isotherm, 0.2 g WASAC and 50 mL of different concentrations (100–350 mgL^{-1}) of MB solutions were stirred for 120 min at the initial pH 7 and at temperature 299.4 K. The amount of MB adsorbed at equilibrium, q_e (mg g^{-1}), was calculated by:

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

Where V (L) is the volume of MB solution, M (g) is the mass of wood apple shell activated charcoal used.

In the adsorption kinetic experiments, batch adsorptions were conducted by shaking each 0.2 g WASAC with 50 mL 100 mg/L of MB solution at the initial pH 7 and the temperature 299.4K for different contact times (20–120 min). The amount of adsorption at time t (min), q_t (mg g^{-1}), was calculated by:

$$q_t = \frac{C_o - C_t}{M} \times V \qquad (3)$$

Where C_t (mg L^{-1}) is the liquid-phase concentrations of MB at time t. All the mixtures after adsorption operation were centrifuged and the MB concentration in the supernatant was estimated by spectrophotometrically, monitoring the absorbance at 660 nm on UV–Visible spectrophotometer (Systronic). To ensure the reproducibility, reliability and accuracy of the collected data, all the batch experiments were carried out in triplicate and the mean values of three data sets are presented. The equilibrium data fitted to the isotherm models used in this study were solved by using the linear regression method.

2.4. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Infrared spectra of wood apple shell activated charcoal were obtained after drying the charcoal at 373K for 24 h. The finely powdered samples were encapsulated with potassium bromide to prepare translucent sample disks, and the spectra were recorded using a Fourier transform infrared spectroscope (SHIMADZU 8400S).

RESULT AND DISCUSSION

3.1. FTIR analysis

FTIR spectroscopy provides qualitative information of characteristic functional groups on the surface. The adsorptive capacity of the activated carbon is also influenced by its surface chemical structure. The FT-IR spectrums of the prepared WASAC were measured within the range of 4000–500 cm^{-1} and are shown in Figure 1. The absorption at 3431.48 cm^{-1} was attributed to (O-H) vibrations in hydroxyl groups or surface-bonded water [16]. The adsorption peaks in the region 1763–1427 cm^{-1} can be assigned to –C=O stretches of aldehydes, ketones, and carboxylates and –C=C- stretches [17]. The bands appearing at 1130.32 and 1043 cm^{-1} are assigned to the –C–O, –C–C, and –C–OH stretching vibrations and the adsorption peaks in the region 750–900 cm^{-1} can be attributed to aromatic –CH stretching vibrations [18].

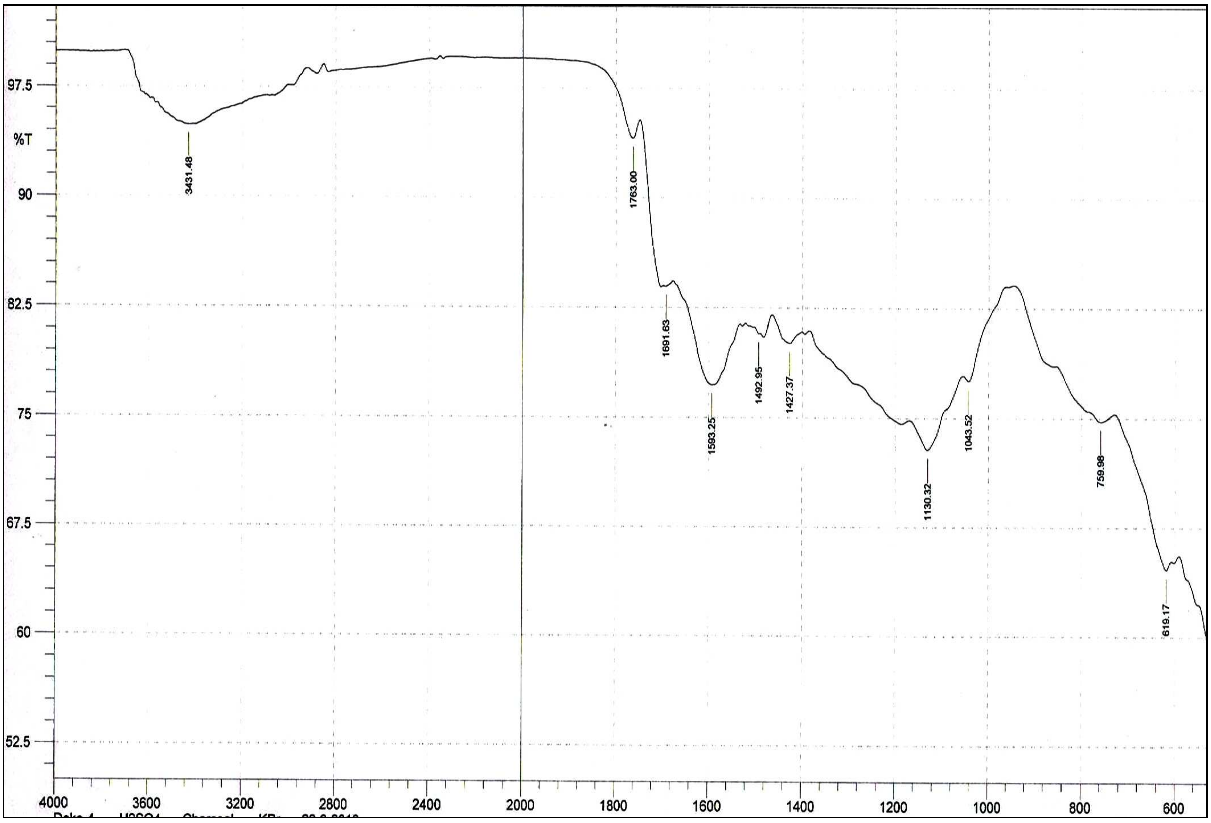

Fig. 1 FTIR spectrum of wood apple shell activated charcoal.

3.2. Effect of system pH on MB Uptake

The pH of the system exerts profound influence on the adsorptive uptake of adsorbate molecules on the surface properties of the adsorbent and ionization or dissociation of the adsorbate molecule. (Fig. 2) shows the variations in the removal of dye from wastewater at different pH.

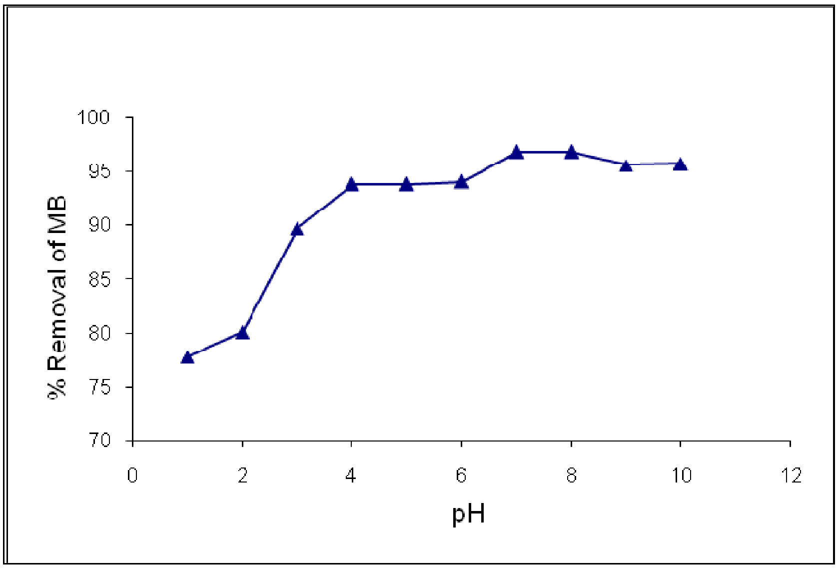

Fig. 2 Effect of pH on the adsorption of MB by WASAC

From the figure, it is evident that the maximum removal of MB color is observed at pH 7.0 to 8.0. Similar trend of pH effect was observed for the adsorption of MB on activated carbon prepared from *Annona Squmosa* Seed [19] *ricinus communis* [20], methyl red on activated carbon prepared from *cucumis sativa* [21] and malachite green on activated carbon prepared from *ricinus communis* [22].

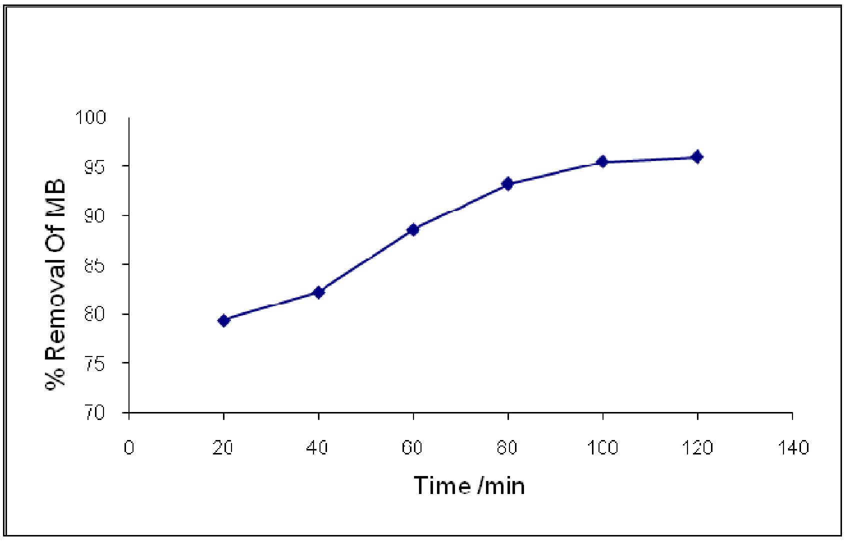

Fig. 3 Effect of contact time on the adsorption of MB by WASAC

Which may be attributed to the hydrophobic nature of the developed carbon which led to absorb hydrogen ions (H^+) onto the surface of the carbon when immersed in water and made it positively charged. Low pH value (1.0 to 3.0) leads to an increase in H^+ ion concentration in the system and the surface of the activated carbon acquires positive charge by absorbing H^+ ions. On the other hand, increase of the pH value greater than 7 led to increase of the number of negatively charged sites. As the activated charcoal surface is negatively charged at high pH, a significantly strong electrostatic attraction appears between the negatively charged carbon surface and cationic dye molecule leading to maximum adsorption of dyes [23] from waste water. The lowest adsorption occurred at pH 1.0 and the highest adsorption occurred at pH 7.0 to 8.0.

3.3. Effect of contact time on adsorption

The adsorption efficiency increases with time, at 120 min the adsorption becomes practically constant (fig 3) and it was the maximum adsorption. There fore the equilibrium contact time for the adsorption process was 120 min.

3.4. Effect of Initial dye concentration

The adsorption capacity of MB dye on WASAC was determined at different initial dye concentrations of MB. Dye removal is highly concentration dependent. The increase in loading capacity of the adsorbent with relation to dye ions is probably due to a high driving force for mass transfer. In fact, the more concentrated the solution, the better the adsorption.

3.5. Equilibrium isotherms

Langmuir isotherm model assumes the uniform energies of adsorption onto the surface. It is a model based on the physical hypothesis that there are no interactions between adsorbed molecules and the adsorption energy over the entire coverage surface. On the other hand in the Langmuir model assumed that intermolecular forces decrease rapidly with distance and this lead to the prediction that coverage of the WASAC is of monolayer type [24].

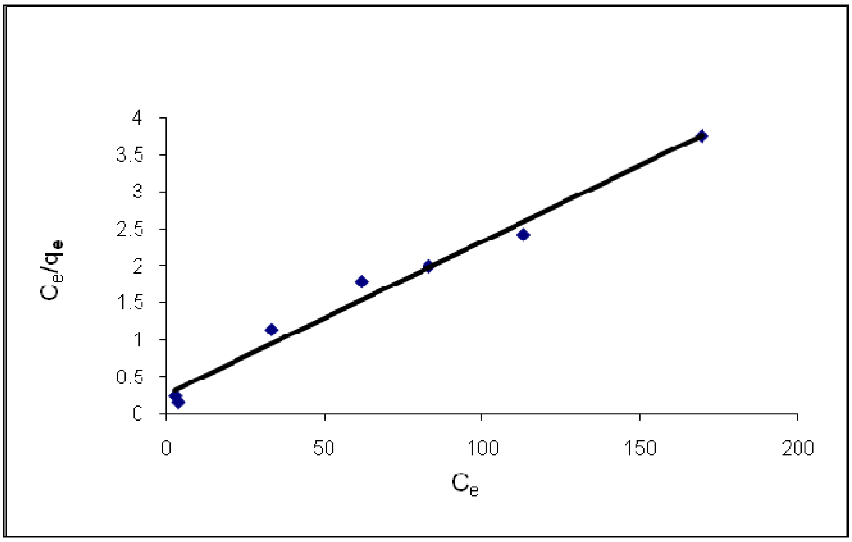

Fig. 4 Langmuir isotherm of adsorption of MB by WASAC at 299.4K

The linear form of Langmuir isotherm equation is given in Eq. 4.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (4)$$

Where q_m (mg g^{-1}) is the maximum adsorption capacity and K_L is the Langmuir constant which is related to the heat of adsorption. Adsorption isotherms were obtained at pH 7. The pH of MB solution was estimated using pH-meter. The constants q_m and K_L are determined plotting the C_e/q_e verses C_e (fig 4) is tabulated in Table 1. The value of q_m was determined from the Langmuir plot (fig 4) at the concentration range 100-350 mg L^{-1} as 48.31 mg g^{-1}. The correlation coefficient of Langmuir isotherm, r^2 is 0.983.

Freundlich isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption [25] and can be represented by Eq. 5

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

Where Ce is the equilibrium concentration of the adsorbate (mg L^{-1}), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), K_F is the adsorption capacity of the adsorbent and n is Freundlich constants giving an indication of how favorable the adsorption process. The slope of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [26].

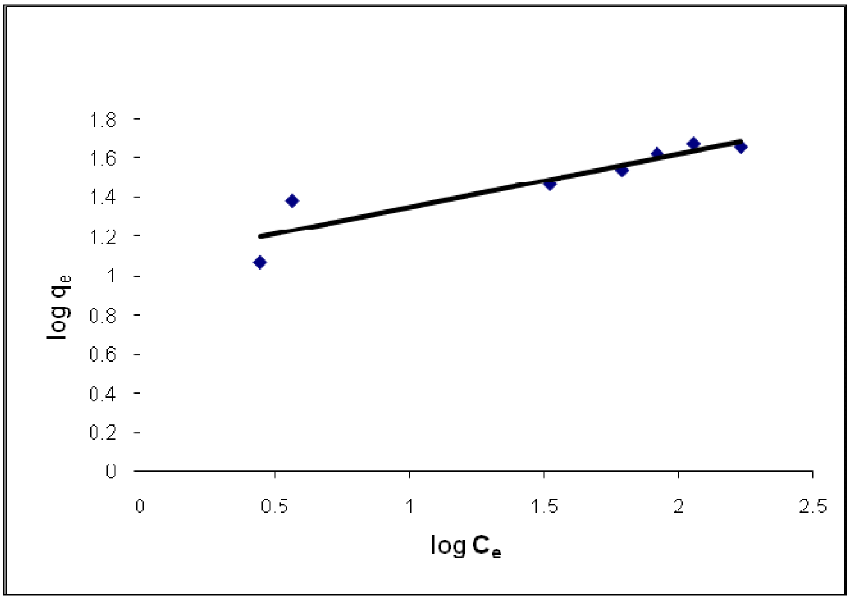

Fig. 5 Freundlich isotherm of adsorption of MB by WASAC at 299.4K

The Freundlich constants were derived from the slopes and intercepts of log C_e versus log q_e (fig 5) and are shown in Table 1.

Table 1 Isotherm parameters for MB adsorption at 299.4K.

Langmuir			**Freundlich**		
q_m (mg g^{-1})	K_L (L mg^{-1})	r^2	K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$)	1/n	r^2
48.31	12.55	0.9824	1.82	3.712	0.8409

3.6. Adsorption kinetics

In order to investigate the adsorption kinetics, the Lagergren pseudo-first order [27], pseudo-second order [28], the Elovich [29] and the Intra-particulate kinetic models [30] were applied. The linearised expression for the Lagergren first order model is:

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1}{2.303} x\ t \qquad (6)$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption amount at equilibrium and time t (min) respectively. K_1 (min^{-1}) is the rate constant in the pseudo-first order adsorption process. The constants were determined experimentally by plotting log (q_e –q_t) versus t (fig 6). The fig. 6 was not fitted by linear regression indicative adsorption was not followed Pseudo-first order.

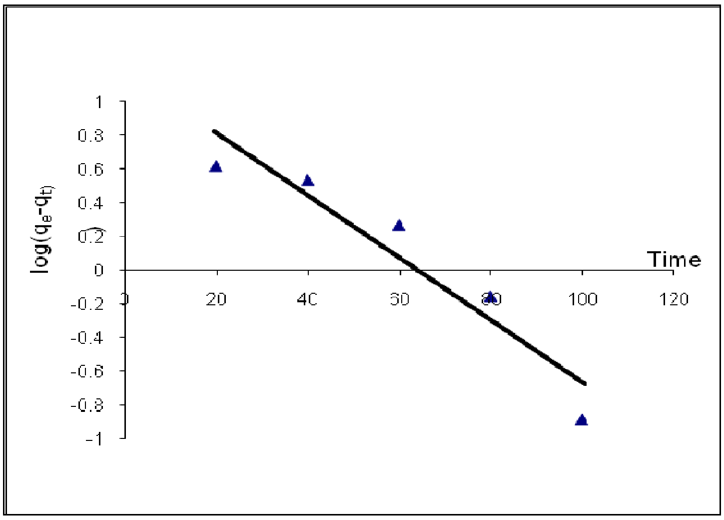

Fig.6 Adsorption kinetics: Pseudo-first order model at 299.4K for MB concentration of 100 mg/L

The linear equation of pseudo-second order model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} x\ t \qquad (7)$$

Where k_2 (g mg^{-1} min^{-1}) is the rate constant of adsorption. By plotting a curve of t/q_t against t, q_e and k_2 can be evaluated. The initial adsorption rate, h_o (mg g^{-1} min^{-1}) is related as [30]:

$$h_0 = k_2 q_e^2 \qquad (8)$$

The values of q_e, k_2, h_o and r^2 are listed in Table 2. The dependence of t/q_t versus t gives an excellent straight line relation (Fig. 7), and the R^2 values are close to 1(Table 2), confirming the applicability of the pseudo-second order equation. The applicability of this model suggested that adsorption of MB on WASAC was based on chemisorptions between MB and active sites of the adsorbent. The FTIR spectra of WASAC also supported this argument.

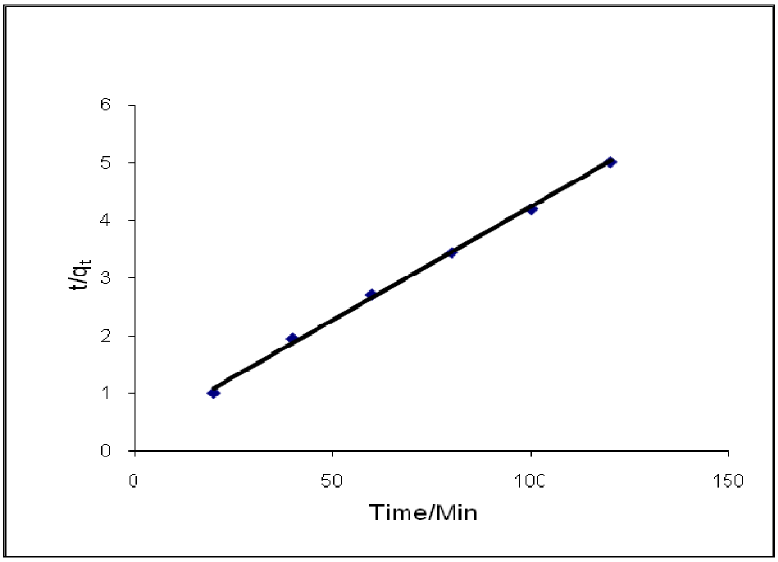

Fig.7 Adsorption kinetics: Pseudo-second order model at 299.4K for MB concentration of 100 mg/L.

The nature of the rate-limiting step in a batch system can also be assessed from the properties of the solute and adsorbent. Weber and Morris [30] stated that if intra-particle diffusion is the rate-controlling factor, uptake of the adsorbate varies with the square root of time. The linear form of intra-particle diffusion model is expressed by Eq. 8:

$$q_t = k_d t^{1/2} + C \qquad (8)$$

Where k_d (mg g^{-1} $min^{-1/2}$) is the intra-particle diffusion rate constant, and C (mg g^{-1}) a constant that gives idea about the thickness of the boundary layer. According to this model, if the plot of q_t versus $t^{1/2}$ gives a straight line, then the adsorption process is controlled by intra-particle diffusion, while, if the data exhibits multi-linear plots, then two or more steps influence the adsorption process. In the present study, the plots presents linearity (Fig. 8), indicating adsorption is totally controlled by intra-particle diffusion.

Values of intercept give an idea about the thickness of boundary layer, i.e., the larger the intercept the greater is the boundary layer effect [31]. The values of, k_d, C and r^2 are listed in Table 2.

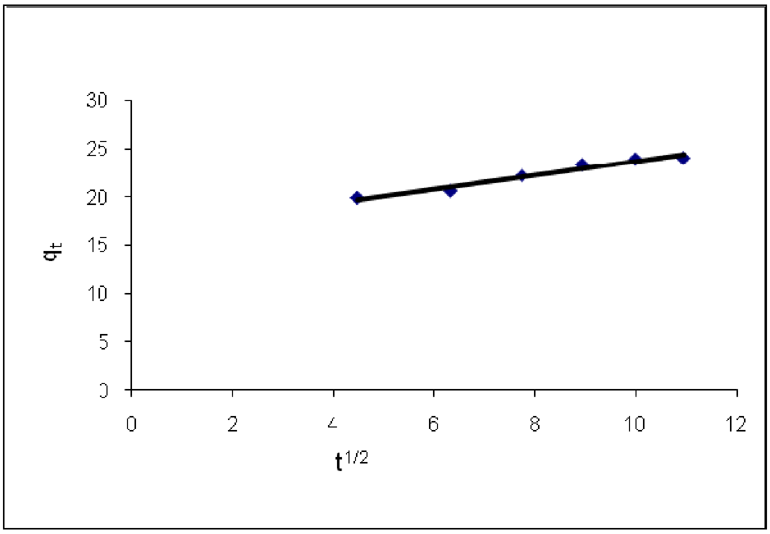

Fig. 8 Adsorption mechanism: intra-particle diffusion model at 299.4K.

Table 2 Kinetic parameters for MB adsorption onto wood apple shell activated charcoal at 299.4K

Pseudo-second order				Intra-particle diffusion		
$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h_o (mg g^{-1} min^{-1})	r^2	k_d (mg g^{-1} $min^{-1/2}$)	C (mg g^{-1})	r^2
25.51	0.00504	3.282	0.9985	0.715	16.51	0.963
Elovich equation model						
α (mg g^{-1} min^{-1})	β (g mg^{-1})	r^2				
426.24	0.4176	0.9351				

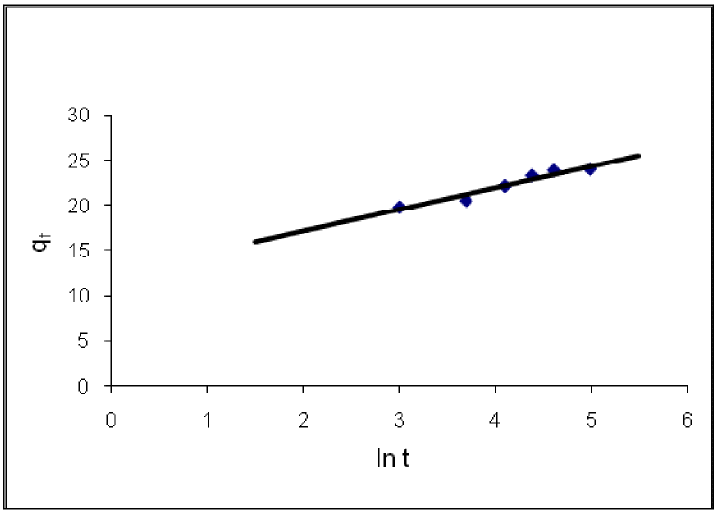

Fig. 9 Adsorption mechanism: Elovich kinetic model at 299.4K.

The Elovich equation based on equilibrium adsorption is generally expressed as:

$$q_t = (\tfrac{1}{\beta}) \ln(\alpha\beta) + (\tfrac{1}{\beta}) \ln t \qquad (9)$$

Where α is the initial adsorption rate (mg g^{-1} min^{-1}), β is the desorption constant (g·mg^{-1}) during any experiment. The adsorption fits the Elovich model; a plot of q_t vs. ln t yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln (αβ) which confirms chemisorptions mechanism. The Elovich model plot for the adsorption of the MB by activated carbon produced from wood apple shell is shown in Fig 9. The values of, α, β and r^2 are listed in Table 2.

CONCLUSION

This study investigated the removal of MB by WASAC from aqueous solution. The microwave activation method for preparation of activated charcoal was efficient and economical. The removal efficiency of MB increased with increasing adsorbent dosage. The equilibrium time was about 120 minutes, depended on the adsorbent dosage. The removal efficiency was maximum across pH range of 7.0 to 8.0 and independent on pH at MB concentration of 100 mg L^{-1} and adsorbent dosage 4.0 g L^{-1}. FTIR studies revealed that the –C=O, –C=C-,–C–O, –C–C, and –C–OH functional groups on activated charcoal were involved in binding with MB. Adsorption dynamics analysis indicates that pseudo-second order equation fitted very well to the adsorption of MB on WASAC. Adsorption system is controlled via intra-particle diffusion mechanism. The Elovich kinetic model confirms chemisorptions mechanism. The adsorption process fits the Langmuir isotherm model better than Freundlich isotherm. The Langmuir maximum monolayer adsorption capacities of MB on WASAC were found to be 48.31 mg g^{-1} at 299.4K. These results suggest that chemical and microwave oven activated charcoal prepared from wood apple shell is a potential adsorbent for the dye removal from industrial wastewater.

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