Chapter-7

Adsorption of methylene blue onto Microwave oven H$_2$SO$_4$ activated carbon

7.1 Introduction

To color products in textiles, paper, plastics, leather, food and cosmetic industries the dyes and pigments are widely used. The major concerning problem of these dyes and pigments industries is colored effluent. The colored effluent wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organisms [1]. Most of the commercial dyes are chemically stable and they are difficult to remove from wastewater [2]. The colored wastewater released from industries may consists of an eco-toxic hazard and bring up the potential danger of bioaccumulation, which ultimately affect man through the food chain. Therefore there is need of suitable method to dispose them off. Methylene blue is a heterocyclic aromatic cationic compound, may causes eye burns, on severe dose responsible for permanent injury to the eyes of human and animals. On consumption, it can give rise to difficult breathing, while swallow through the mouth produces a burning sensation. Further, methylene blue dye may cause vomiting, nausea, excessive sweating, mental confusion and disorder characterized by methemoglobin [3, 4]. Therefore, due to its esthetic impacts on receiving waters the treatment of effluent containing dyes is of necessity. The most widely used techniques to remove pollutants from wastewater using activated carbons are adsorption processes. In adsorption techniques the activated carbon is used as adsorbent. Since, the commercially available activated carbon is expensive, special emphasis on the preparation of activated carbon from several agricultural by-products has been given. Researchers have studied the preparation of activated carbon from various low-cost biomasses such as 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 main advantages for preparation of activated carbon using agricultural by-products as the raw materials are renewable and potentially less expensive. Waste biomass of plants is a natural renewable resource and 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 result of a reaction between the adsorbent and the adsorbate.

In the present work, the activated carbon was prepared by chemical activation using H$_2$SO$_4$ along with microwave activation method from wood apple shell (Limonia acidissima L.). The common Langmuir and Freundlich adsorption isotherms and kinetics of methylene blue adsorption on the prepared activated carbon were analyzed. Adsorption kinetic study describes the adsorbate uptake rate and apparently this rate controls the equilibrium time of adsorbate uptake at the solid-solution interface. The conformation of model between experimental data and the predicted values was expressed by the correlation coefficients ($R^2$, values close to or equal to 1). A relatively higher value of correlation coefficients indicates that the model successfully describes the isotherms and kinetics of MB adsorption.

7.2 Experimental

7.2.1 Preparation of adsorbent and its characterization

The activated carbon was prepared from the wood apple shell. The shells were cut into smaller pieces and soaked in concentrated H$_2$SO$_4$ (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 thus obtained was dried at 373 ± 1K for nearly 2 hours to remove the moisture and stored in desiccators. The prepared charcoal was called as SAMAC.

The prepared sulphuric acid microwave activated carbon (SAMAC) was characterized by SEM, XRD and FTIR analysis method. X-ray diffraction pattern of SAMAC was recorded by using a diffractometer (Bruker, AXS D-8 Advance) equipped with a rotating target X-ray tube and a wide-angle goniometer [12]. The source X-ray was K$_\alpha$ radiation from a copper target with graphite monochromater. The X-ray tube was operated at a potential of 50 kV and a current of 150 mA. The range (2θ) of scans was from 10° to 90° at a speed of 2° per minute at increments of 0.1°. The Surface morphology of SAMAC was examined by Scanning Electron Microscope (SEM; Jeol JST-6360A). Samples were dispersed onto carbon tabs (double-adhesive carbon coated tape) adhered to aluminum stubs. These sample stubs were coated with a thin layer (30 Å) of gold by employing Jeol JFC-1600 auto fine coater.
were subsequently examined by SEM and photographed under various magnifications with direct data capture of the images onto a computer [11]. Infrared spectra of wood apple shell activated charcoal were obtained after drying the charcoal at 100°C for 24 h. The finely powdered samples were encapsulated with potassium bromide to prepare translucent sample disks, and the spectra was recorded using a Fourier transform infrared spectroscope (SHIMADZU 8400S).

7.2.2 Preparation of adsorbate solutions

Stock solution of methylene blue (MB) was prepared (1000 mg L⁻¹) by dissolving the 1 g of A. R. Grade MB in 1 liter distilled water. The test solutions were prepared by diluting the stock solution to the desired concentrations. The chemical structure of MB is shown in Fig. 7.1

![Fig. 7.1 Chemical structure of methylene blue](image)

7.2.3 Adsorption experiments

In batch pH studies, 0.2 g SAMAC 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 thermostated 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 was determined as:

\[
\% \text{ MB removal} = \left(1 - \frac{C_e}{C_o}\right) \times 100
\]  

(7.1)

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 SAMAC and 50 mL of different concentrations (100–350 mg L⁻¹) of MB solutions were stirred for 120 min at the
initial pH 7 and at temperature 299.4±1 K. The amount of MB adsorbed at equilibrium, $q_e$ (mg g$^{-1}$), was calculated by:

$$q_e = \frac{C_0 - C_e}{M} \times V \tag{7.2}$$

Where $V$ (L) is the volume of MB solution, $M$ (g) is the mass of SAMAC used.

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

$$q_t = \frac{C_0 - C_t}{M} \times V \tag{7.3}$$

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 solution was estimated from calibration curve obtained spectrophotometrically, monitoring the absorbance at 660 nm on UV–Visible spectrophotometer (Systronic) [16]. A calibration curve of absorbance versus concentration was constructed at maximum wavelength of 660 nm (Fig.7.2). To ensure the accuracy, reproducibility and reliability of the data collected, all the batch experiments were carried out in triplicate and the mean values of three data sets are reported. The equilibrium data fitted to the isotherm models used in this study were solved by using the linear regression method.

![Calibration curve](Fig. 7.2) Calibration curve for evaluation of MB at 660 nm
7.3. Result and Discussions

7.3.1 Scanning Electron Microscope (SEM) analysis

Analysis of surface characteristics with SEM photographs showed that the adsorbent is not uniformly porous (Fig. 7.3). The carbon surface showed relatively smooth regions as well as cracked and pitted morphology. The presence of small pores on the surface showed that carbon was starting to develop an elementary pore network. Thus the impregnation of sulphuric acid on powdered wood apple shell was effective for the developing the wide range of pores with different sizes and shapes and hence leading to large surface area activated carbon [12, 17]. The similar trends were reported by other authors in their research works related to the characterizations of prepared activated carbon from apricot stones [18], jute and coconut fiber [19] and bamboo waste [20], pomegranate seeds [21].

![SEM image of SAMAC](image)

**Fig.7.3** SEM image of SAMAC

7.3.2 X-ray diffraction analysis

X-Ray diffraction analysis has been used to analyze crystalline and amorphous nature of the prepared activated carbon. For analyzing SAMAC, the powder X-ray diffraction study was conducted. The powder X-Ray diffraction pattern of SAMAC is shown in Fig.7.4.
The appearance of a broad peak centered at the 2θ angle of 13° in the X-ray diffraction analysis of activated carbon indicated the presence of silica and was essentially amorphous in nature. Further, X-ray diffraction analysis of activated carbon shows the graphitic basal planes at a 2θ angle of 43° [22]. The similar trends were reported in the literature of the activated carbon prepared from other biomasses [23], such as synthesis of coir pith carbon [24], petroleum cokes [25], and graphitization process of activated carbon [26].

Figure 7.4 X-ray diffraction analysis of SAMAC

7.3.3 FT-IR 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 7.5. The absorption at 3431.48 cm\(^{-1}\) was attributed to (O-H) vibrations in hydroxyl groups or surface-bonded water [27]. 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 [28]. 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 –P–O, –S–O, and aromatic –CH stretching vibrations [29].
7.3.4 Effect of pH

Fig. 7.5 FTIR spectrum of SAMAC

Fig. 7.6 Effect of pH on the adsorption of MB by SAMAC
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. 7.6) and it shows the variations in the removal of dye from wastewater at different pH. From the figure 7.6, 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 Squamosa Seed [30] ricinus communis [31]. It may be attributed to the hydrophobic nature of the developed carbon which led to adsorb 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 adsorbing 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 from waste water [32]. The lowest adsorption occurred at pH 1.0 and the highest adsorption is occurred at pH 7.0 to 8.0.

**7.3.5 Effect of contact time on adsorption**

It was found that initially adsorption was fast and rapid followed by slower adsorption contributed significantly to equilibrium uptake (Fig. 7.7).

![Fig. 7.7 Effect of contact time on the adsorption of MB by SAMAC](image)

At the beginning adsorption rate was fast due to the larger driving force between MB and SAMAC due to instantaneous external surface adsorption. Then the driving force between
MB and SAMAC becomes smaller and the adsorption rate is also slowed. So the adsorption of MB onto SAMAC may be controlled by external mass transfer followed by intra particle diffusion mass transfer [33a]. The adsorption efficiency increases with increase in contact time between MB and SAMAC, at 120 min the adsorption becomes practically constant (Fig. 7.7).

7.3.6 Effect of initial dye concentration

The adsorption capacity of MB dye on SAMAC was determined at different initial dye concentrations of MB (50 to 350 mg L\(^{-1}\)). Dye removal is highly concentration dependent. The increase in adsorbent loading capacity with relation to dye ions is probably due to a high driving force for mass transfer [33b]. In fact, the more concentrated the solution, the better the adsorption. The plot of % MB removal versus MB concentration is depicted in Fig. 7.8, indicating a considerable influence of initial MB concentration on its removal. Increase in MB concentration increases the value of MB uptake but decreases the removal percentage from 95% to 50% with increase in concentration of MB 50 to 350 mg L\(^{-1}\). Therefore, the increase of initial MB concentration resulted in a reduction of its adsorption percentage due to limited adsorption sites. The reduction of removal percentage of MB with the increase of its initial concentration since the mass of SAMAC was constant for all concentrations, the MB molecules must compete for sites onto which they can adsorb. In fact, when the MB concentration is higher, the ratio of MB to SAMAC is greater, and therefore the percentage of MB removed is lower [33b].

![Fig. 7.8 Effect of Concentration of MB on the adsorption onto SAMAC](image)

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7.3.7 Effect of adsorbent dose

The effect of adsorbent dose for the uptake of Methylene blue by activated carbon was found to increase by increasing the adsorbent dose [34a]. It is due to the increase of the activated site available for adsorption. The effect of adsorbent dose on MB adsorption was tested in a range of 0.75 – 4 g/L at pH 7. The results are shown in Fig. 7.9 in terms of % MB removal as a function of adsorbent doses. The degree of removal reached a maximum from 63% to 95% after 120 min when in contact with adsorbent dose of 0.75 to 4 g/L. The enhancement of MB removal as a function of adsorbent dose was due to the presence of a greater surface for adsorption and thus more available sites for MB molecules to be adsorbed [34b]. Similar trends were reported previously for adsorption of MB onto papaya seeds [35] and jackfruit peels [34b].

![Fig. 7.9 Effect of adsorbent dose on MB adsorption](image)

7.3.8 Adsorption isotherms

Equilibrium relationship between the concentration of MB in the aqueous solution and the concentration of adsorbed MB at a constant temperature is represented by an adsorption isotherm. In the present study, the adsorption equilibrium data of MB on activated carbon prepared from wood apple shell by H₂SO₄ activation were analyzed in terms of linear form of Langmuir and Freundlich isotherm models. The linear graphs of Langmuir and Freundlich isotherms were plotted as $C_e/q_e$ against $C_e$ and $\log q_e$ against $\log C_e$, respectively at constant temperature 299.4±1K (Fig. 7.10a and 7.10b). The isotherm parameters were evaluated from
the slope and intercept of respective linear plots for each isotherm along with linear regression coefficient and are listed in Table 7.1. The adsorption isotherms based on parameter values are compared; relatively higher $R^2$ value of the Langmuir isotherm model indicates that the adsorption of MB onto SAMAC follows the Langmuir isotherm model better than Freundlich isotherm. The value of monolayer adsorption capacity 48.31 mg g$^{-1}$ was determined from the Langmuir isotherm. This finding supports the assumption that the MB is adsorbed as a homogeneous monolayer onto SAMAC particles sites and has a same energy change for all adsorption sites [36]. The $R_L$ values at initial concentrations of 50 to 350 mg/L MB were calculated and are in the range of 0.206 to 0.035, which is indicative of the favorable uptake process of MB adsorption. Lower $R_L$ values at higher concentration showed that the adsorption was more favorable at higher concentrations. The value of 1/n (0.269) lie between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The calculated value of $K_F$ from the Freundlich models 12.02 reveals that the prepared activated carbon has high affinity toward MB.

![Figure 7.10a](image1.png) **Figure 7.10a** Langmuir isotherm of MB adsorption onto activated carbon at 299.4±1K

![Figure 7.10b](image2.png) **Figure 7.10b** Freundlich isotherm of MB adsorption onto activated carbon at 299.4±1K
Table 7.1 Isotherm parameters for MB adsorption at 299.4±1K

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<th>Freundlich</th>
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<td>$q_m$ (mg g$^{-1}$)</td>
<td>$K_L$ (L mg$^{-1}$)</td>
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7.3.9 Adsorption kinetics

The present study employed three different models to investigate the kinetics of the adsorption: pseudo-first-order, pseudo-second-order, and Elovich kinetic models and were considered to interpret the experimental data. A good correlation of the kinetic data explains the adsorption mechanism of the metal ions on the SAMAC.

The pseudo-first order model was the first equation employed to the kinetics data of present system and from the plot of log ($q_e - q_t$) versus $t$, the constants, $k_1$ (min$^{-1}$) and $q_e$ (mg g$^{-1}$) were determined from the slope and intercept of linear portion (Fig. 7.11a) of MB dye and are listed in Table 7.2. The experimental data, $q_e$, exp differ from theoretical values ($q_e$, cal), suggests that the adsorption of MB on activated carbon does not follow the pseudo-first order adsorption kinetics.

The Pseudo-second order plot of $t/q_t$ versus $t$, gives the values of $q_e$, and $k_2$ from intercept and slope, respectively. The initial rate of adsorption, $h_0$ were obtained from the values of $q_e$, and $k_2$ ($h_0 = 1/ k_2 q_c^2$). The plot of $t/q_t$ versus $t$ gives an excellent straight line relation for adsorption of MB on SAMAC (Figure 7.11b). The kinetic parameters for adsorption of MB by SAMAC are given in Table 7.2. Based on the obtained correlation coefficients ($R^2 > 0.998$), the pseudo second-order model equation was the best fit for the experimental kinetic data of MB. The calculated $q_e$, cal values from the pseudo-second order kinetic model exhibit excellent agreement with the experimental $q_e$ values. Thus, the adsorption process was pseudo-second order, suggesting chemical adsorption as the rate-limiting step of the adsorption mechanism. Similar kinetic trends have been reported previously for adsorption of MB onto other low-cost adsorbents such as papaya seeds [35], modified wheat straw [37], and rejected tea [38].
Elovich equation was initially applied to evaluate the kinetics of chemisorption of gases onto heterogeneous solids [39]. Recently, the Elovich equation has been applied to describe the kinetics of chemisorption of heavy metals and dyes from liquid phase onto the solid adsorbent [40-43]. The MB dye adsorption on SAMAC fits the Elovich model, since the plot of $q_t$ versus $\ln (t)$ yields linear relationship (Fig. 7.12a) with regression coefficient $R^2=0.935$. It further, confirms that the adsorption of MB onto SAMAC was due to chemisorptions mechanism [44, 45]. The Elovich constants ($\alpha$ and $\beta$), were evaluated from the intercept and slope from the linear plots, respectively and are listed in Table 7.2. The relatively higher magnitude of Elovich initial rate of adsorption, $\alpha$ indicates that chemisorptions was faster for MB and the smaller fractional values of desorption constant, $\beta$ suggests that the adsorbed MB can easily be desorbed from the SAMAC surface.

To realize the exact diffusion mechanism, the adsorption kinetic data were further analyzed by a Weber and Morris intra-particle diffusion model [46]. 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 and if the data exhibits multi-linear plots, then two or more steps controls the adsorption process [47]. The intra-particle diffusion parameters such as rate constant, $K_d$ and thickness of boundary layer $I$, were also evaluated from the plot of $q_t$ versus $t^{1/2}$ (Fig. 7.12b) and are listed in Table 7.2. In the present study, the plots presents linearity not passing through origin, indicating adsorption was not totally controlled by intra-particle diffusion. This indicates that intra-particle diffusion mechanism was involved in the adsorption of MB onto SAMAC and the deviation of straight lines from the origin indicates that the intra-particle diffusion is not the sole rate-controlling mechanism [48, 49].
Fig. 7.11a Pseudo-first order plot of MB onto SAMAC at 299.4±1K

Fig. 7.11b Pseudo-second order plot of MB onto SAMAC at 299.4±1K

Fig. 7.12a Elovich plot of MB onto SAMAC at 299.4±1K

Fig. 7.12b Intra-particle diffusion plot of MB onto SAMAC at 299.4±1K
Table 7.2 Kinetic parameters for MB adsorption onto SAMAC at 299.4±1K

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<td>( k_1 ) (min(^{-1}))</td>
<td>( R^2 )</td>
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<td>0.715</td>
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7.4 Conclusions

This study investigated the removal of methylene blue (MB) by sulphuric acid microwave activated carbon (SAMAC) from aqueous solution. The microwave activation method for preparation of activated charcoal was efficient and economical. The removal efficiency of MB is 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 SAMAC. Adsorption system is not totally controlled by 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 SAMAC were found to be 48.31 mg g\(^{-1}\) at 299.4±1K. These results suggest that microwave oven activated charcoal prepared from wood apple shell is a potential adsorbent for the dye removal from industrial wastewater.
References: