

Kinetic and Equilibrium Adsorption Studies of Methylene Blue from Aqueous Solution Using Low-Cost Adsorbent

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Abstract--- *This study investigates the potential use of activated carbon prepared from copper pod flowers for the removal of methylene blue dye from simulated wastewater. The parameter studied included contact time, initial dye concentration, carbon dosage, temperature, and pH. The characterization of the adsorbent was carried out using Fourier transform infrared spectroscopy, scanning electron microscope, and X-ray diffraction data. The kinetic data were modeled using pseudo-first-order model, pseudo-second-order kinetic model, and intraparticle diffusion. The adsorption followed second-order rate equation. The adsorption equilibriums were analyzed with Langmuir and Freundlich isotherms. The experimental data were better interpreted by Freundlich isotherm model Langmuir isotherm model. Adsorption capacity values obtained from the Activated carbon developed from the copper pod flowers can be used as an alternative to highly efficient and low-cost abundant materials for methylene blue dye removal from wastewater.*

Keywords--- *Adsorption, Percentage Dye Removal, Kinetics, Isotherm, Copper Pod.*

I. INTRODUCTION

Dye wastewater discharged into environmental water bodies deteriorates the water quality and light penetration, and may cause a significant impact on human health (Vadivelan and kumar, 2005). In addition, most of the dyes or their metabolites are toxic, carcinogenic, mutagenic, or teratogenic [Jan et al.2008](Jayaranajn et al.2011).Several chemical, biological, and physical methods have been used for dye wastewater treatment (Guo et al.2003). Conventional methods used to treat colored effluents are coagulation, flocculation, ultra-filtration, membrane technology, electrochemical techniques, reverse osmosis, biological process, chemical reaction, photo-oxidation, and precipitation (Wang et al.2005) . Most of these methods are expensive due to their high capital and operational costs (Sarioghu and Atay, 2006). Therefore, there is a need to search for a new and economical process that could remove dyes that are commonly used in the industry. Among various methods, adsorption occupies a prominent place in dye removal (Namasivayam et al.2001). Adsorption techniques are widely used to remove certain classes of pollutants from waters; especially those that are not easily biodegradable. There are many advantages of adsorption process, such as requirement of less land area, lower sensitivity to diurnal variation, resistance to toxic chemicals, greater flexibility in the design and operation, and superior removal of organic contaminants. Adsorption process is

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an effective and low-cost physical and chemical method for removing dyes from wastewater (Tehrani – Bagha et al.2011). In the past years, several investigations reported the removal of dyes using activated carbons developed from industrial or agricultural wastes (Salleh et al.2011). Activated carbon is the most widely used adsorbent in the industries due to its capability to adsorbing many types of dyes with high adsorption capacity. Generally, a low-cost adsorbent can be defined as the one that requires little processing and is abundant in nature. Agricultural by-products and industrial waste can be seen as having a great potential to be developed as a low-cost adsorbent. Natural adsorbents play an important role in removing dyes from wastewater; such adsorbents include activated corn husk carbon (Khodaie et al.2013), jute fiber (Senthilkumar et al.2005), wheat shells (Bulut and Audin, 2006),rice husk(Malik, 2003), bamboo dust(Kannan and Sundaram,2011), sugarcane(Ho et al.2005), fly ash (Janos et al.2003), bottom ash(Dincer at al.2007), clay(Ozdemir et al.2004), peanut hull(Gong et al.2005), lemon peel(Kumar,2007),peat of Brunei Darussalam III(Chieng et al.2013), *Artocarpuscamansi* Blanco core (Lim et al.2016), and Cempedak durian(Dahri et al.2015).

The objective of this study was to investigate the ability of copper pod flower for the removal of methylene blue from aqueous solution. Literature survey revealed that numerous biological materials have been used as adsorbents. However, no study has reported the adsorption of methylene blue dye by activated carbon prepared from copper pod. The effects of various operating parameters such as initial pH, dye concentration, and adsorption temperature on the adsorption were investigated in controlled batch experiments.

II. MATERIALS AND METHODS

2.1 Preparation of adsorbents

The copper pod flowers were collected locally and were thoroughly washed twice by ordinary tap water and distilled water to remove dust and other impurities. The washed materials were dried in sunlight to evaporate the moisture present in them. The dried materials were kept in a muffle furnace. The carbonized material was ground and sieved to 125- μm particle size. The sieved adsorbent sample prepared was kept in a plastic container for use in adsorption studies.

2.2 Preparation of adsorbate

A stock solution of 1000mg/L methylene blue was prepared by dissolving 1 g methylene blue dye in 1L distilled water. Other concentrations (10, 20, 30, 40, and 50 mg/L) were obtained from this stock solution by serial dilution. All working solutions used in tests were prepared by diluting the stock solution with distilled water to get the appropriate concentration. The methylene blue dye concentration in supernatant solution was determined using UV/visible spectrometer at a λ_{max} value of 663nm. All chemicals used in this study were of analytical reagent grade.

2.3 Adsorption experiment

Adsorption experiments were performed following the batch technique to obtain rate and equilibrium data. The adsorption parameters such as contact time, initial dye concentration, pH, and temperature were studied. The experiments were carried out in 150ml conical flasks by mixing a preweighed amount of adsorbent with 50ml of methylene blue dye solution. The adsorbent dosages on dye removal were checked from 0.1 to 1g for better

adsorption. The isotherm study was carried out at different temperatures ranging from 30 to 60°C with the initial dye concentrations of 10–50mg/L. The kinetic study was conducted by varying time from 0 to 100min. The isotherm study was carried out with different initial dye concentrations of 10–50mg/L. The kinetics of adsorption was measured by varying time intervals ranging from 0 to 100 min. The effect of pH in the range from 2 to 12 was analyzed on the adsorption of methylene blue dye. The pH of the solution was controlled with 0.1M HCl or 0.1M NaOH solution by using a pH meter (pH 510; Eutech Instrument). The equilibrium adsorption capacity was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

Where q_e is the equilibrium adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentrations (mg/L) of dye solution used, V is the volume of the dye solution used (mL), and M is the weight of adsorbent used (g).

III. RESULTS AND DISCUSSION

3.1 Effect of contact time and initial dye concentration

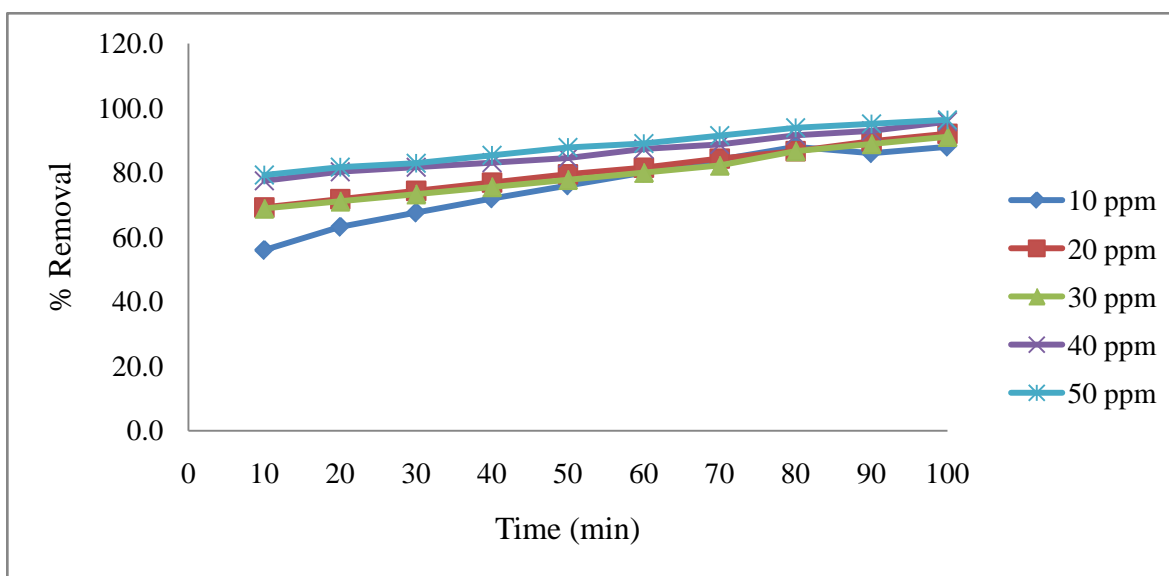


Figure 1: Effect of initial concentrations on the adsorption of methylene blue onto copper pod.

The effect of contact time on the percentage removal of methylene blue by copper pod flowers from aqueous solution at different concentrations is shown in Figure 1. It can be seen that the percentage removal of methylene blue increases rapidly with an increase in contact time and attains equilibrium after 100 min (Hameed et al.2006)(Bazrafshan et al.2017). The result indicates that the adsorption takes place rapidly at the initial stage on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate-determining step. In addition, the fast adsorption at the initial stage also may be because a large number of binding sites are available for adsorption (Jamasih et al.2005). The results indicate that for lower initial dye concentration, the adsorption is fast. The percentage dye removal decreases with increase in initial concentration and takes longer time to reach equilibrium because of the fact that with increase in concentration of dye, there will be increased

competition for the active adsorption sites and the adsorption process will increasingly slow down. This explains the more adsorption time for higher concentration.

3.2 Effect of adsorbent dosage

Adsorbent dose is an important parameter influencing adsorption process because it determines the adsorption capacity of an adsorbent. The effect of adsorbent dosage with activated carbon used as adsorbent for removal dye is shown in Figure 2. From the figure, it is readily understood that increased adsorbent dosages increase the percentage removal of dye (Gupta et al.2004)(Asfaram et al.2017).This is due to the increase in the surface area of adsorbent from 0.1 to 1.0 g and availability of more binding sites (Emad et al.2006).

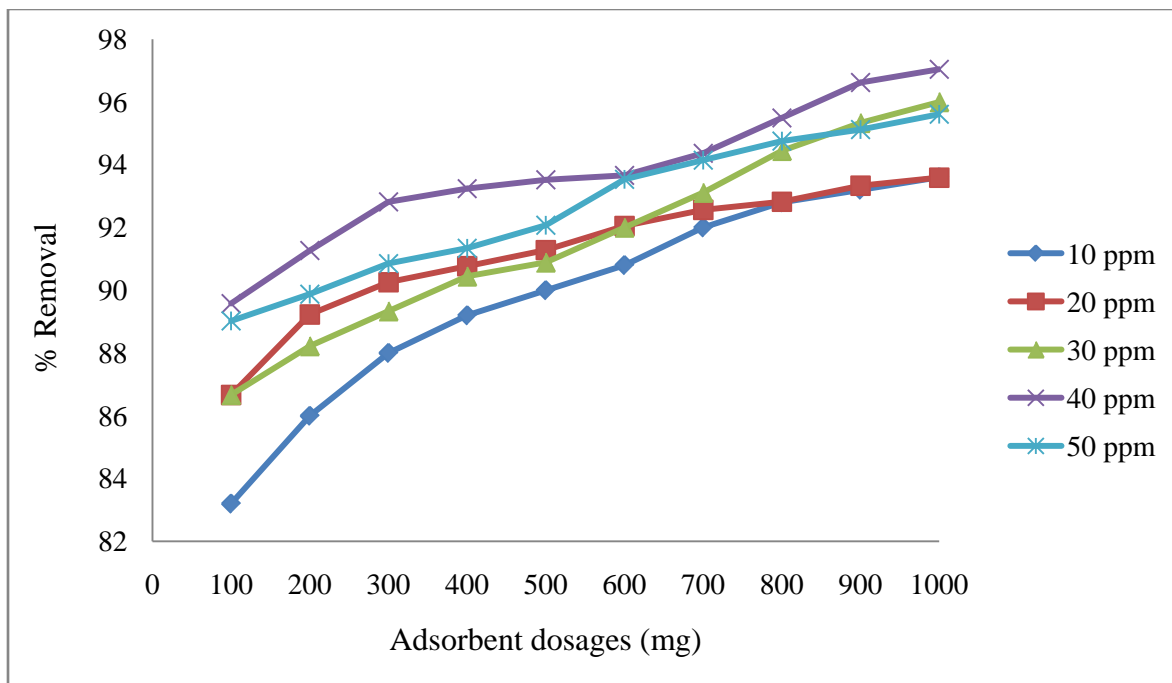


Figure 2: Effect of adsorbent dosages on the adsorption of methylene blue onto copper pod.

3.3 Effect of pH

The effects of pH on the percentage removal of methylene blue dye are shown in Figure 3. From the figure, it is clear that the percentage of dye removal increases up to pH 7 and it decreases gradually until pH 12. Removal of dyes occurs at pH 7 when the concentration of dye is increased from 10 to 50 mg/L (Gupta et al.1997) (Bagheri et al.2016).The surface charge of adsorbent may get negatively charged at lower pH and positively charged at higher pH. In addition, the negative charge in acidic medium and the positive charge in basic medium develop on the adsorbent surface. It can be explained by the formation of electrostatic forces of attraction between negatively charged adsorbent surface and cationic methylene blue at lower pH (Gupta et al.2011). At high pH, the adsorbent surface becomes positively charged and high concentration of H⁺ ions that compete with cationic methylene blue dye causes decrease in dye uptake (Kadirvelu et al.2003) (Dil et al.2017). The reduction in methylene blue dye removal could be due to the reduction of color intensity of the dye itself (Mittal, 2006).

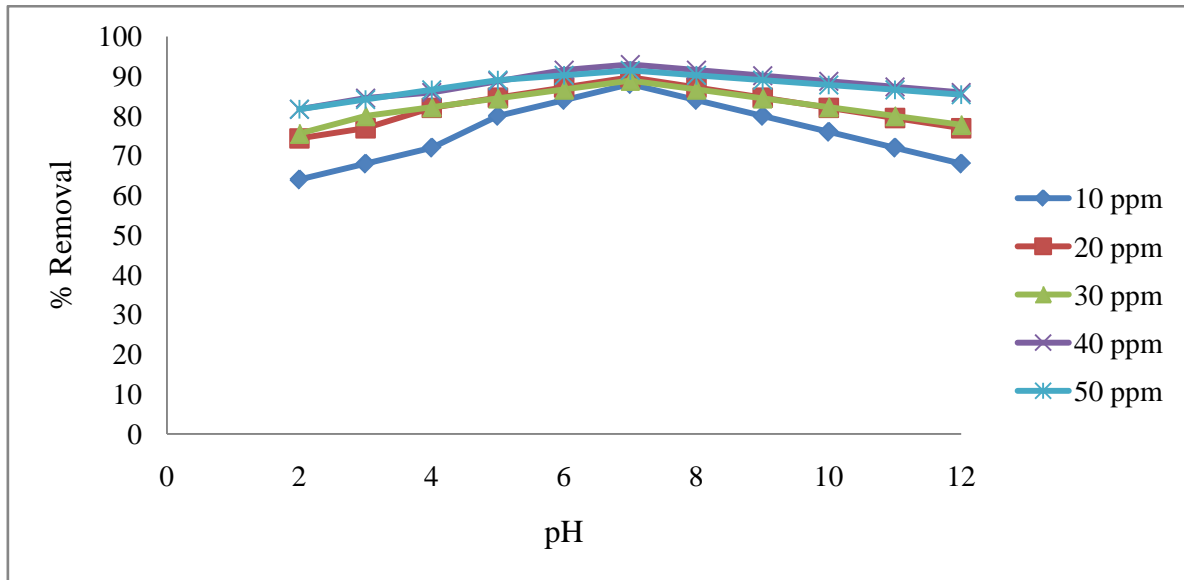


Figure 3: Effect of pH on the adsorption of methylene blue onto copper pod.

3.4 Effect of temperature

The effect of temperature on the percentage of dye removal is shown in Figure 4. The result shows that the equilibrium adsorption capacities of methylene blue dye decreased while increasing the solution temperature from 30 to 60°C for 40 mg/L. It is because higher temperature may decrease the adsorptive forces between the dye molecules and active sites on the adsorbent (Rahman et al.2005). The maximum percentage removal of methylene blue dye is observed at 30°C. Therefore, the result indicates that the adsorption reaction of methylene blue adsorbed by copper pod flower is exothermic in nature (Senthil kumar et al.2005).

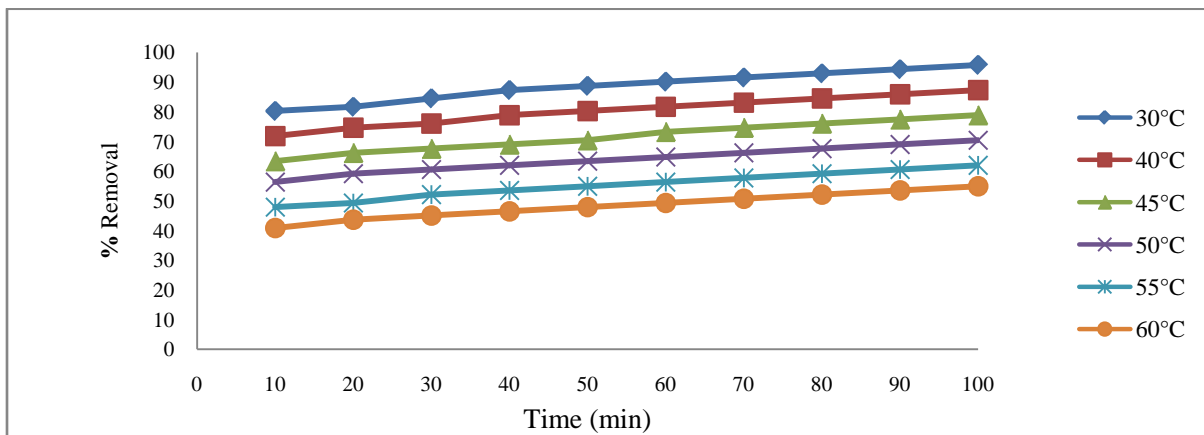


Figure 4: Effect of temperature on the adsorption of methylene blue onto copper pod.

3.5 Scanning electron microscope analysis

The scanning electron microscope (SEM) image of the adsorbent is shown in Figure 5. The figure shows wide varieties of pores on the adsorbent surface (Kumar, 2007). Pore development in an adsorbent is important because pores act as binding sites (Khafri et al. 2017). Pores formed on the surface of an adsorbent are binding sites for dye to be adsorbed onto the adsorbent.

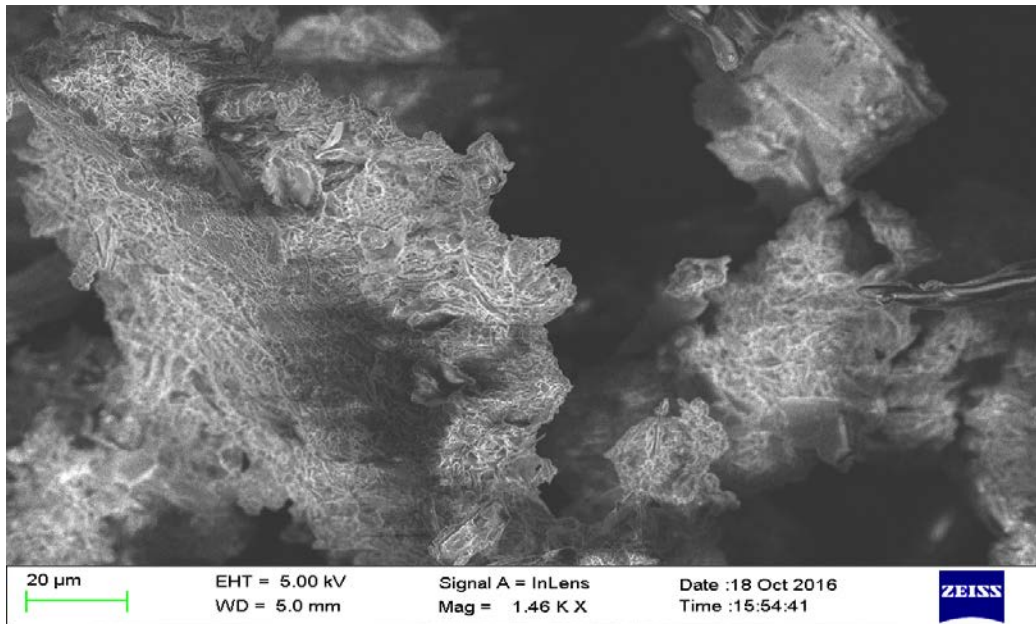


Figure 5: SEM images of activated carbon.

3.6 Powder X-ray diffraction study

The powder X-ray diffraction spectrum of the adsorbent is shown in Figure 6. This spectrum clearly shows broad peaks, indicating the presence of amorphous form of carbon which is disorderly stacked up by carbon rings (Sharma et al.2010).

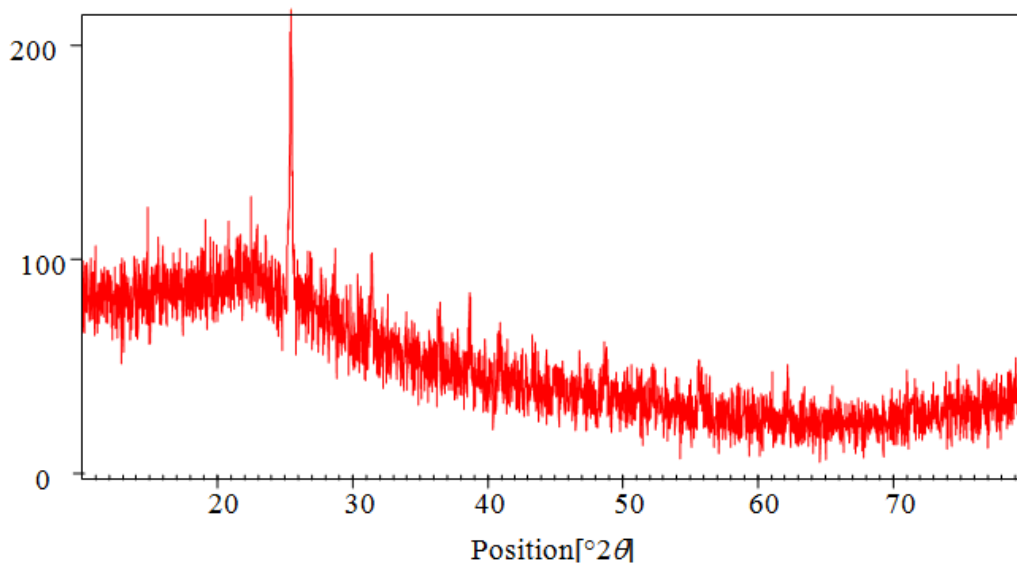


Figure 6: XRD pattern for the prepared activated carbon

3.7 Fourier transform infrared spectroscopy analysis

The Fourier transform infrared spectroscopy (FTIR) spectra of the copper pod flower and the dye-loaded copper pod flower are shown in figure 7 & 8. The adsorbent spectrum was measured within the range of 4000–400 cm^{-1} wave number. The absorption peak around 3437 cm^{-1} could possibly be due to the presence of OH groups. The peaks

observed at 2924.09cm^{-1} can be assigned to stretching vibration of the C–H group. The absorption peaks at 1847.81 , 1620.21 , and 1033.85 cm^{-1} are associated with the presence of C=O, C=C, and C–O bonds, respectively. These bands shifted to higher frequencies after adsorbing the dyes, which indicated an aromatic carbon or carbonyls could combine with the dye molecules on the surface of the activated carbon (Jain et al. 2006). The band at 1161.15 cm^{-1} may belong to C–O stretching in alcohol or ether or hydroxyl groups. It could be seen that the absorbance peaks in dye-loaded copper pod flower shifted to 1165.0 cm^{-1} for methylene blue (Mckay et al.1998) (Venceslau et al.1994). The above results indicate that functional groups on the surface of copper pod flower affected the adsorption process.

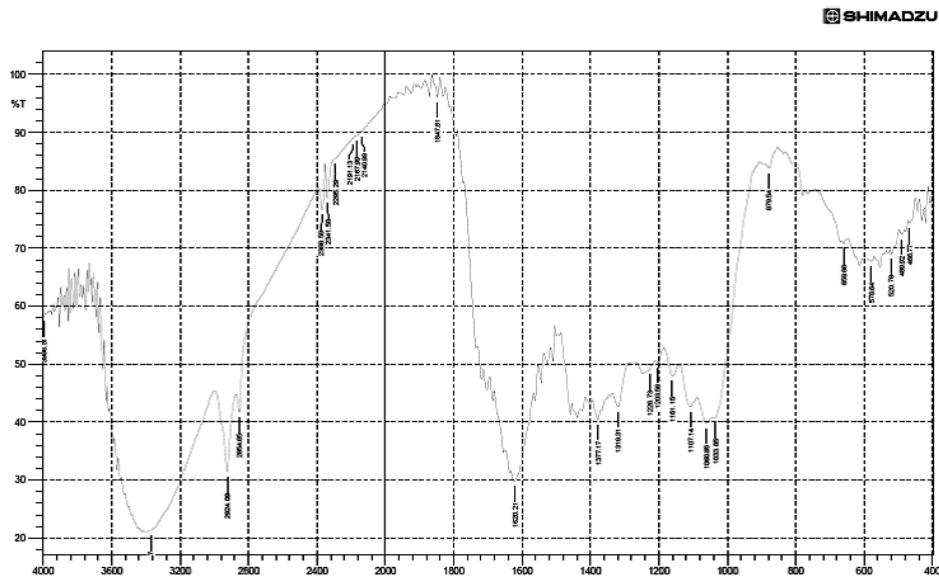


Figure 7: FTIR spectrum of activated carbon.

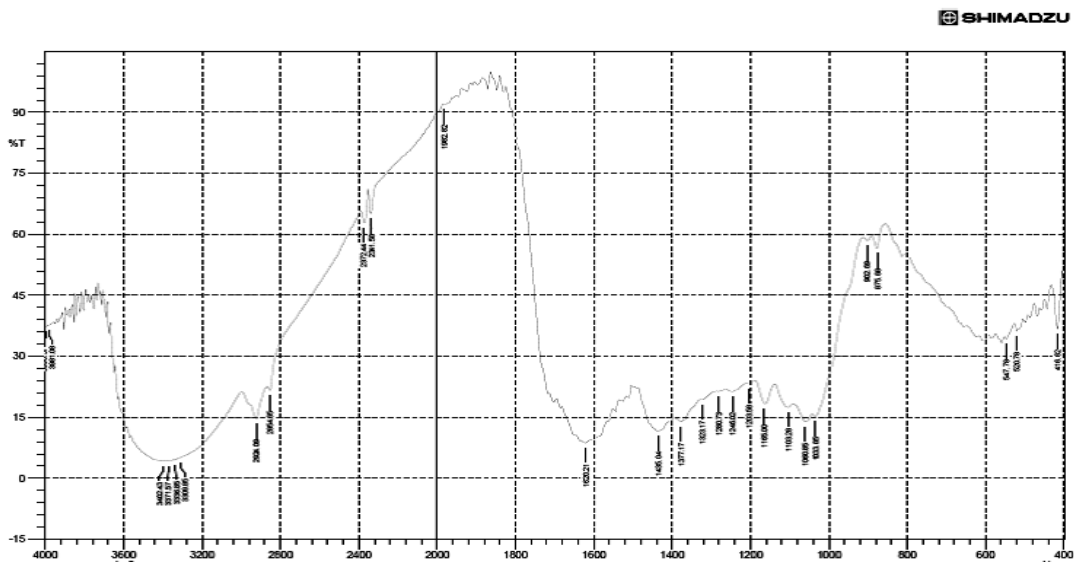


Figure 8: FTIR spectrum of methylene blue dye-loaded activated carbon.

3.8 Analysis of adsorption kinetics

Adsorption kinetics are used to examine the rate of the adsorption process and rate-controlling step (Bagheri et al.2017). Various kinetic models can be used to analyze the adsorption process. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to analyze the experimental data.

3.8.1 Pseudo-first-order equation

The pseudo-first-order equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

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

A plot of $\log(q_e - q_t)$ versus time (t) gives a linear line and is shown in Figure7. The values of q_e and k_1 can be determined from the slope and intercept of the plot, respectively, and are given in Table1. From the table, it can be seen that the experimental q_e values are not close to the calculated q_e values obtained from the linear plots (Asku et al.1992). It suggests that the adsorption of methylene blue dye on copper pod flower did not follow the pseudo-first-order reaction.

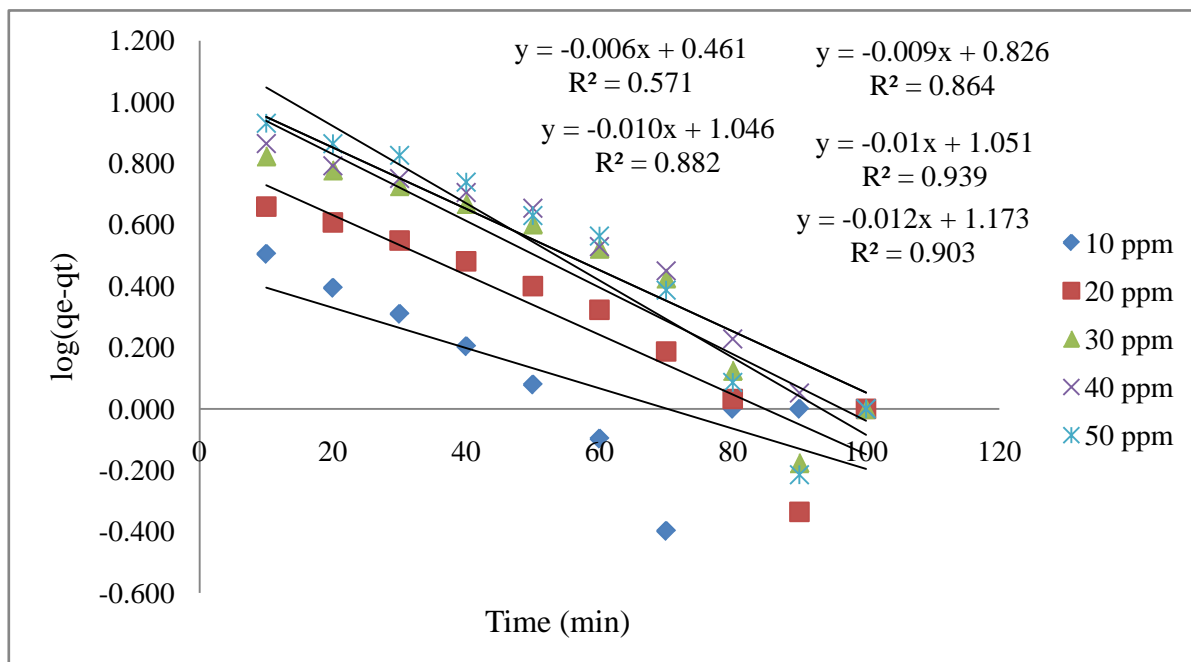


Figure 9: Pseudo-first-order kinetics for adsorption of methylene blue onto the prepared activated carbon at 30°C.

3.8.2. Pseudo-second-order equation

The pseudo-second-order equation is expressed as follows:

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

Where q_e is the amount of dye removed at equilibrium (mg/g), q_t is the amount of dye removed at time t (mg/g), and k_2 is the pseudo-second-order rate constant (min^{-1}).

A plot of $\frac{t}{q_t}$ versus t should give a linear relationship and is shown in Figure 8. q_e and k_2 values can be calculated from the slope and intercept of the plot. The pseudo-second-order rate constant, correlation coefficients (R^2), experimental data (q_e), and calculated q_e values are shown in Table 1. From the table, the correlation coefficients (R^2) values for the pseudo-second-order kinetic model reveal the applicability of the pseudo-second-order kinetic model to describe the adsorption process (Tehrani – Bagha et al. 2011). In view of these results, it can be concluded that the pseudo-second-order kinetic model provided a good correlation for the adsorption of methylene blue dye onto copper pod flower in contrast to the pseudo-first-order kinetic model.

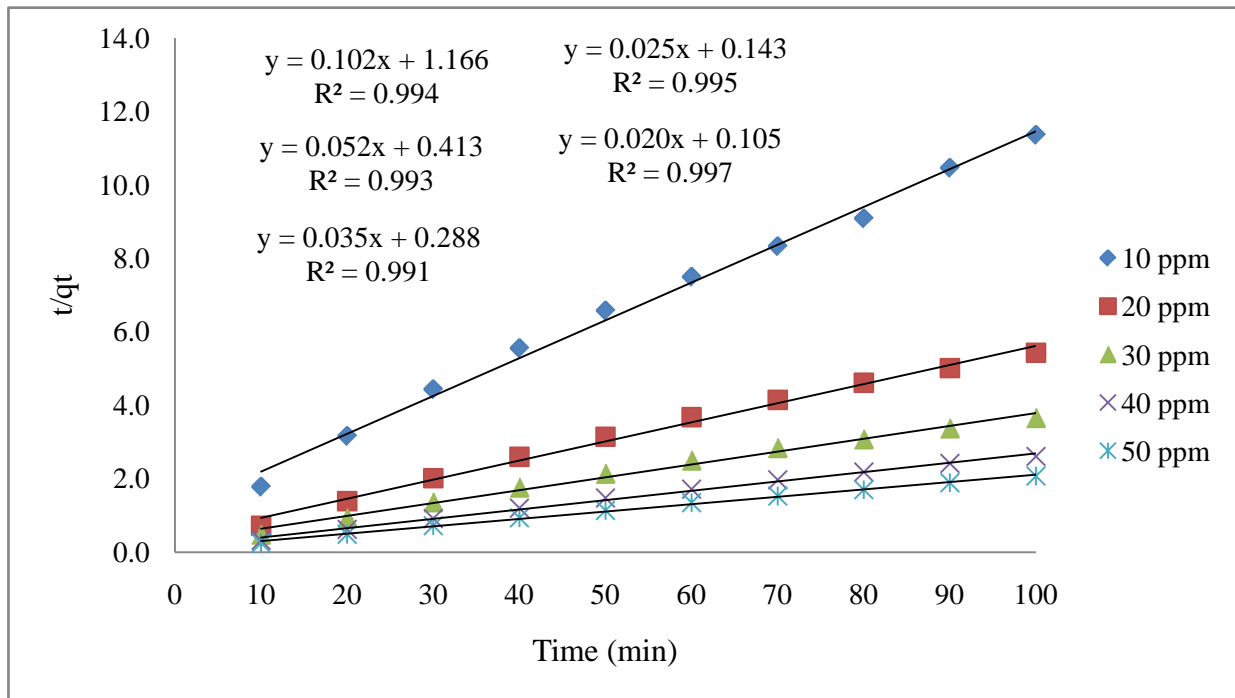


Figure 10: Pseudo-second-order kinetics for adsorption of methylene blue onto prepared activated carbon at 30°C.

Table 1: Results of kinetic plots for the adsorption of methylene blue onto copper pod flower.

Concentration (mg/L) 10 20 30 40 50					
Pseudo-first-order					
q_{exp} (ppm)	8.80	18.41	27.33	38.31	48.17
q_{ecal} (ppm)	2.89	6.69	11.11	11.24	14.89
k_1 (ppm)	0.0138	0.0207	0.0230	0.0230	0.0276
R^2	0.571	0.864	0.882	0.939	0.903
Pseudo-second-order					
q_{ecal} (ppm)	9.80	19.23	28.57	40.00	50.00
k_2 (ppm)	0.0089	0.0065	0.0042	0.0043	0.0038
R^2	0.994	0.993	0.991	0.995	0.997
Intraparticle					
C	4.106	11.32	16.78	27.14	34.84
K_d (mg/g·min)	0.492	0.675	0.996	1.039	1.309
R^2	0.981	0.976	0.955	0.960	0.980

3.8.3 Intraparticle diffusion studies

The intraparticle diffusion model is used for confirming the mechanism of the adsorption process. Intraparticle diffusion (k_d) is expressed as follows:

$$q_t = k_d t^{1/2} \quad (3)$$

Where q_t is the amount adsorbed (mg/g) at time t (min) and k_d is the rate constant of intraparticle diffusion (mg/g·min).

The plot of amount adsorbed (q_t) versus time gives a straight line and is shown in Figure 9. The rate constant of intraparticle diffusion (k_d) can be determined from the slope of the straight line and the values are given in Table 1. When the plots do not pass through the origin, the linear portion of the plot does not pass through the origin, suggesting that some degree of boundary layer control. This further shows that the intraparticle diffusion was not the only rate-limiting step (Gong et al. 2006). This variation from the origin may be due to the variation of mass transfer in the initial and final stages of adsorption. The high correlation coefficient (R^2) values ($R^2 = 0.955-0.981$) obtained at each concentration prove that the pore diffusion plays a significant role for the adsorption of methylene blue dye onto copper pod flower.

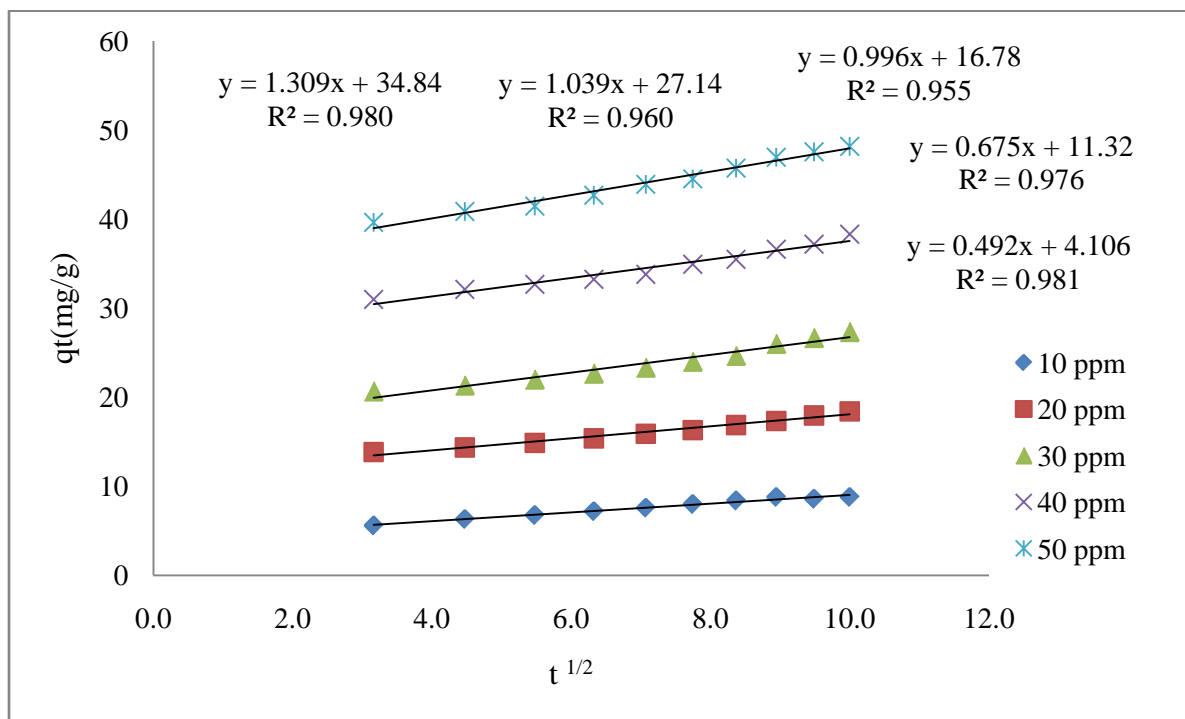


Figure 11: Intra particle diffusion for the adsorption of methylene blue onto the prepared activated carbon at 30°C.

3.9 Adsorption isotherm

The adsorption isotherm describes the mechanism of the adsorption process between the adsorbate and the adsorbent. There are several isotherm equations. For this study, Langmuir and Freundlich isotherms were used. The Langmuir isotherm assumes that the adsorption process takes place as a homogeneous monolayer of adsorbate on the outer surface of the adsorbent, and after that no further adsorption occurs.

3.9.1 Langmuir isotherm

The Langmuir isotherm equation is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (6)$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of dye solution (mg/L), Q_0 is the Langmuir constant related to adsorption capacity (mg/g), and b is the Langmuir constant related to rate of adsorption (L/mg).

A linear plot obtained for Langmuir isotherm is shown in Figure 11. A plot of $\frac{C_e}{q_e}$ versus C_e gives a straight line with slope of $\frac{1}{Q_0}$ and intercept of $\frac{1}{Q_0 b}$. The constant Q_0 and b values can be calculated from slope and intercept of the plots are given in Table 2.

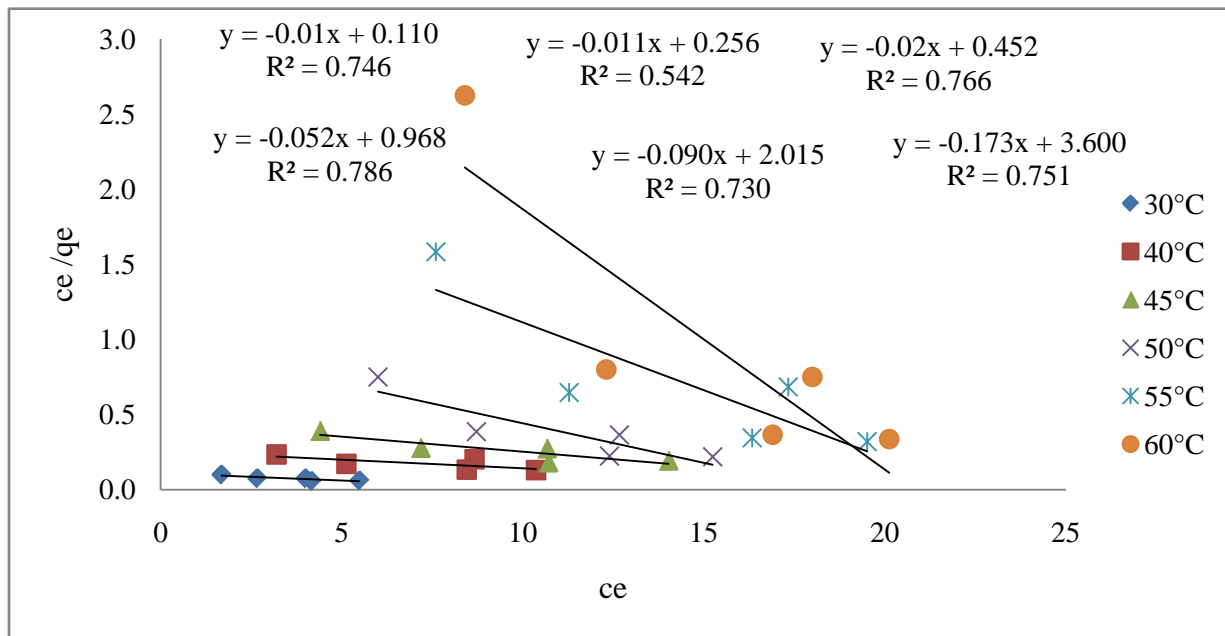


Figure 12: Langmuir isotherm for the adsorption of methylene blue onto the prepared activated carbon.

Table 2: Langmuir and Freundlich isotherm constants for the adsorption of methylene blue onto copper pod flower.

Temp.(°C)	Langmuir Isotherm Constants			Freundlich Isotherm Constants		
	R^2	Q_0 (mg/g)	b (L/mg)	R^2	n	k_f (mg/L)
30	0.746	100.00	0.0909	0.978	0.7032	8.184
40	0.542	90.90	0.0429	0.939	0.7163	2.773
45	0.766	50.00	0.0442	0.961	0.6226	1.051
50	0.786	19.23	0.0537	0.947	0.4452	0.153
55	0.730	11.11	0.0446	0.905	0.4053	0.036
60	0.751	5.78	0.0480	0.915	0.3201	0.004

The essential characteristics of Langmuir equation can be expressed in terms of dimensionless separation factor (R_L) and can be expressed by the following equation:

$$R_L = \frac{1}{1 + bC_0}$$

Where C_0 is the initial concentration of dye solution (mg/L) and b is the Langmuir constant. R_L values indicate the type of the adsorption isotherm to be linear ($R_L = 1$), favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), or irreversible ($R_L = 0$). Table 3 shows the values of R_L at different temperatures, which are in the range between 0 and 1, indicating the favorable adsorption process (Velmurugan et al.2011).

Table 3: R_L values at various initial dye concentrations.

Initial Dye Concentration (ppm)	R_L Value					
	30°C	40°C	45°C	50°C	55°C	60°C
10	0.5238	0.6964	0.6932	0.6505	0.6912	0.6754
20	0.3548	0.5378	0.5305	0.4820	0.5281	0.5099
30	0.2682	0.4368	0.4296	0.3829	0.4273	0.4095
40	0.2156	0.3678	0.3610	0.3175	0.3588	0.3422
50	0.1803	0.3176	0.3112	0.2713	0.3092	0.2938

3.9.2 Freundlich isotherm

The Freundlich isotherm model is an empirical equation assuming that the adsorption process takes place on a heterogeneous surface through a multilayer adsorption mechanism. It is generally expressed as

$$\log q_e = \log k_f + \left(\frac{1}{n}\right)\log C_e \quad (7)$$

Where q_e is the amount of dye adsorbed (mg /g), C_e is the equilibrium concentration of dye solution (mg /L), k_f is the Freundlich adsorption constant related to the adsorption capacity of adsorbent, and n is the adsorption intensity.

A plot of $\log q_e$ versus $\log C_e$ gives a straight line with slope and intercept and is shown in Figure2. The values of k_f and n can be determined from the slope and intercept of the plot and are listed in Table2.

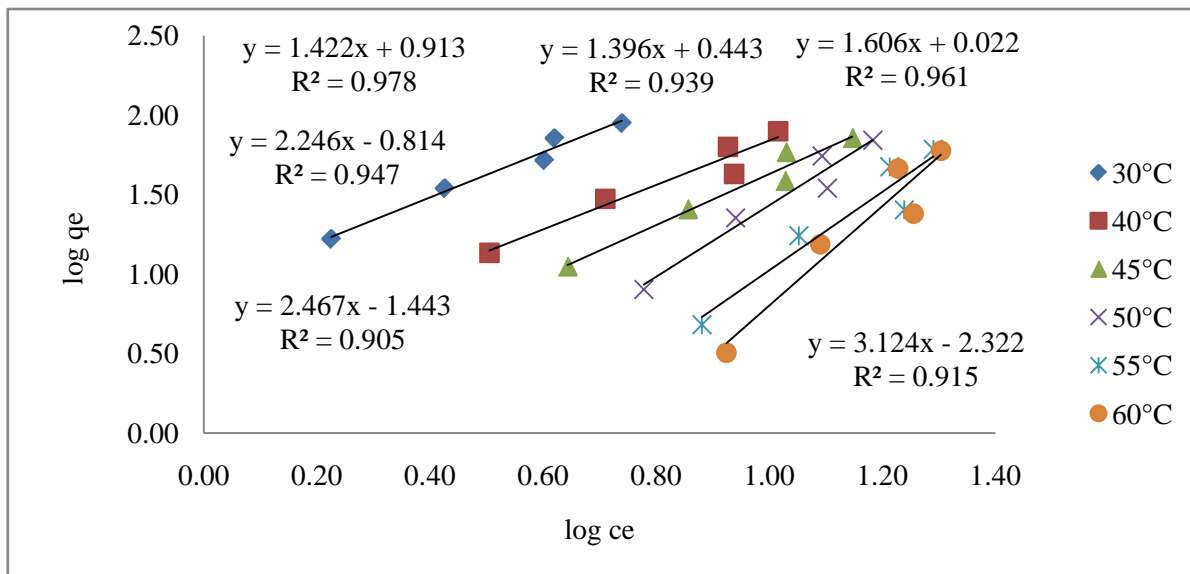


Figure 13: Freundlich isotherm for the adsorption of methylene blue onto the prepared activated carbon.

In general $n > 1$ illustrates that dye is favorably adsorbed on the adsorbent surface whereas $n < 1$ shows the adsorption process is chemical in nature (Dojan et al.2000). The value of n ranging between 0 and 1 is a measure of adsorption intensity, becoming more heterogeneous as its value gets closer to 0 (Dahri et al.2014). In this study, the

values found for n were around 0.3201–0.7163, which proves that adsorption conditions are favorable and the process is chemical in nature. The Freundlich adsorption constant (k_f) decreases with incremental temperature. The correlation coefficient (R^2) values for Freundlich isotherm model are higher than those of the Langmuir isotherm. The values of correlation coefficient (R^2) are closer to unity ($R^2 = 0.905$ – 0.978), which indicates the data are also well described by the Freundlich isotherm model. The results suggest that there is better fitting of the Freundlich isotherm model than the Langmuir isotherm model. This indicates that the adsorption of methylene blue dye on copper pod flower takes place as multilayer adsorption on the surface of the adsorbent.

IV. CONCLUSIONS

In this study, copper pod flowers were successfully used for the removal of methylene blue dye from aqueous solution. It was found that pH 7 and temperature 30°C are optimum for the removal of methylene blue dye from aqueous solution. The equilibrium adsorption of methylene blue onto copper pod flowers was suitably described by the Freundlich isotherm model than the Langmuir isotherm model. The adsorption process was best explained by the pseudo-second-order kinetics and the intraparticle diffusion model. The shifting of peaks in FTIR spectrum confirmed the adsorption of methylene blue dye onto copper pod flower. The SEM study also supported it by observing difference in the surface morphology of the adsorbent. The adsorption process was contact time, adsorbent dosage, pH, and initial metal ion concentration dependent. The equilibrium adsorption isotherm data were best represented by the Freundlich isotherm model better than the Langmuir isotherm model. From the kinetic data, it was found that adsorption of methylene blue dye using activated carbon is explained well by the pseudo-second-order kinetic model. Kinetic data results indicate that intraparticle diffusion is not the only rate-limiting step of the adsorption process. R_L values indicate favorable adsorption process. From the experimental results, it was observed that the optimum pH was 7. Findings indicated that the waste materials of copper pod flower could be used as an alternative to highly efficient low-cost and abundant materials for removal of methylene blue dye from contaminated aqueous solutions.

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