CHAPTER 5

ADSORPTION OF METHYLENE BLUE BY THE PREPARED FIVE ACTIVATED CARBONS

5.1 Introduction

Activated carbon was prepared with highly porous structures using a chemically activating agent from natural by-products (Yahya et al., 2015). The surface modification techniques are used for improving the adsorption capacity of activated carbon (Lee et al., 2016). The optimization process can be obtained using a different chemical agent such as zinc chloride, sulphuric acid, phosphoric acid, sodium carbonate, and sodium nitrate buffer solution. The inorganic species were eliminated from adsorbents by this demineralization process. After completing this process, the surface area and porosity of adsorbents are enlarged. The aim of this study is to investigate the removal of methylene blue from wastewater using activated carbon of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark to investigate the performance of the prepared activated carbon treated with a chemically activating agent using batch equilibrium tests, adsorption isotherm, and adsorption kinetics studies.

5.2 Materials and Chemicals

5.2.1 Sample of Agricultural By-Products

The same samples were taken as in Chapter 3 for this study.

5.2.2 Chemicals

Methylene blue (MB) was an analytical grade obtained from Sigma, Aldrich. Standard solution and Stock solution of methylene blue were obtained by dissolving 1g

MB in 1000 mL deionized water. Working solutions were prepared like 5 mg/L, 10 mg/L, 20 mg/L and 50 mg/L by diluting the stock solutions (1000 mg/L). Others chemicals were used 0.5 M HCl (70 %), 0.5 M H_2SO_4 (>98 %), 0.5 M HNO_3 (70 %), 1 M NaOH, 0.05 M $NaNO_3$ buffer, (10 %) $ZnCl_2$, 1 M H_3PO_4.

5.3 Adsorption Experiments

The stock solution of 1000 mg/L methylene blue was prepared in distilled water. Batch adsorption experiments were conducted for adsorption of methylene blue from waste water by the treated five activated carbons. The effects of pH in the solution, dosage, initial concentration, contact time, and percentage removal of the adsorption process were studied. This experiment was conducted by mixing 0.025 g activated carbon in 100 mL of methylene blue solutions (50 mg/L) in a volumetric flask. The solution was kept in a shaker at 25±1 °C for 3 hours at the speed of 200 rpm. The pH was controlled at 6 for methylene blue adsorption to obtain the best adsorption capacity (Jawad et al. 2016). It was observed the effect of pH of the solution were adjusted ranging from 2-11 by 0.1N (HCl and NaOH) solutions with sodium nitrate ($NaNO_3$) 0.5M buffer solution. Then the samples were run for 10, 20, 40, 80, 100, 120, and 180 minutes. The flasks were taken out at some intervals. After adsorption, the adsorbent and the supernatants were separated by centrifugation at 4000 rpm for 10 min and samples for analyses (10 mL) withdrawn with a clinical syringe and analysed for residual dye concentration using a UV– Visible Spectrophotometer (Cary 50 Varian, Agilent Technologies, USA) by monitoring the absorbance changes at the wavelength of 668 nm. The calibration curve was attained from the spectra of the standard solutions (5, 10, 20, 50 mg/L). To prevent decolourization and degradation from sunlight, the stock and working solution were kept in a dark place. The amount of adsorbate adsorbed, q_e (mg/g) and the percent removal of adsorbate at equilibrium were calculated according to Equation 3.1 and Equation 3.2 (as presented in Chapter 3).

5.3.1 Effect of Initial Adsorbate Concentration

The effect of the initial concentration of methylene blue was carried out ranging (5, 10, 20, 50 mg/L) in the batch adsorption process. A 100 mL of methylene blue solution was added with 0.025 g of each activated carbon into each 250 mL flask. The flask was then placed in a shaker at constant temperature (25±1 °C). The rotation speed of the shaker was 200 rpm. After 2 hours reaching the equilibrium point then it was tested by UV-vis Spectrophotometer (Cary 50 Varian, Agilent Technologies, USA).

5.3.2 Effect of Contact Time

The effect of contact time of methylene blue was conducted for 10, 20, 40, 80, 100, 120, and 180 minutes in the batch adsorption techniques. To investigate the adsorption uptake and percent removal, 100 mL of methylene blue solution with known initial concentration (50 mg/L) was prepared. The prepared solution was added into each flask containing the activated carbon and was fixed at 0.025 g with rotation speed of 200 rpm.

5.3.3 Effect of Solution pH

The adsorption capacity of methylene blue was conducted at different pH ranging from 2 to 11 to investigate the effect of pH in solution. The pH of the solution was maintained using hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M). Each activated carbon was 0.025 g and added with 5 mg/L initial concentration of methylene blue (100 mL) solution into each flask at pH (2-11). After 120 minutes, the adsorption plot was steady. The batch adsorption process was carried out for 180 minutes at 25±1 °C.

5.3.4 Effect of Adsorbent Dosage

The effect of adsorbent dosage was conducted ranging from 0.005 g to 0.05 g of each activated carbon during removal of methylene blue. The prepared solution (5

mg/L) of methylene blue (100 mL) was added into each flask containing the activated carbon and was fixed at (0.005 g, 0.01 g, 0.025 g, 0.05 g) with rotation speed of 200 rpm at 25±1 °C.

5.4 Results and Discussion

5.4.1 Effect of Initial adsorbate Concentration

The effect of initial concentration for the removal of methylene blue from spiked aqueous solution using activated carbon such as rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark as shown in Figure 5.1. The initial concentration was set at 5, 10, 20, 50 mg/L. It may be described from the graph that with increasing the initial concentration, the removal percentage of methylene from aqueous solution was decreased but the adsorption quantity of methylene blue also was increased using all activated carbon. At lower initial concentration (5 mg/L), The percent (~100%) of methylene blue were removed using most of the activated carbon and the adsorption quantity was 20.40 mg/g but with increasing the initial concentration up to 50 mg/L, the removal percentage and the adsorption quantity of methylene were 53.40 %, 52.80 %, 52.80 %, 53.60 %, 53.00 % and 108.94, 107.71, 107.71, 109.34, 108.12 mg/g for rice husk, coconut coir, corn cobs, neem bark and *Moringa oleifera* bark, respectively. It can be occurred due to possession of active functional group on to activated carbon. The higher mass transfer for most of the adsorbents was due to the increased in the driving force which was the initial concentration of methylene blue (Ahmad & Alrozi, 2011). The removal percentage of methylene blue were better (99.40 %, 99.60 %, 100 %) for coconut coir, corn cobs and neem bark than rice husk (94.60 %) as well as *Moringa oleifera* bark (94.20 %). It was happened due to possessing more available active sites onto activated carbon of coconut coir, corn cobs and neem bark for adsorbing methylene blue from spiked aqueous solution (Jawad et al., 2016). Figure 5.1 shows a slightly different behaviour for the removal percentage of methylene blue for corn cobs and *Moringa oleifera* bark, with increasing the initial concentration from 5 to 50 mg/L, the graph was not plotted in a gradually decreasing trend. The percentage removal firstly decreased from 100% to about 50.00 % for (5 to 20 mg/L) then increased slightly (52.80

% for corn cobs and 53.00 % for *Moringa oleifera* bark) for 50 mg/L of methylene blue solution. This pattern of adsorption indicated that monolayer formation of methylene blue can be formed on the adsorbent surface (Ahmad & Alrozi, 2011). Another side, the removal percentage of methylene blue for coconut coir was better gradually than others. The percentage of adsorption decreased with an increase in the initial concentration and increased as the contact time prolonged. However, the increase in the initial dye concentration caused an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial dye concentration (Bulut and Aydin, 2006). In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of the initial number of dye molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of the initial concentration.

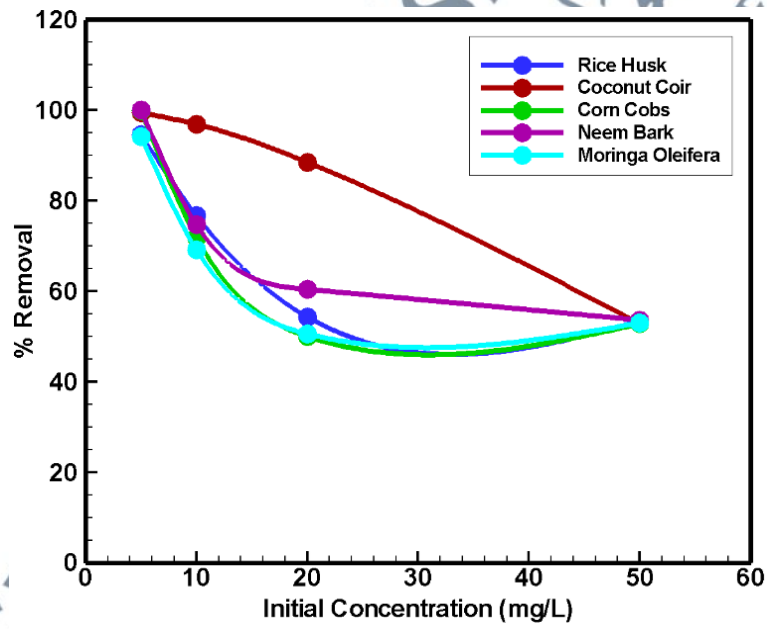

Figure 5.1 Effect of initial concentration on methylene blue removal by rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

5.4.2 Effect of contact time

The effect of contact time to the adsorption of methylene blue in 180 minutes of experiments was shown in Figure 5.2. The contact time between the activated carbon and the solute is an important parameter to determine the equilibrium time of an adsorption process. The graph shows the pattern of the adsorption capacity of methylene blue with time at 25±1 °C. The graph indicates that the quantity of adsorbate adsorbed at time, q_t is not significantly increased with the increase in contact time. During first 10 minutes, the q_t of methylene blue was 104.04, 103.22, 106.80, 106.08, and 105.22 mg/g for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark, respectively. After 120 minutes, the q_t could only increase up to 108.94, 107.71, 107.71, 109.34, and 108.12 mg/g for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark, respectively. Hence, the adsorbents need greater contact time to reach the equilibrium state and remove the maximum concentration of the adsorbates. The adsorption capacity of all activated carbon were better for the initial stage due to available active sites of adsorbents. The starting stage was shown at a fast rate indicating a rapid adsorption process. The subsequent stage was much horizontal due to a slower adsorption process.

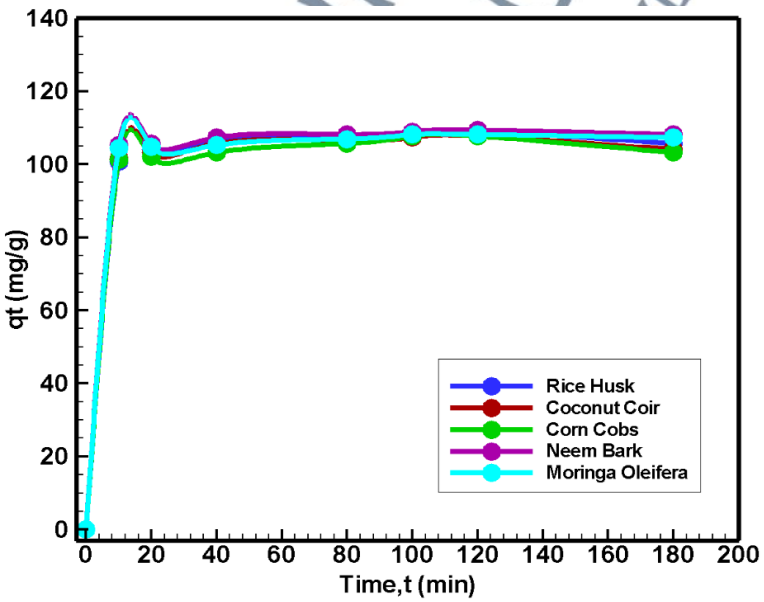

Figure 5.2 Adsorption capacity on methylene blue (50 mg/L) removal by rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

5.4.3 Effect of pH Solution

The effect of pH in the adsorption process was conducted ranging pH from 2 to 11 which was shown in Figure 5.3. At pH 6, the removal of methylene blue from aqueous solution was good about (~100%) by the adsorbents of coconut coir, corn cobs and neem bark but other two activated carbon (rice husk and *Moringa oleifera* bark) can remove more than 94% of methylene blue from aqueous solution. With increasing the pH value, the percent removal also increased and at pH 6, the removal percentage was highest. After increasing the pH values from 6 to 11, the removal percentage was decreased. It can be observed that methylene blue contains basic properties and cation formed (MB^+) was attracted to a negative surface of adsorbents due to the zero-point charge on most of the activated carbon being about below 6. When the pH > pH(pzc), the surface of activated carbon contains negative charges. For this reason, at pH 6, there can be better adsorption of methylene blue by electrostatic attraction between the negative surface of adsorbents and positive charges of methylene blue.

At pH 2, the methylene blue (MB) adsorption was lower due to high concentration of H^+ ions. This H^+ ions competed with MB^+ ions for the adsorption sites, hindering the adsorption of MB^+ ions by adsorbent. Protonated adsorption sites were not capable of binding MB^+ ions due to electrostatic repulsion. As the pH increased, H^+ ions decreased. Therefore, extra negatively anionic sites were made and methyl blue cation (MB^+ ions) adsorption increased by electrostatic attraction. So, the technique of MB^+ in adsorption can be conducted by electrostatic forces. The Methylene blue adsorption on activated carbon is also described by the ion-exchange technique. The major functional groups of adsorbents are the carboxyl, hydroxyl, aromatic ring that are responsible for ion exchange. The removal percentages of MB using coconut coir was good which indicated that the electrostatic mechanism was not the only mechanism for dye adsorption in the solution but was also affected by the chemical reaction between the adsorbent and dye molecules (Al-Degs et al., 2008).

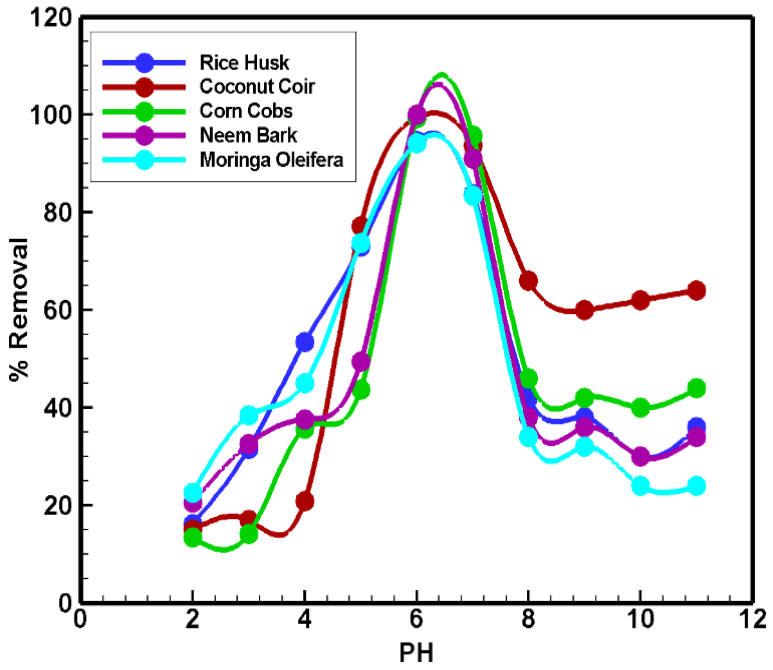

Figure 5.3 Effect of pH change for methylene blue (5 mg/L) of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

5.4.4 Effect of Adsorbent Dosage

The effect of dosage of activated carbon for the removal of methylene blue from wastewater is shown in Figure 5.4. From the graph, it can be observed that with increasing the adsorbent dosage, the removal of methylene blue also was increased. The removal percentage of methylene blue were 31.60 %, 42.20 %, 26.00 %, 33.60 %, and 25.00 % using 0.005 g of the activated carbon of rice husk, coconut coir, corn cobs, neem bark and *Moringa oleifera* bark, respectively and also were removed 94.60 %, 99.40 %, 99.90 %, 100 %, and 94.20 % using 0.025 g of adsorbents. It was reached at an equilibrium state using 0.025 g dosage of adsorbents for 100 mL solution. This can be obtained due to having more binding sites of adsorbents for complexation of methylene blue. Further increasing the adsorbent dose above 0.025 g, the methylene blue reduction was not increased significantly. This occurred due to the equilibrium state between binding adsorbate and unadsorbed adsorbate in the adsorption process.

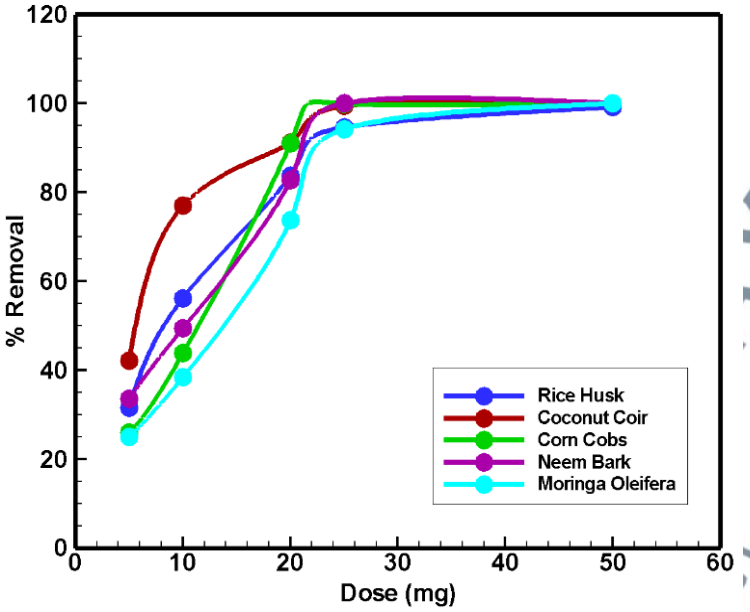

Figure 5.4 Effect of dosage for methylene blue (5 mg/L) of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

5.4.5 Adsorption Isotherms of Methylene Blue

The adsorption isotherm and kinetic isotherm of methylene using activated carbon of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark were shown in Figures 5.5-5.7 respectively. At equilibrium state, the adsorption isotherm designated how the adsorbate molecule distributes between adsorbent and solution. At the initial stage, the adsorbent contains available vacant active sites and shows well adsorption capacity (Ahmad et al., 2012). Using the adsorption data, the Langmuir, Freundlich, and Dubinin Radushcavick model have been successfully plotted for the removal of methylene blue from wastewater. The coconut coir was well fitted with the Langmuir isotherm which was a closed to the correlation coefficient, R^2 value to 0.999 but other activated carbon of rice husk, corn cobs, neem bark, *Moringa oleifera* bark were closely fitted with Freundlich isotherm. For the Langmuir adsorption process, the dimensionless constant, R_L, is an important characteristic and has a value of $0 < R_L < 1$, which indicates a favourable isotherm as shown in Table 5.1. The R_L value is defined as in equation 5.1.

$$R_L = 1/1+bCi \quad (5.1)$$

From the developed plots, the summary for the constant isotherm value of methylene blue was shown in Table 5.2. A high value of b for coconut coir and a low value of R_L (0.587, 0.108, 0.602, 0.545, and 0.587 for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark, respectively) indicate a high and favorable solute adsorption process. The values of Langmuir for coconut coir and Freundlich for other activated carbons indicated a favourable condition for methylene blue adsorption onto all activated carbon. From the Dubinin-Radushkevich model, adsorption energy values (E) indicated that the adsorption process was occurred by physical adsorption for all activated carbon (E< 8) but only corn cobs adsorption was shown chemical adsorption (E > 8-16).

Table 5.1 Separation factor, R_L (Ahmad & Alrozi, 2011)

R_L value	Nature of adsorption process	Calculated R_L value
$R_L > 1$	Unfavourable	X
$R_L = 0$	Linear	X
$0 < R_L < 1$	Favourable	0.108-0.602
$R_L < 1$	Irreversible	X

It can be carried out by some mathematical equation. All graphs were given in Figures 5.5–5.7 for the standard Langmuir and Freundlich and Dubinin-Radushkevich models. The higher value of b has described the affinity of activated carbon to bind pollutants. Other hand, q_{max} is considered as the entire number of active sites of adsorbents. From the above data, the affinity, b (1.62) of adsorbent was good for coconut coir but the affinity (b) of other activated carbons were not well.

Langmuir isotherm expressed as a monolayer of pollutants that was designed on activated carbon. From the plot of log q against log C_f of Freundlich isotherm were obtained the constant values k and 1/n. The Freundlich constants k and 1/n are adsorption capacity and adsorption intensity which are summarized in Table 5.2.

Adsorption properties can not be detected clearly by the Langmuir and Freundlich isotherm model. It can be described by the D-R isotherm (Azouaou et al., 2010). If the mean adsorption energies (E) are below 8 kJmol^{-1} indicates that the adsorption process is physical adsorption. When the E values are ranging 8-16 kJmol^{-1} that the adsorption

process follows chemical bonding. Table 5.2 of adsorption energy values of rice husk, coconut coir, neem bark, and *Moringa oleifera* bark were 2.39, 4.83, 0.49, and 2.4 kJmol^{-1} indicate physical adsorption (E<8) for the methylene blue adsorption process. On the other hand, the adsorption energy value of corn cobs was 11.24 (E > 9) indicated that methylene blue was adsorbed by chemical adsorption process. The constant data of all activated carbon without coconut coir were well fitted for Freundlich like ($1/n$ < 1, K > 1). The Freundlich equation represents multilayer and heterogeneous adsorption on the surface of the activated carbon. Overall, coconut coir, corn cobs, and neem bark showed high adsorption capacity to remove methylene blue from wastewater. The relatively high adsorption quantity was consistent with the results obtained earlier due to possessing high surface areas and pore volumes by mesopores. Besides, the adsorption capacity was affected by the presence of functional groups such as carboxylic, hydroxyl, and aromatic (C=C) groups on the surfaces which was described in Chapter 4. The functional groups became negatively charged sites by dissociation, which fascinates the positive charge of methylene blue cations in electrostatic interaction. So, methylene blue can be removed from the aqueous solution by the ion exchange method.

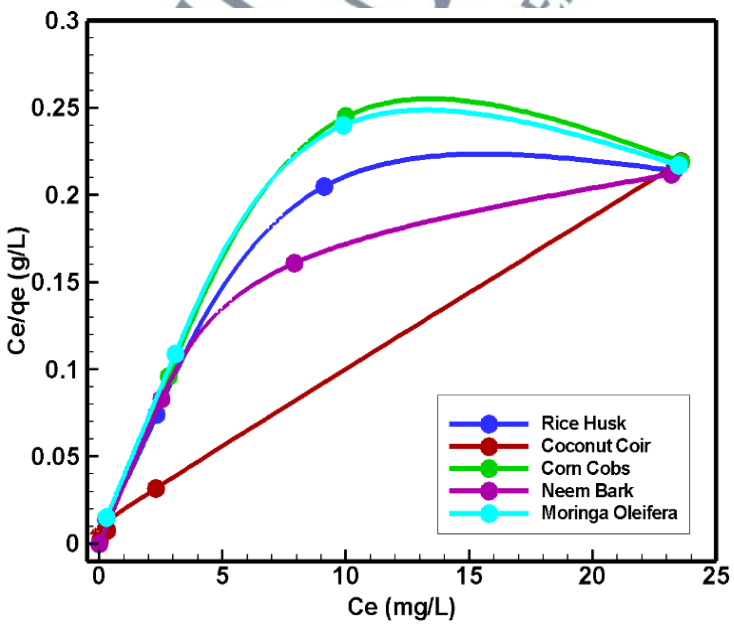

Figure 5.5 Langmuir adsorption for methylene blue (50 mg/L) of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

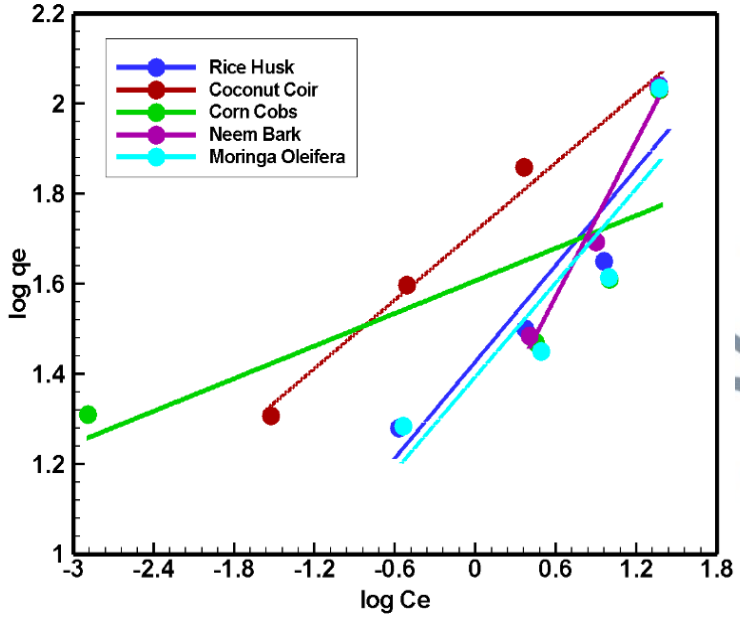

Figure 5.6 Freundlich adsorption for methylene blue (50 mg/L) of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

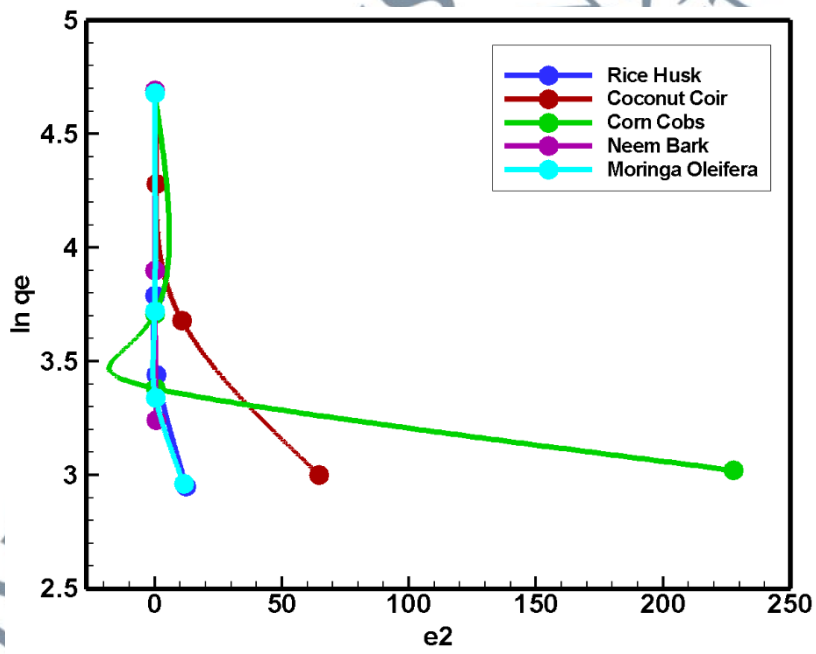

Figure 5.7 Dubinin-Radushkevich plot for methylene blue adsorption of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

Table 5.2 Isotherm constants for adsorption of methylene blue by all activated carbon

Methylene blue	Langmuir model			Freundlich model			Dubinin-Radushkevich		
	R^2	q_{max} (mg/g)	B (L/mg)	R^2	$1/n$	K	R^2	q_{max} (mg/g)	E (kJmol^{-1})
Rice husk	0.70	125.00	0.14	0.88	0.35	6.45	0.52	54.80	2.39
Coconut coir	0.99	109.89	1.66	0.61	33.71	0.67	0.81	74.99	4.83
Corn cobs	0.60	119.05	0.13	0.58	0.12	4.85	0.40	50.63	11.24
Neem husk	0.78	126.58	0.16	0.97	0.57	11.25	0.80	81.90	0.49
***Moringa oleifera* bark**	0.58	129.87	0.10	0.80	0.34	6.94	0.44	51.07	2.40

5.4.6 Adsorption Kinetic Studies

The kinetics of the adsorption process were evaluated in the pseudo-first-order and pseudo-second-order kinetic models. Figures from 5.8 to 5.10 indicated the adsorption kinetics plot for the first, second, and intra-particle graph. All constant values (k_1, k_2, k_d, R^2) of adsorption kinetics for methylene blue adsorption were shown in Table 5.3. There is a far difference for q_e values of the first order equation between experimental values (108.94, 107.71, 107.71, 109.34, and 108.12 mg/g) and calculative values (8.34, 7.62, 8.01, 5.59, and 4.54 mg/g) for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark, respectively. The coefficient regression value (R^2) was not close to 1. So, these graphs were not fitted with the first-order model. On the other hand, the experimental value (q_{exp} ~ 108.94, 107.71, 107.71, 109.34, and 108.12 mg/g) and calculative values (q_{cal} ~ 111.1, 108.69, 108.69, 111.1, and 108.69 mg/g) for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark, respectively were closed for the pseudo-second-order model and also coefficient regression constant (R^2) was almost equal to unity (~1) for all activated carbon. So, the adsorption of methylene blue kinetics parameter for all activated carbon was well fitted to the second order model. The results indicate that there are several steps involved in the adsorption process. It may be conducted that the rate limiting step is the physical adsorption process proved by the D-R model for most of the activated carbon.

The rate of adsorption for methylene blue was evaluated by external transport or intra-particle transport. Linear lines of the graph were obtained in Figure 5.10. Most of the lines developed did not pass through the origin. According to Kumar et al., (2011), if the linearity was achieved and the line passes through the origin, it indicates the internal diffusion is the slowest step in the adsorption process. The graph line of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark were not linear and did not pass through the origin. It is indicated that the adsorption process was controlled by film diffusion (Kumar et al., 2011). The adsorption of methylene blue by all activated carbon were conducted by film diffusion, external transport was shown to be more prominent than internal transport. There are two steps of this operation: (1) external mass transfer during the initial adsorption process followed by intra-particle diffusion. (2) The rate limiting process is controlled by film diffusion that has a high adsorbate affinity for the adsorbent (Ahmad et al., 2012).

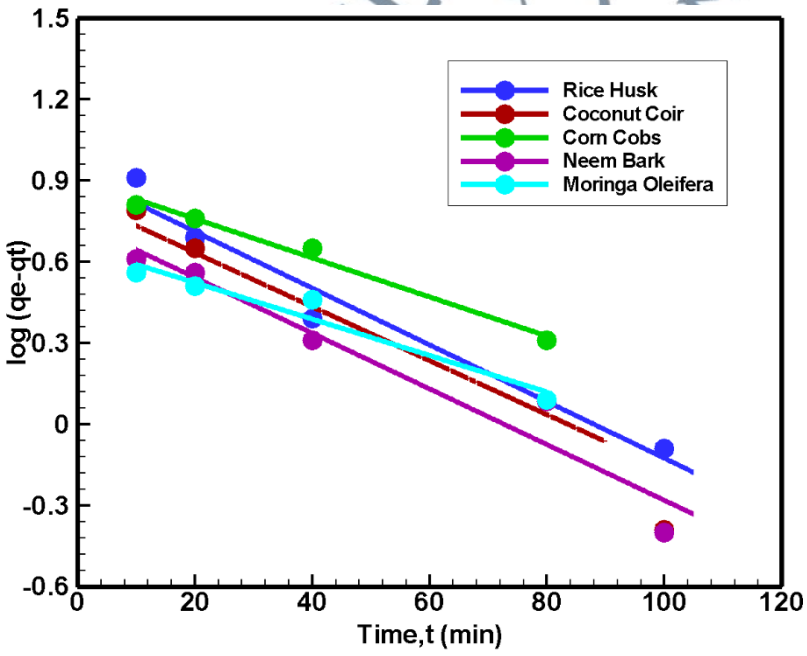

Figure 5.8 Pseudo-first-order of methylene blue (50 mg/L) kinetic adsorption for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

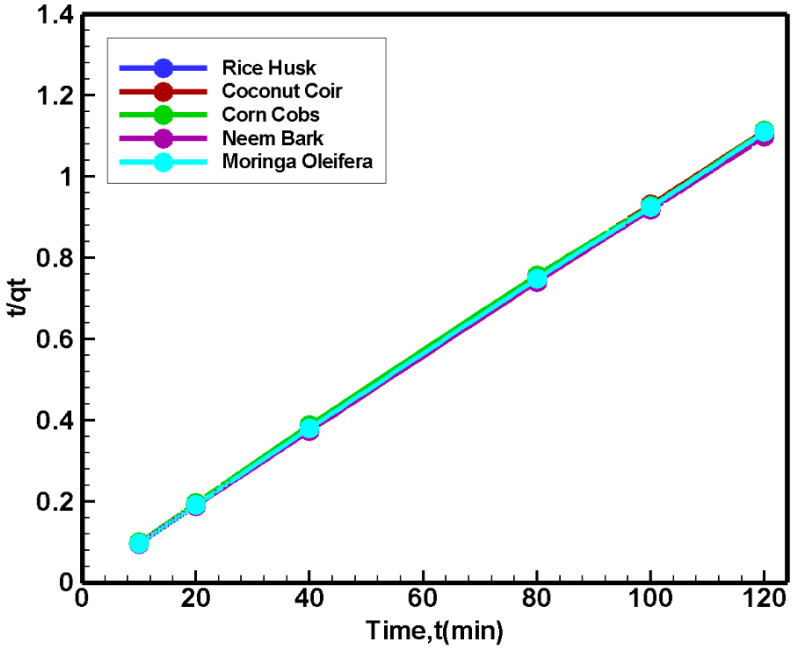

Figure 5.9 Pseudo-second-order of methylene blue (50 mg/L) kinetic adsorption for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

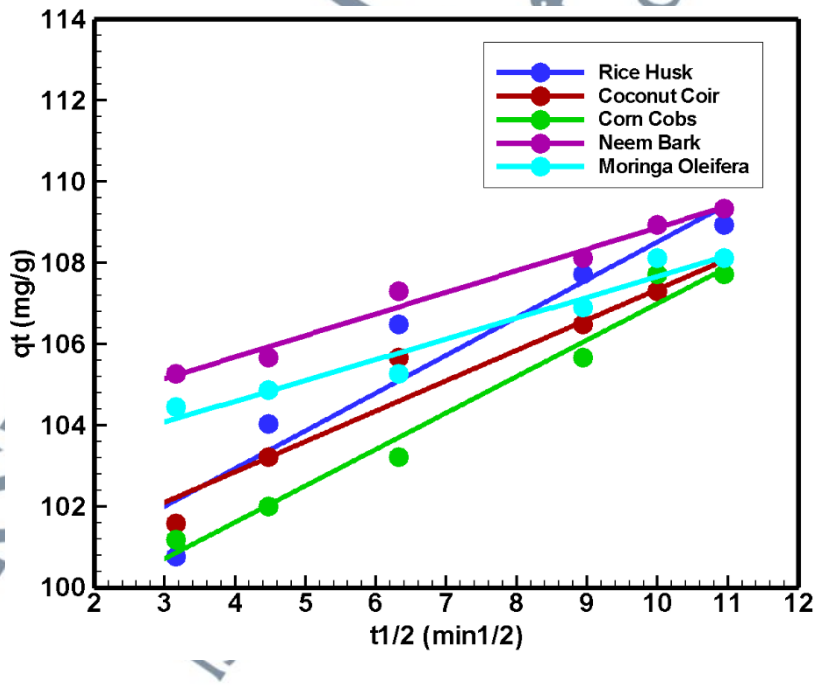

Figure 5.10 Intra-particle diffusion of methylene blue (50 mg/L) for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark

Table 5.3 Adsorption kinetics parameters for methylene blue adsorption

Methylene blue			First order			Second order		Intra Particle diffusion	
	q_{exp} mg/g	R^2	q_{cal} mg/g	k_1 min^{-1}	R^2	q_{cal} mg/g	K_2 min^{-2} gmg^{-1}	k_d mgl^{-1} $min^{-1/2}$	R^2
Rice husk	108.94	0.96	8.34	0.02	1.00	111.11	0.008	0.93	0.90
Coconut coir	107.71	0.95	7.62	0.01	1.00	108.69	0.009	0.74	0.94
Corn cobs	107.71	0.98	8.00	0.01	0.99	108.69	0.006	0.89	0.97
Neem bark	109.34	0.93	5.59	0.02	1.00	111.10	0.012	0.53	0.98
Moringa oleifera bark	108.12	0.94	4.54	0.01	0.99	108.69	0.011	0.51	0.95

5.5 CONCLUSION

The adsorption of methylene blue using the activated carbon such as rice husk, corn cobs, neem bark, and *Moringa oleifera* bark were closely fitted by Freundlich model (R^2~0.97) but activated carbon of coconut coir was well fitted with Langmuir model (R^2~0.99). Most of the activated carbon showed physical adsorption by D-R model (E<8) without corn cobs (E >8). The adsorption kinetics parameter was well fitted by pseudo-second order model (R^2 > 0.99) than pseudo-first-order model and intra-particle diffusion for all activated carbon. The adsorption kinetic model indicates that the adsorption process was carried out by several mechanisms. It may be caused by an active site on the surface, diffusion and adsorption into the interior pore of the adsorbents. The adsorption capacity of adsorbent can be influenced by the interaction of positive ions with surface functional groups of adsorbents. This study suggests that all activated carbon can be used as an essential adsorbent for the removal of methylene blue from wastewater.