Adsorption Studies on The Removal of Methylene Blue Dye Using AMC

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Abstract- *Generally, dyes are organic compounds used as colouring products in chemical, textile, paper, printing, leather, plastics and various food industries. The need for the treatment of dye contaminated waste water passed out from the industry.The research of the present work was to investigate the removal of methylene blue dyes from aqueous solution by using Activated Mullugo Cerviana Leaves Carbon (AMC). The experimental data were fitted into the pseudo-second order kinetic model. The equilibrium of adsorption was modeled by using the Langmuir and Freundlich isotherm models*

Keywords- Activated Mullugo Cerviana Leaves Carbon (AMC); Methylene blue

I. INTRODUCTION

Dyes are widely used, generally in the textiles, plastics, paper, leather, food industry to color products. In process of washing and finishing coloured products, waste water contaminated with dyes is generated. The contaminated waste waters are hazardous, which is a great threat to environment [1-3]. Dye contamination in wastewater causes problems in various ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters; retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies. These materials are the complicated organic compounds and they resist against light, washing and microbial invasions [4-7]. The need for the treatment of dye contaminated waste water arose from the environmental impact [8]. Activated minerals are one of the most popular adsorbents used for the removal of toxic substances from waste water. This could be related to their extended surface area [9]. The major use of Activated Mullugo Cerviana Leaves Carbon is in solution purification and for the removal of colour, odors and other unpleasant impurities from liquids, water supplies and vegetable and animal oils.

In recent years it has been increasingly used for the prevention of environmental pollution and antipollution laws have increased the sales of low-cost activated minerals for control the of air and water pollution. Various techniques like precipitation, ion exchange, chemical oxidation and adsorption have been used for the removal of toxic pollutant from, wastewater. Methylene blue (MB) is selected as a model compound for evaluating the potential of AMC to remove dye from aqueous solution.

II. MATERIALS AND METHODS

2.1 Adsorption studies

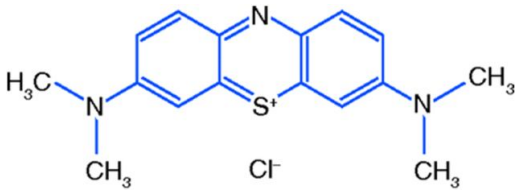
Methylene blue (MB) was used as an adsorbate in the adsorption experiments. Adsorption from the liquid phase was carried out to verify the porosity characteristics of the samples. An aqueous solution with a concentration of 50-250 mg/L was prepared by mixing an appropriate amount of MB with distilled water adsorption experiments were conducted by placing 0.025 g of AMC samples and 50 ml of aqueous solution in 250 ml of glass stoppered flask. The flask was kept in shaker at 150 rpm with constant temperature of 30 ±2°C. The isothermal adsorption experiments were performed at 30 ±2°C.

2.2 Preparation of adsorbent materials

The *Mullugo Cerviana* Leaves collected from agricultural area nearby Ariyalure districts, it was carbonized with concentrated Sulphuric acid and washed with water and activated around 600°C in a muffle furnace for 5 hrs the it was taken out, ground well to fine powder and stored in a vacuum desiccators.

2.3 Preparation of adsorbate

Methylene blue was chosen in this work because of its strong adsorption onto solids and it recognized usefulness in characterizing adsorptive material Methylene blue is employed to evaluate the adsorption characteristics of carbon. A known weight of 1000 mg of MB was dissolved in about one litre of distilled water to get the stock solution.



Structure of Methylene Blue

2.4 Batch equilibrium method

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60˚ C. A known weight of AMC was added to 50 ml of the dye solutions with an initial concentration of 50 mg/L to 250 mg/L, which is prepared from 1000 mg/L of methylene blue stock solution. The contents were shaken thoroughly using a mechanical shaker with a speed of 150 rpm. The solution was then filtered at present time intervals and the residual dye concentration was measured.

III. RESULT AND DISCUSSIONS

3.1 Characteristics of the adsorbent

Activated Mullugo Cerviana Leaves Carbon is an effective adsorbent for the abatement of many pollutant compounds (organic, inorganic, and biological) of concern in water and wastewater treatment. Most of the solid adsorbents possess micro porous fine structure, high adsorption capacity, high surface area and high degree of surface, which consists of pores of different sizes and shapes. The wide usefulness of AMC is a result of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity.

3.2 Effect of contact time and initial dye concentration

The effect of contact time on the amount of dye adsorbed was investigated at 1000 mg/L concentration of the dye (Fig. 1). It is observed that the percentage removal of dye increases rapidly with an increase in contact time initially, and thereafter, beyond a contact time of about 40 min, no noticeable change in the percentage removal is observed the percentage removals after 40 min were 85%. Therefore, the optimum contact time is considered to be 40 min. this is also the equilibrium time of the batch adsorption experiments, since beyond a contact time of 40 min, adsorption is not changed. The rapid removal of dye is observed at the beginning of the contact time due to the percentage of large number of binding sites available for adsorption. The experimental results of adsorptions at different concentrations (50 to 250mg/L) collected in Table 2 observed that percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of AMC increased leads to increase in dye concentration. This means that the adsorption is highly dependent on initial concentration of dye. At lower concentration, the ratio of the initial number of dye molecules to the available surface area is low. Subsequently, the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption become less and hence the percentage removal of dye is dependent upon initial concentration [10, 11].

3.3 Effect of adsorbent dosage

The adsorption of the methylene blue dye on AMC was studied by varying the adsorbent dose (25–125 mg/50ml) for 50 mg/L of dye concentration. The percentage of adsorption increased with increases in the AMC concentration, which is attributed to increased carbon surface area and the availability of more adsorption sites [12, 13]. Hence, all studies were carried out with 0.025g of adsorbent /50 ml of the varying adsorbate solutions.50, 100, 150, 200 and 250. The results obtained from this study are shown in Fig. 2. The amount of MB adsorbed per gram reduced with increase in the dosage of AMC. This reveals that the direct and equilibrium capacities of MB are functions of the activated AMC dosage.

3.4 Effect of solution pH

The solution pH is one of the most important factors that control the adsorption of dye on the sorbent material. The adsorption capacity can be attributed to the chemical form of dye in the solution at specific pH. In addition, due to different functional groups on the adsorbent surface, which become active sites for the dye binding at a specific pH the effect of adsorption can vary substantially. Therefore, an increase in pH may cause an increase or decrease in the adsorption, resulting different optimum pH values dependent on the type of adsorbent. To examine the effect of pH on the % removal of MB dye , the solution pH were varied from 2.0 to 10.0 by adding acid and base to the stock solution This increases may be due to the presence of negative charge on the surface of the adsorbent AMC that may be responds for the dye binding. However, as the pH is lowered, the hydrogen ions compete with dye for the adsorption sites in the adsorbent AMC, the overall surface charge on the particles become positive and hinds the binding of positively charged dye. On other hand, decrease in the adsorption under pH >6.3 may be due to occupation of the adsorption sites by OH^- ions which retard the approach of such dye further toward the adsorbent AMC surface. From the experimental results, the optimum pH range for the adsorption of the MB dye is 2.0 to 6.5 shown in Fig.3.

3.5. Adsorption isotherms

3.5.1 Langmuir isotherm

The theoretical Langmuir isotherm is used for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir non-linear equation is commonly expressed as follows:

$$C_{eq}/Q_{eq} = 1/Q_m b + C_{eq}/Q_m \quad \text{..... (1)}$$

Where C_{eq} is the equilibrium concentration of adsorbate in the solution (mg/L), Q_{eq} is the amount adsorbed at equilibrium (mg/g), Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of Ceq/ Q_{eq} vs. C_{eq} suggest the applicability of the Langmuir isotherms (Fig.5.17). The values of Q_m and *b* were calculated from slope and intercepts of the plots are given in Table 3. From the results, it is obvious that the value of adsorption efficiency Q_m and adsorption energy *b* of the AMC increases on increasing the temperature. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with endothermic nature of adsorption [14, 15]. To confirm the favorability of the adsorption process, the separation factor (R_L) was determined and given in Table 4.The values were established to be between 0 and 1 and confirm that the ongoing adsorption process is favorable [16].

3.5.2 The Freundlich isotherm

The Freundlich isotherm model is the earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. The Freundlich equation was employed for the adsorption of methylene blue dye on the adsorbent. The Freundlich isotherm was represented by the following equation.

$$\log Q_e = \log K_f + 1/n \log C_e \quad \text{……..(2)}$$

Where Q_e is the amount of methylene blue dye adsorbed (mg/g), C_e is the equilibrium concentration of MB dye in solution (mg/L), and K_f and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log Q_e versus log C_e shows that the adsorption of methylene blue obeys the linear plots of log Q_e versus log C_e shows that the adsorption of methylene blue dye obeys the Freundlich adsorption isotherm (Fig. 5.18). The values of K_f and *n* are given in Table 4 shows that the increase of negative charges on the adsorbent surface makes electrostatic force like Vanderwaal's between the AMC surface and dye ion. The molecular weight and size either limit or increase the possibility of the adsorption of the dye onto adsorbent. However, the values clearly show the dominance in adsorption capacity.

The intensity of adsorption is an indication of the bond energies between dye and adsorbent, and the possibility of slight chemisorptions rather than physisorption [17, 18]. However, the multilayer adsorption of methylene blue through the percolation process may be possible. The values of *n* are less than one, indicating the physisorption is much more favorable [19].

3.6 Effect of temperature

To study the effect of temperature on the adsorption of dye adsorption by AMC, the experiments were performed at temperatures of 30, 40, 50, 60°C. As it was observed that, the equilibrium adsorption capacity of MB onto AMC was found to increase with increasing temperature, especially in higher equilibrium concentration, or lower adsorbent dose because of high driving force of adsorption. This fact indicates that the mobility of dye molecules increased with the temperature. The adsorbent shows the endothermic nature of adsorption. The adsorption capacity of the AMC increased with increase of the temperature in the system from 30° to 60°C. Thermodynamic parameters such as change in free energy ($^{\Delta}G°$) (kJ/mol), enthalpy ($^{\Delta}H°$) (kJ/mol) and entropy ($^{\Delta}S°$) (J/K/mol) were determined using the following equations.

$$K_0 = C_{solid}/C_{liquid} \quad \text{……. (3)}$$

$$^{\Delta}G° = -RT \ln K_O \quad \text{……...(4)}$$

$$\log K_0 = {}^{\Delta}S°/(2.303R) - {}^{\Delta}H°/(2.303RT) \quad (5)$$

Where K_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), *T* is the temperature in Kelvin, and *R* is the gas constant. The $^{\Delta}H°$ and $^{\Delta}S°$ values obtained from the slope and intercept of Van't Hoff plots are given in Table 5.The values of $^{\Delta}H°$ is the range of 9 to 17 kJ/mol, indicate the physisorption. The results show that physisorption is much feasible for the adsorption of

methylene blue. The positive values of $\Delta H°$ show the endothermic nature of adsorption which governs the possibility of physical adsorption [19, 20]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, there is no possibility of chemisorption. The negative values of $\Delta G°$ (Table 5) show that the adsorption is highly favorable and spontaneous. The positive values of $\Delta S°$ (Table 5) show the increased disorder and randomness at the solid solution interface of methylene blue with AMC adsorbent. The enhancement of adsorption capacity of the activated AMC at higher temperatures was ascribed to the enlargement of pore size and activation of the adsorbent surface.

3.7. Adsorption kinetics

The study of adsorption dynamics describes the solute up take rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface .The kinetics of MB dye adsorption on the AMC were analyzed using pseudo second-order[21] Elovich [22] and intra-particle diffusion[23] kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation co- efficient (γ) and the values are close or equal to 1. A relatively high correlation coefficient (γ) value indicates that the pseudo second-order model successfully describes the kinetics of MB dye adsorption.

3.7.1 The pseudo second- order equation

The pseudo second-order adsorption kinetic rate equation is expressed as

$$dq_t/d_t = k_2(q_e-q_t)^2 \text{ ……..(6)}$$

Where: k_2 is the rate constant of pseudo second-order adsorption (g mg/min). For the boundary conditions t = 0 to t= t and $q_t = 0$ to $q_t = q_t$ the integrated form of Eq. (6) becomes:

$$1/(q_e – q_t) = 1/q_e + K_2t \text{ ……. (7)}$$

This is the integrated rate law for a pseudo second-order reaction. Equation (7) can be rearranged to obtain Eq.(8),which has a linear form:

$$t/q_t=(1/k_2q_e^2)+ ((1/q_e)t \text{ …….(8)}$$

If the initial adsorption rate (h)(mg $g^{-1}min^{-1}$) is :

$$h=k_2q_e^2 \text{ ……. (9)}$$

Equation (8) and (9) becomes,

$$t / q_t = 1 / h + 1 / q_e\, t \text{ …….. …(10)}$$

The plot of (t/q_t) and t of Eq. (10) gives a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The pseudo-second order rate constants K_2, the calculated h values, and the correlation coefficients (γ) are summarized in Table (5).At all studied initial MB dye concentrations, the straight lines with extremely high correlation co-efficient (>0.99) were obtained. From table 5, the values of the rate constant k decrease with in increasing initial MB dye concentration for AMC. This is shows that the sorption of MB dye on AMC follows pseudo second order kinetic model [24, 25].

3.7.2 The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t / d_t = \alpha \exp(-\beta q_t) \text{ ……..…..(11)}$$

Where; α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation [22]. assumed $\alpha\beta t >> t$ and by applying boundary conditions $q_t = 0$ at t= 0 and $q_t = q_t$ at t = t Eq.(11) becomes:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \text{ ……. (12)}$$

If MB dye adsorption fits with the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with a slope of $(1/\beta)$and an intercept of $(1/\beta)\ln(\alpha\beta)$. The Elovich model parameters α, β, and correlation coefficient (γ) are summarized in table 5. The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second–order kinetics models. This may be due to increase the pore or active site on the AMC adsorbent.

3.7.3 The intra particle diffusion model

The intra-particle diffusion model used here refers to the theory proposed by Weber and Morris [23] based on the following equation for the rate constant:

$$q_t = k_{id}\, t^{(1/2)} + C \text{……(13)}$$

Where k_{id} is the intra-particle diffusion rate constant (mg/g/min) and C is the constant. Since the rate limiting step is intra-particle diffusion, the graph drawn between (q_t) (mg/g) verses square root of the contact time ($t^{1/2}$) yields a straight line passing through the origin [23]. The slope of the will give the value of the intra-particle diffusion coefficient (k_{id}) and correlation coefficient (γ) indicate the fitness of this model. The value of C gives an idea about the thickness of the boundary layer. The intercept value indicates that the lines were not passing through origin, there are some other process affect the adsorption. But the correlation coefficient (γ) value is very high, so that the intra-particle diffusion takes place along with other process that may affect the adsorption. The values are given in table 5.

3.7.4 Desorption studies:

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dye can be desorbed using neutral pH water, then the attachment of the dye molecule of the adsorbent is by weak bonds. The effect of various reagents used for desorption studies. The results indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed dyes. The reversibility of adsorbed dyes in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of dye molecules by mineral acids and alkaline medium indicates that the dye was adsorbed onto the AMC through physisorption as well as by chemisorptions mechanisms.

TABLE: 1. EQUILIBRIUM PARAMETERS FOR ADSORPTION OF MB DYE ONTO AMC

M_0	Ce (Mg / L)				Qe (Mg / L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
50	4.383	3.809	3.318	3.013	91.234	92.38	93.36	93.97	91.23	92.38	93.36	93.97
100	20.75	18.32	15.04	12.69	158.50	163.4	169.9	174.6	79.25	81.68	84.96	87.31
150	46.43	41.01	35.80	31.20	207.15	218.0	228.4	237.6	69.05	72.66	76.13	79.20
200	90.31	83.44	35.80	69.05	219.37	233.1	328.4	261.9	54.84	58.28	82.10	65.47
250	140.9	132.2	76.22	115.6	218.1	235.5	347.6	268.9	43.63	47.11	69.51	53.78

TABLE: 2. LANGMUIR AND FREUNDLICH ISOTHERM PARAMETER FOR ADSORPTION OF MB ONTO AMC

Temp. (°C)	Langmuir Parameters		Freundlich Parameters	
	Q_m	b	K_f	n
30°C	231.39	0.1420	66.788	3.8027
40°C	250.05	0.1372	69.137	3.6435
50°C	415.24	0.0576	55.094	2.2974
60°C	285.37	0.1483	75.505	3.4063

TABLE: 3. DIMENSIONLESS SEPERATION FACTOR (R_L) FOR ADSORPTION OF MB ONTO AMC

(C_i)	Temperature °C			
	30°C	40°C	50°C	60°C
50	0.1235	0.1273	0.2576	0.1189
100	0.0658	0.0680	0.1478	0.0632
150	0.0448	0.0464	0.1037	0.0430
200	0.0340	0.0352	0.0798	0.0326
250	0.0274	0.0283	0.0649	0.0263

TABLE: 4. THERMODYNAMIC PARAMETER FOR THE ADSORPTION OF MB ONTO AMC

(C_0)	ΔG°				ΔH°	ΔS°
	30°C	40°C	50°C	60°C		
50	-5901.1	-6494.0	-7100.4	-7604.7	11.440	57.281
100	-3375.7	-3890.4	-4649.7	-5339.4	16.763	66.278
150	-2021.4	-2544.0	-3115.2	-3701.6	14.975	56.038
200	-489.50	-869.80	-4090.4	-1771.8	21.701	73.920
250	-645.60	-301.4	-2213.3	-419.4	18.553	59.670

TABLE: 5. THE KINETIC PARAMETERS FOR THE ADSORPTION OF MB ONTO AMC

C_0	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
50	30	109.76	0.0007	0.9897	7.917	23.17	0.0469	0.9905	0.2864	0.9919	1.4428
	40	109.39	0.0007	0.9918	8.515	28.09	0.0491	0.9926	0.2672	0.9940	1.4807
	50	108.98	0.0008	0.9889	9.225	34.62	0.0514	0.9897	0.2498	0.9911	1.5158
	60	109.93	0.0008	0.9900	9.234	33.78	0.0506	0.9908	0.2527	0.9922	1.5142
100	30	195.40	0.0003	0.9891	12.177	31.04	0.0249	0.9899	0.3179	0.9913	1.3241
	40	199.09	0.0003	0.9902	13.067	35.82	0.0252	0.9910	0.3017	0.9924	1.3646
	50	202.95	0.0004	0.9893	15.037	45.82	0.0257	0.9901	0.2796	0.9915	1.4228
	60	208.43	0.0004	0.9914	15.801	48.25	0.0251	0.9922	0.2782	0.9936	1.4392
150	30	271.57	0.0002	0.9895	12.904	28.41	0.0167	0.9903	0.3761	0.9917	1.1597
	40	276.07	0.0002	0.9888	15.183	35.63	0.0170	0.9896	0.3449	0.9910	1.2380
	50	284.12	0.0002	0.9888	17.542	43.99	0.0170	0.9896	0.3216	0.9910	1.3034
	60	290.71	0.0002	0.9907	15.138	47.05	0.0182	0.9915	0.2921	0.9929	1.3368
200	30	343.36	0.0001	0.9890	9.263	18.69	0.0126	0.9898	0.5167	0.9912	0.8093
	40	342.47	0.0001	0.9901	10.979	22.21	0.0126	0.9909	0.4721	0.9923	0.9142
	50	345.89	0.0001	0.9912	13.005	26.75	0.0126	0.9920	0.4330	0.9934	1.0102
	60	347.28	0.0001	0.9903	16.126	34.51	0.0129	0.9911	0.3881	0.9925	1.1189
250	30	540.21	0.0000	0.9927	5.837	13.52	0.0102	0.9935	0.7297	0.9949	0.3349
	40	484.39	0.0000	0.9928	7.170	15.64	0.0100	0.9936	0.6620	0.9950	0.4855
	50	489.41	0.0000	0.9914	8.095	17.34	0.0096	0.9922	0.6325	0.9936	0.5664
	60	442.81	0.0001	0.9921	10.482	21.26	0.0098	0.9929	0.5541	0.9943	0.7351

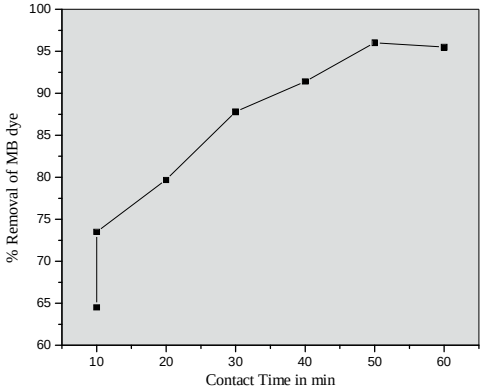


Fig: 1 -Effect of Contact Time for the Removal of MB dye
[MB]=50 mg/L; adsorbent dose=25 mg/50 ml; pH-6.5;Temp 30°C

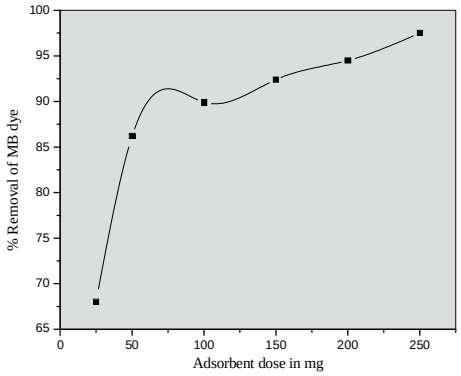


Fig. 2-Effect of adsorbent dose for the removal of MB dye
[MB]=50mg/L: Contact time=60 min: pH=6.5: Temp 30°C

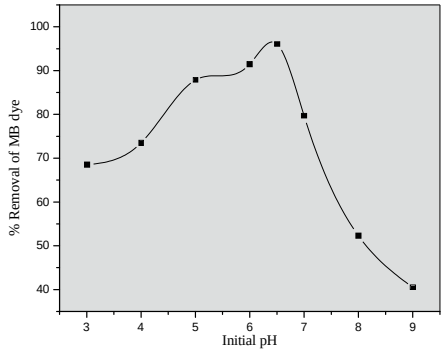


Fig. 3- Effect of Initial pH for the removal of MB dye
[MB]=50 mg/L;Temprature 30°C;Adsorbent dose=25 mg/50ml

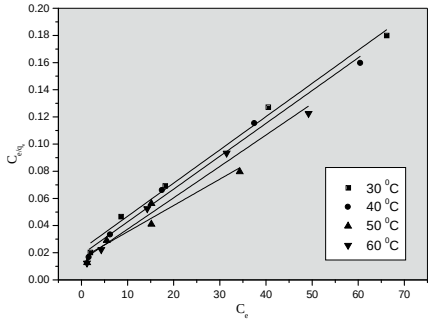


Fig. 5.17 Linear Langumuir isotherm for the removal of MB dye

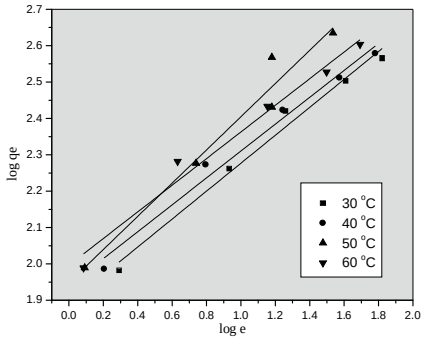


Fig:5.18- Linear Freundlich Isotherm for the removal of MB dye

IV. CONCLUSION

The present study has shown the effectiveness of using AMC in the removal of methylene blue dye from aqueous solutions. Activated Mullugo Cerviana Leaves Carbon in different forms has a great role in modern life to clean environment. Mullugo Cerviana Leaves Carbon can be good precursors for producing highly porous Activated Mullugo Cerviana Leaves Carbon by simple preparative methods. An adsorption test has been carried out for industrial pollutants (methylene blue) under different experimental conditions in batch mode. The adsorption of methylene blue was dependent on adsorbent surface characteristics, adsorbent dose, methylene blue concentration, time of contact and temperature. A study of the kinetic models on sorption showed that sorption fitted the pseudo second- order kinetics model. The ΔG^0, ΔH^0, and ΔS^0 reveal the favorability of adsorption. The thermodynamic parameters suggested that the adsorption on AMC was a spontaneous and endothermic process.

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