

A Comparative Study On The Removal Of Methyl Blue By Activated Carbon And Bentonite

Dr. S. Sivakumar

Assistant Professor,
Post Graduate Department of Chemistry,
Hajee Karutha Rowther Howdia College,
Uthamapalayam, Tamilnadu, India

V. Veeramani

Post Graduate Department of Chemistry,
Hajee Karutha Rowther Howdia College,
Uthamapalayam, Tamilnadu, India

K. Shahul Hameed

Assistant Professor,
Post Graduate Department of Chemistry,
Hajee Karutha Rowther Howdia College,
Uthamapalayam, Tamilnadu, India

Abstract: *The present study explains the removal of Methyl Blue (MB) dye from aqueous solution by the adsorbents Commercial Activated Carbon (CAC) and Bentonite Clay (BC). The adsorption batch experiments were conducted to study the effect of initial concentration, contact time, dose of adsorbent and pH. The optimum initial concentration for adsorption of dye MB on CAC was 40 ppm and 200 ppm for MB on BC. The equilibrium data for the removal of MB by CAC and BC were used in the Freundlich and Langmuir isotherm. The separation factor, R_L indicate the nature of isotherm and the feasibility of adsorption process. The adsorption of MB on CAC and BC was found to be first order with the intra-particle diffusion as one of the rate determining step. The basic pH was highly favourable for the removal of MB by adsorbents CAC and BC. The result shows that the Bentonite Clay (BC) has more adsorption capacity than Commercial Activated Carbon (CAC) in the removal of MB dye from waste water.*

Keywords: *Methyl Blue, Commercial Activated Carbon, Bentonite Clay, kinetic, Isotherm.*

I. INTRODUCTION

The production of dyes and pigments has been on increase to meet the needs of textile, paper, plastics, paints, leather and cosmetics industries [Khan *et al.*, 2004]. These industries consume more amount of water. The waste water emerge out from these industries mainly contains dyes and other chemicals. A very little amount of dyes in water are visible and they affect the eco system of water [Mishra and Tripathy 1993]. The dye should be removed from the waste water before it is discharged into water bodies. Even though so many methods are available, adsorption method [Kannan and Meenakshisundaram 2002] is the best one to remove dye from waste water. The Literature collections show that Activated

Carbon [Wang (2015), Kannan and Jeyaganesh (2001), Aysu and kucuk (2015), Danish *et al.*, (2013), Mahmoudi *et al.*, (2014), Manoj Kumar Reddy *et al.*, (2015) and Clay materials [Eren and Afsin (2009), Rytwo *et al.*, (2002), Almedia *et al.*, (2009), Yener *et al.*, (2006), Nandi *et al.*, (2009)] can be used as an adsorbent in the removal of dye from waste water. In this study, Commercial Activated Carbon (CAC) and Bentonite Clay (BC) were used as adsorbents for the removal of Methyl Blue (MB) dye from aqueous solution and their adsorption capacities were determined.

II. MATERIALS AND METHODS

Dye MB used in the present study was AR grade sample (Merck, India). Commercial Activated Carbon (CAC) was purchased from Thermo Fisher scientific and Bentonite Clay (BC) from Thomas Baker. The other chemicals and reagents employed in the present work was Laboratory reagent supplied by SD fine chemicals, Merck, India. The measuring maximum absorbance of Methyl Blue (MB) dye was analysed in UV-visible double beam spectrophotometer (model name: V-630, JASCO, Japan). The λ_{max} value for Methyl blue is 574 nm. The structure of Methyl blue is shown below (Figure 1). The adsorption studies were carried out by varying the experimental parameters (Table 1) (Kannan and Meenakshisundaram 2002).

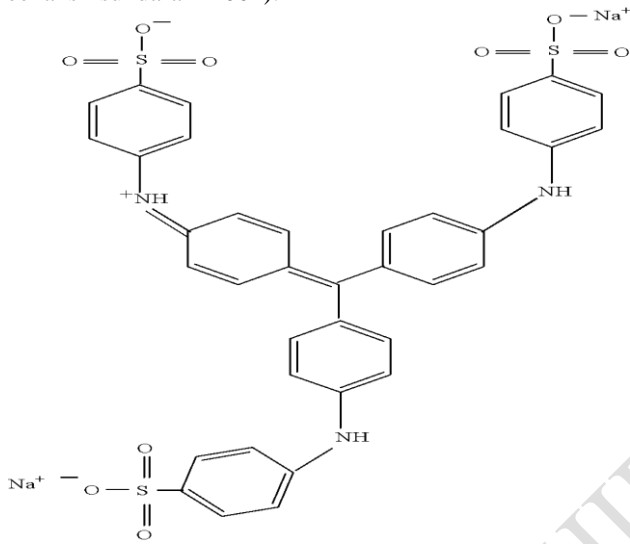


Figure 1: Structure of Methyl blue

Experimental Parameters	Initial concentration (ppm)		Contact time (min)		Dose of adsorbent (g/L)		pH	
	CAC	BC	CAC	BC	CAC	BC	CAC	BC
Initial concentration	20-60	50-350	30	30	2	2	7.4	7.4
Contact time	40	200	5-60	5-60	2	2	7.4	7.4
Dose of adsorbent	40	200	30	30	1.6-2.4	1.6-2.4	7.4	7.4
pH	40	200	30	30	2	2	2-11	2-11

Table 1: Experimental Parameters for the Adsorption of MB on CAC and BC

III. RESULTS AND DISCUSSION

EFFECT OF INITIAL CONCENTRATION

The removal of dye Methyl Blue (MB) by Commercial Activated Carbon (CAC) and Bentonite Clay (BC) was carried out by varying initial concentration of the dye and other parameters kept constant (Table 1). The percentage removal of dye MB was found to increase with decrease of initial concentration of dye (Figure 2). This was due to saturation of active sites by dye molecules at lower concentration. At an

optimum initial concentration of dye (200 ppm for BC and 40 ppm for CAC), the values of percentage removal was 82% for BC and 65% for CAC.

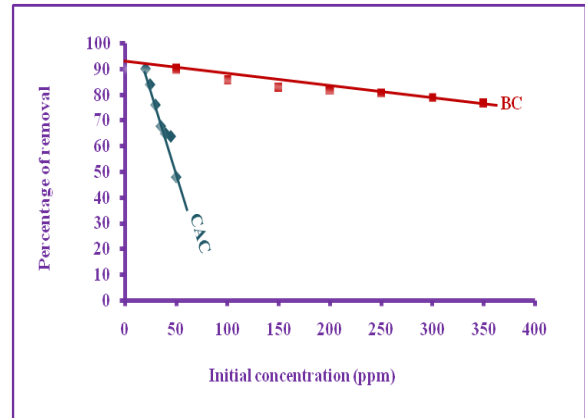


Figure 2: Effect of Initial Concentration

ADSORPTION ISOTHERM

The equilibrium data for the removal of Methyl Blue (MB) by Commercial Activated Carbon (CAC) and Bentonite Clay (BC) at 26°C were used in the Freundlich and Langmuir isotherm.

Freundlich isotherm: $\log (x/m) = \log K + (1/n) \log C_e$ -----1

Langmuir isotherm : $(C_e / q_e) = (1/Q_0 b) + (C_e / Q_0)$ -----2

K and (1/n) are the measure of adsorption capacity and intensity of adsorption respectively, q_e or (x/m) is the amount of dye adsorbed per unit mass of adsorbent (in mg g⁻¹) and b is the Langmuir constant related to energy of adsorption (in mg g⁻¹). The plot of $\log q_e$ against $\log c_e$ and (c_e/q_e) against C_e , are shown in Figures 3 and 4. The values are correlated with one another (Table 2) (Kannan and Meenakshisundaram 2002). The result indicates the applicability of these adsorption isotherms and mono layer coverage of dye molecules MB exist on the surface of CAC and BC. The separation factor or equilibrium factor R_L , is defined by the Equation

$R_L = [1/(1+bc_i)]$3

The separation factor, R_L indicate the nature of isotherm and the feasibility of adsorption of MB on CAC and BC (Table 2). The adsorption capacity (Q_0 value) of Commercial Activated Carbon (CAC) was 52.36 and adsorption capacity (Q_0 value) of Bentonite Clay (BC) was 625.

The Q_0 values show that the Bentonite Clay (BC) has more adsorption capacity than Commercial Activated Carbon (CAC) in the removal of MB dye from waste water.

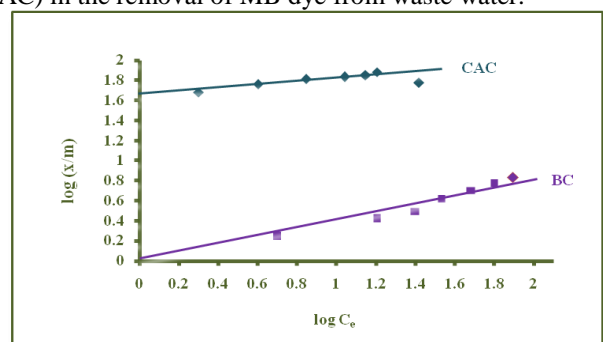


Figure 3: Freundlich isotherm

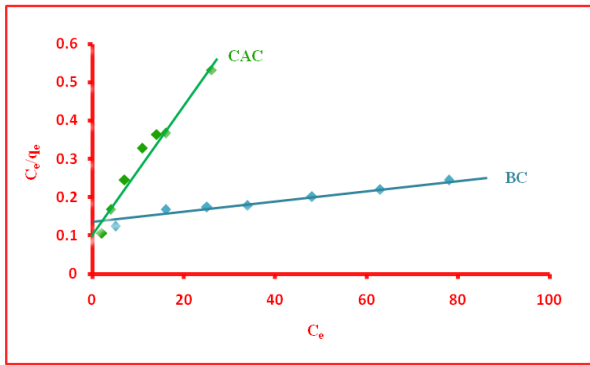


Figure 4: Langmuir isotherm

ISOTHERM MODELS	PARAMETERS	MB on CAC	MB on BC
FREUNDLICH ISOTHERM	Slope 1/n	0.2266	0.6748
	Intercept	0.6131	0.4415
	Correlation coefficient (r)	0.9871	0.9960
LANGMUIR ISOTHERM	Slope (1/Q ₀)	0.0191	0.0016
	Intercept (1/Q ₀)	0.0903	0.1217
	Correlation coefficient (r)	0.9791	0.9483
	Q ₀ (mg g ⁻¹)	52.36	625.0
	b (g L ⁻¹)	0.2115	0.1314
	R _L	0.1057	0.0366

Table 2: Results of correlation analysis on testing the applicability of adsorption isotherm for the removal of MB by CAC and BC

Amount adsorbed per unit mass of adsorbent (g L⁻¹) at equilibrium, q_t= Amount adsorbed per unit mass of adsorbent at any given time (g L⁻¹)

C_e= Concentration at equilibrium time. The results indicate the applicability of these kinetics equation and first order nature of adsorption kinetics for MB on CAC and MB on BC. The possibility of intra – particle diffusion process was explored by applying the intra –particle diffusion model.

$$q_t = k_p t^{1/2} + C \dots\dots\dots 7$$

Where, q_t is the amount of dye adsorbed at time t, C is the intercept and k_p is the intra – particle diffusion rate constant. The k_p values were calculated by using correlation analysis (Table 3).

KINETIC EQUATIONS	PARAMETERS	MB on CAC	MB on BC
Natarajan and Khalaf equation	Correlation coefficient (r)	0.9876	0.9744
	K (min-1)	0.0404	0.1076
Lagergren equation	Correlation coefficient (r)	0.9511	0.9733
	K (min-1)	0.1795	0.1566
Bhattacharya and Venkobachar equation	Correlation coefficient (r)	0.9544	0.9734
	K (min-1)	0.2619	0.1536
Intra - particle diffusion	Correlation coefficient (r)	0.9836	0.9814
	Intercept	0.5978	7.1052

Table 3: Effect of contact time on the extent of removal of MB on CAC and BC at 26±1 °C

The Intra - particle diffusion study shows that the intercept (C) value for adsorbent BC was maximum (7.1052) and minimum for CAC (0.5978). Therefore the boundary layer effect is maximum in BC and minimum in CAC.

EFFECT OF CONTACT TIME

The adsorption experiments were carried out at different contact time (5 to 60 min) at constant optimum initial concentration of dye (200 ppm for MB on BC and 40 ppm for MB on CAC) with 2 g L⁻¹ of CAC and BC. The values of percentage removal and amount of dye adsorbed exponentially increases with increase in contact time for MB on CAC and MB on BC (Figure 5).

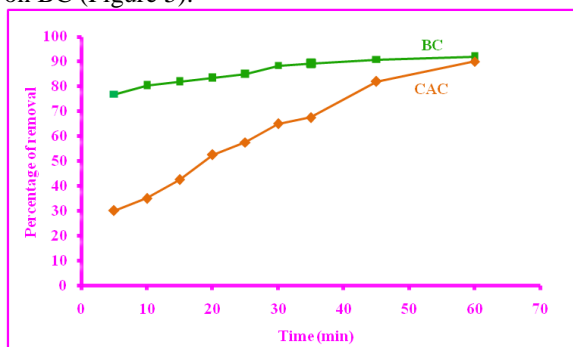


Figure 5: Effect of Contact time

The following kinetics equations were employed to study the kinetics and dynamics of adsorption of dye MB on CAC and MB on BC under the correlation of first order kinetics (Table 3) (Kannan and Meenakshisundaram 2002).

- Natarajan – Khalaf equation : $K = (2.303/t) \log (C_0/C_t)$ ----- 4
- Lagergren equation : $\log (q_e - q_t) = \log q_e - (k/2.303) t$ -----5
- Bhattacharya – Venkobachar equation : $\log [1 - U(t)] = - (k/2.303) t$ -----6

Where, $U(t) = [(C_0 - C_t)/(C_0 - C_e)]$

C₀ = Initial concentration of dye solution (in ppm), C_t= Concentration of dye solution at various time (in ppm), K = First order rate constant for adsorption of dyes (in min⁻¹), q_e=

EFFECT OF DOSE OF ADSORBENT

The percentage of removal of dye Methyl Blue (MB) by adsorption increases with increase in the dose of adsorbents CAC and BC (Figure 6). This may be due to the increase in the availability of the active sites on the surface of the adsorbents CAC and BC. The percentage removal of MB at the optimum dose of BC was found to be 76%. The percentage removal of MB at the optimum dose of CAC was found to be 50%.

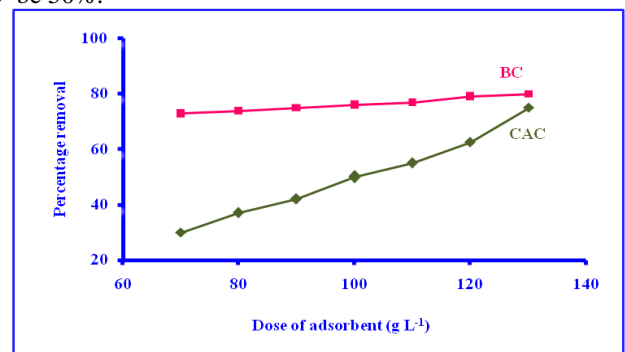


Figure 6: Effect of dose of adsorbent

EFFECT OF pH

The effects of initial pH on adsorption process for dye Methyl Blue (MB) on adsorbents Commercial Activated Carbon (CAC) and Bentonite Clay (BC) were studied at

different pH values range from 2-11 (Table 2). The basic pH is highly favourable for the removal of MB by adsorbents CAC and BC (Figure 7). The maximum percentage removal of MB by CAC was found to be 88 % at pH 11. The maximum percentage removal of MB by BC was found to be 96% at pH 11.

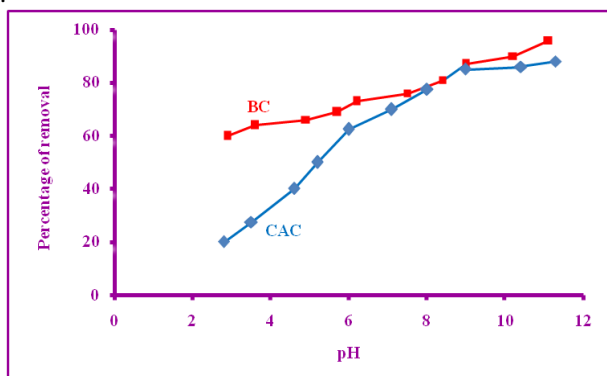


Figure 7: Effect of pH

IV. CONCLUSION

The equilibrium data for the removal of MB by CAC and BC were fitted in the Freundlich and Langmuir isotherm. The adsorption was found to be first order with the intra-particle diffusion as one of the rate determining step. The basic pH was highly favourable for the removal of MB by adsorbents CAC and BC. The percentage of removal of dye MB increases with the increase in dose of adsorbents CAC and BC. The adsorption capacity (Q_0 value) of Commercial Activated Carbon (CAC) was 52.36 and adsorption capacity (Q_0 value) of Bentonite Clay (BC) was 625. It is inferred that the Bentonite Clay (BC) has more adsorption capacity than Commercial Activated Carbon (CAC) in the removal of MB dye from waste water.

ACKNOWLEDGEMENT

The authors are very much thankful to the principal, secretary and correspondent, president and managing committee of Hajee Karutha Rowther Howdia College, Uthamapalayam for providing the necessary facilities to carry out this investigation successfully.

REFERENCES

[1] Khan, T. A., Singh, V. V., & Kumar, D. (2004). Removal of some basic dye from artificial textile waste water by adsorption on Akash Kinari coal. *J. Sci. Ind. Res*, 63, 355- 364.

[2] Mishra, G., & Tripathy, M.A. (1993). Critical review of the treatments for decolourization of textile effluent. *Colourage*, 40, 35–38.

[3] Kannan, N., & Meenakshisundaram, M. (2002). Adsorption of congo red on various activated carbons- a comparative Study. *Water Air Soil Pollut*, 138, 289–305.

[4] Wang, Z. (2015). Efficient adsorption of dibutyl phthalate from aqueous solution by activated carbon developed from phoenix leaves. *Int. J. Environ. Sci. Technol*, 12, 1923 - 1932.

[5] Kannan, N., & Jeyaganesh, R.V. (2001). Studies on the removal of malachite green from aqueous solution of mixed adsorbent. *Indian J. Env. Prot*, 23(2), 127-133.

[6] Aysu, T., & Kucuk, M.M. (2015). Removal of crystal violet and methylene blue from aqueous solutions by activated carbon prepared from *Ferula orientalis*. *Int. J. Environ. Sci. Technol*, 12, 273-284.

[7] Danish, M., Hashim, R., Mohamad Ibrahim, M. N., & Sulaiman, O. (2013). Characterization of physically activated acacia mangium wood-based carbon for the removal of methyl orange Dye. *Bio Resources*, 8, 4323-4339.

[8] Mahmoudi, K., Hamdi, N., & Srasra, E. (2014). Preparation and characterization of activated carbon from date pits by chemical activation with zinc chloride for methyl orange adsorption. *J. Mater. Environ. Sci*, 5, 1758-1769.

[9] Manoj Kumar Reddy, P., Krushnamurty, K., Mahammadunnisa, S. K., Dayamani, A. & Subrahmanyam, C. H. (2015). Preparation of activated carbons from bio-waste: effect of surface functional groups on methylene blue adsorption. *Int. J. Environ. Sci. Technol*, 12, 1363-1372.

[10] Eren, E., & Afsin, B. (2009). Removal of basic dye using raw and acid activated bentonite samples, *J. Hazard. Mater.* 166, 830–835.

[11] Rytwo, G., Tropp, D., & Serban, C. (2002). Adsorption of diquat, paraquat and methyl green on zeolite: experimental results and model calculations. *Appl. Clay Sci*, 20, 273–282.

[12] Almedia, C.A.P., Debacher, N.A., Downs, A.J., Cottet, L. & Mello, C.A.D. (2009). Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *J. Colloid Interface Sci*, 332, 46–53.

[13] Yener, J., Kopac, K., Dogu, G., & Dogu, T. (2006). Adsorption of Basic Yellow 28 from aqueous solutions with clinoptilolite and amberlite, *J. Colloid Interf. Sci*, 294, 255–264.

[14] Nandi, B. K., Goswami, A., & Purkait, M. K. (2009). Adsorption characteristics of brilliant green dye on kaolin. *J. Hazard. Mater*, 161, 387–395.