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ISOTHERM AND KINETIC STUDIES ON THE ADSORPTION OF COMMASSIE BRILLIANT BLUE ON COMMERCIAL ACTIVATED CARBON AND KAOLIN

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ABSTRACT

Batch mode adsorption of Coomassie brilliant blue dye on Commercial Activated Carbon and kaolin were carried out with various experiment parameters like initial concentration, contact time, dose and pH. Adsorption isotherm models like Langmuir and Freundlich were applied to test the equilibrium data. Both isotherms are well fitted. The monolayer adsorption capacities were found to be 73.62 mg g^{-1} for commercial activated carbon and 41.31 mg g^{-1} for kaolin. The separation factors R_L were found to be 0.1838 for kaolin and 0.1879 for commercial activated carbon, indicating favorable adsorption. Various kinetic equations like Natarajan – Khalaf , Lagergren and Bhattacharya – Venkobachar were tested for kinetic study. Intra particle diffusion model showed boundary layer effect and larger intercepts indicate greater surface adsorption. The percentage removal of dye Coomassie brilliant blue decreases with increases in pH. The adsorption maximum was observed at pH 5.

Keywords: Commercial Activated Carbon (CAC), kaolin, Coomassie brilliant blue, Adsorption isotherm.

1. INTRODUCTION

The textile industry consumes a substantial amount of water in its manufacturing processes used mainly in the dyeing and finishing operations of the plants. The wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition. In addition, the increased demand for textile products and the proportional increase in their production, and the use of synthetic dyes have together contributed to wastewater becoming one of the substantial sources of severe pollution problems in current times. Color is usually the first contaminant to be recognized in a wastewater because a very small amount of synthetic dyes in water (< 1 ppm) are highly visible, affecting the aesthetic merit, transparency and gas solubility of water bodies. They prevent the sunlight entering water, thereby interfering with the aquatic species growth and hindering photosynthesis [1,2]. Additionally, they can have acute and/ or chronic effects on organisms depending on their concentration and length of exposure. Dyes lead to number of environmental and health hazards. Some of the dyes and their reaction products are highly carcinogenic [3]. The complex structures of the most dyes and their high recalcitrance to degradation are considered a great challenge for decolorization and complete mineralization [4]. Hence the removal of dyes from wastewater is environmentally essential.

Several physicochemical methods have been proposed to remove dyes from textile waste waters. Methods like sedimentation and flotation, do not remove color effectively without simultaneous chemical treatment. Processes such as membrane separation,

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coagulation and ion exchange are also used to remove color from dye wastewater, but these are not feasible due to high cost involved [5]. Activated carbon adsorption is an effective method for removing various organic contaminants and textile dyes. However, the high volume of effluent produced by textile industries generates greater expense during the regeneration of the activated carbon. Substitutes for activated carbons using low-cost alternative adsorbents have been proposed based on their availability as either natural or industrial/agricultural waste or by-products [6]. Natural clays are gaining importance among low-cost adsorbents because of their easy and abundant availability and high adsorption capabilities. There are a large number of clays like montmorillonite [7], bentonite [8], clinoptiolite [9] kaolin [10] and zeolite [11], which are widely used to remove dyes from wastewater. In the present study kaolin is used for the removal of Coomassie brilliant blue.

2. EXPERIMENTAL

2.1 Materials

The sample of Coomassie brilliant blue R 250 (C.I.No.42660) dye was used as an adsorbate. The dye sample (figure 1) was obtained from Thomas Baker chemicals Mumbai. Commercial Activated Carbon (CAC) and kaolin were used as adsorbents. CAC and kaolin were supplied by Merck and Thomas Baker chemicals Mumbai respectively. The other chemicals and reagents employed in the present work was laboratory reagents supplied by SD fine chemicals, E Merck, India. ELICO CL 223 photocolorimeter was used for measuring optical densities at 595nm (λ_{max}).
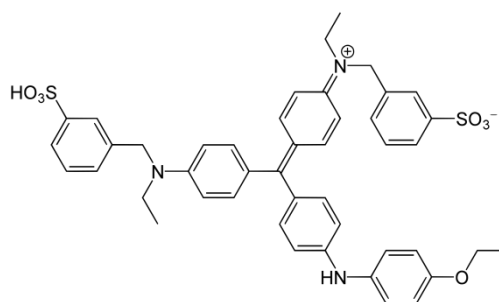
Figure1: Structure of Coomassie brilliant blue

2.2 Adsorption experiment

Stock solution of dye (1000 ppm) was suitably diluted to the required initial concentration of dye with distilled water. Batch type adsorption experiments were carried out in a mechanical shaker and shaken vigorously for a required period of contact time at room temperature.

Adsorption of the Coomassie brilliant blue dye on Commercial Activated Carbon (CAC) and kaolin were studied under four different experimental conditions by varying the following experimental parameters with other parameters kept constant (Table 1).

1. Initial concentration of the dye
2. Contact time
3. Dose of CAC and kaolin
4. Initial pH of the dye solution

Table 1: Experimental conditions of adsorption experiments for the removal of Coomassie brilliant blue

variation	Initial concentration mg/L	Contact time min	Dose of adsorbent g/L	Initial pH
Initial concentration mg/L				
CAC	40-100	30	1	7.8
kaolin	40-55	30	10	7.8
Contact time				
CAC	60	5-60	1	7.8
kaolin	45	5-60	10	7.8
Dose of adsorbent				

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CAC	60	30	0.6-1.4	7.8
kaolin	45	30	6-14	7.8
Initial pH				
CAC	60	30	1	5-9
kaolin	45	30	10	5-9

In all the batch adsorption experiments, the extent of removal of dye in terms of the values of percentage removal of dye and amount adsorbed (q in mg g^{-1}) have been calculated using the following relationships.

Percentage of removal = $\dfrac{C_i - C_e}{C_i} \times 100$

Amount of dye adsorbed = $\dfrac{x}{m} = \dfrac{C_i - C_e}{m}$

Where

C_i = initial concentration of dye (ppm)

C_e = equilibrium concentration of dye (ppm)

x = concentration of dye adsorbed (mg L^{-1})

m = mass of adsorbent (g L^{-1})

A standard curve is drawn by plotting optical density against concentration, a straight line is obtained. From this line the concentration of dye solution before and after adsorption experiment is calculated.

3. RESULT AND DISCUSSION

3.1 Effect of initial concentration

Exactly 10g/L of kaolin and 1g/L of commercial activated carbon were used as adsorbents with 50mL of dye solution were kept constant (initial concentrations of dye 40-100 ppm for CAC and 40-55 ppm for kaolin). The dye solutions were placed in a mechanical shaker and shaken vigorously for 30 minutes. The percentage removal decreases with the increase in dye concentration (figure 2). The optimum initial concentration for CAC and kaolin are 60 ppm and 45 ppm respectively. For lower concentrations, the total removal was caused by the large number of vacant sites available for the lower number of dye molecules, therefore, the driving force of the concentration gradient between adsorbate in solution and adsorbate in the adsorbent increased [12].
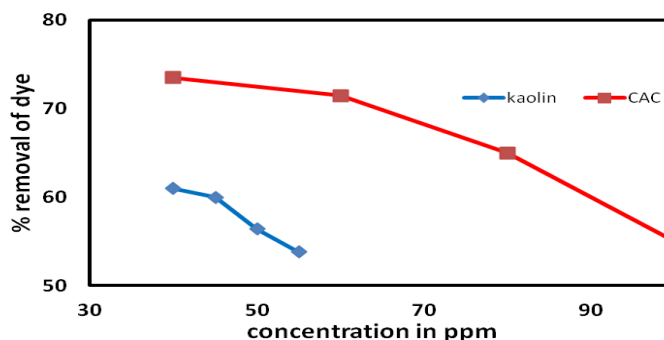
Figure 2: Effect of initial concentration of the adsorption of Coomassie brilliant blue dye on CAC and kaolin

3.2 Adsorption isotherm

The study of adsorption isotherm has been of important and significant in the waste water treatment by adsorption technique [13], as they provide an approximate estimation of the adsorption capacity of the adsorbent. The equilibrium data for the removal of Coomassie brilliant blue dye by CAC and kaolin were used in the Freundlich and Langmuir isotherm [14].

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

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

The data obtained from the adsorption experiments were fitted into Freundlich and Langmuir isotherms respectively by plotting log x/m against log C_e and (C_e/q_e) against C_e. They are found to be linear (figures 3 and 4) indicating the formation of monolayer adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The monolayer adsorption capacities of the adsorbents (Q_0 values) are found to be in the following order (Table 2).
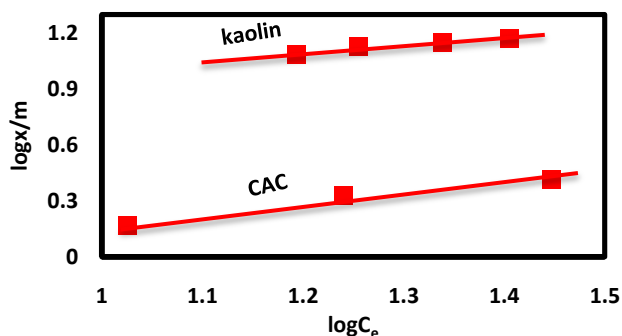
kaolin < CAC

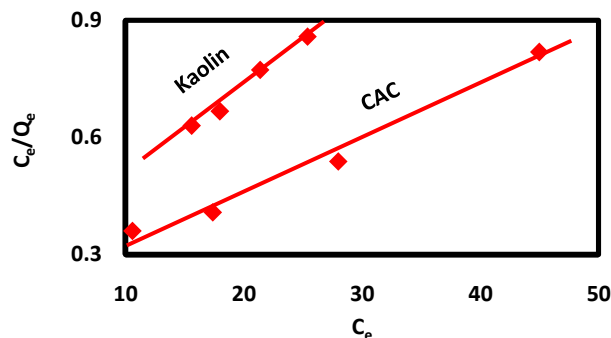**Figure 3. Freundlich adsorption isotherm**

Figure 4. Langmuir adsorption isotherm

Further the essential characteristic of the Langmuir isotherm is the prediction of possibility of the adsorption process, which is expressed in terms of the dimensionless constant 'R_L'. The separation factor, R_L indicate the nature of isotherm and the feasibility of adsorption process as, unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<<R_L<<1$) and irreversible ($R_L=0$). Adsorption of Coomassie brilliant blue on CAC and kaolin are found to be favorable. The data were given in the Table 2.

Table 2. Result and correlation analysis for the adsorption of Coomassie brilliant blue dye by CAC and kaolin

Parameters	Coomassie brilliant blue on CAC	Coomassie brilliant blue on kaolin
Freundlich isotherm		
Slope 1/n	0.0137	0.3735
Intercept	0.0478	0.6493
Correlation coefficient (r)	0.9872	0.9686
Langmuir isotherm		
Slope ($1/Q_0$)	0.2020	0.0242
Intercept ($1/Q_0$)	0.1884	0.2453
Correlation coefficient (r)	0.9908	0.9945
Q_0 (mg g^{-1})	73.62	41.31
b (g L^{-1})	0.0721	0.0987
R_L	0.1879	0.1838

3.3 Effect of contact time

In order to study the kinetics and dynamics of adsorption of Coomassie brilliant blue dye on CAC and kaolin, adsorption experiments were carried out at different contact time (5 to 60 min) at constant optimum initial concentration of dye (60ppm for CAC and 45ppm for kaolin) with 1 g L^{-1} of CAC and 10 g L^{-1} of kaolin. The values of percentage removal and amount of dye adsorbed exponentially increases with increase in contact time (figure 5). The removal of dye by adsorption on CAC and kaolin were found to be rapid at the beginning and then become slow with increase in contact time.
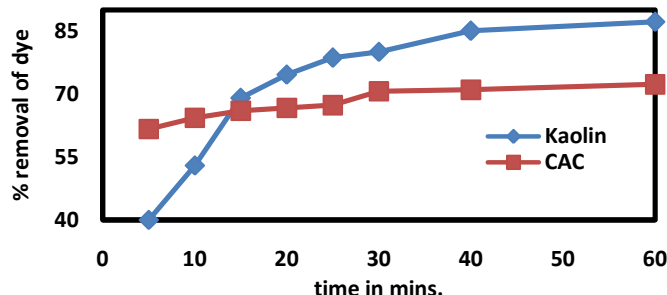
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Figure 5. Effect of Contact time

3.4 Kinetics and Dynamics of adsorption

The following kinetics equations were employed to study the kinetics and dynamics of adsorption of Coomassie brilliant blue on CAC and kaolin.

Natarajan -Khalaf equation: $k = (2.303/t) \log (C_o/C_t)$ -----------------(4)

Lagergren equation: $\log (q_e\text{-}q_t) = \log q_e - (k/2.303)\ t$ -----------(5)

Bhattacharya – Venkobachar equation : $\log [1- U (t)] = - (k/2.303)\ t$ -------------(6)

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

C_o = 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 = Amount of dye adsorbed per unit mass of adsorbent (mg/g) at equilibrium.

q_t = Amount of dye adsorbed per unit mass of adsorbent at any given time (mg/g)

C_e = Concentration at equilibrium time (mg L^{-1}).

The values of $\log (C_o - C_t)$, $\log (q_e – q_t)$ and $\log [1- U (t)]$ were plotted against time. The kinetic plots are found to be linear (figures 6 to 8). These values are also noted to be linearly correlated to each of other as evidenced from the values of correlation coefficients close to unity (Table 3). The results indicate the applicability of these kinetic equations and first order nature of adsorption kinetics.
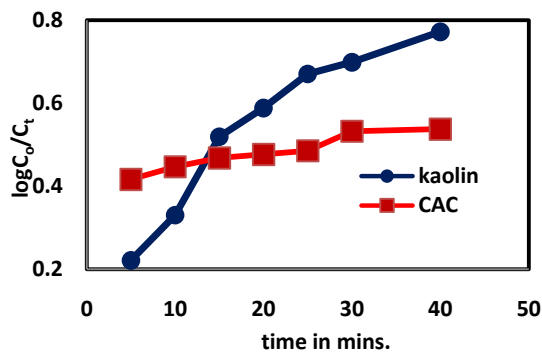

Figure 6. Natarajan-Khalaf plot

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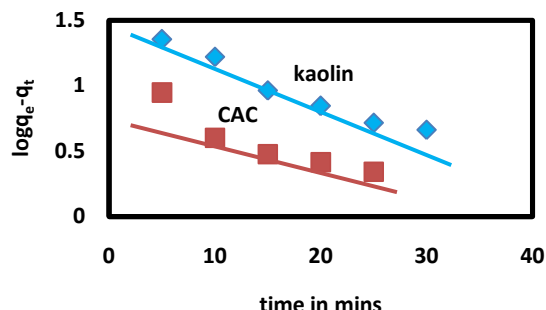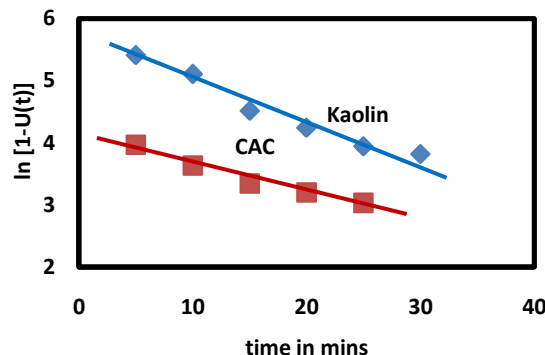*(Scholarly Peer Review Publishing System)*

Figure 7. Lagergren   plot

Figure 8. Bhattacharya –Venkobachar plot

3.5 Intra-particle diffusion study

The possibility of intra particle diffusion process was explored by applying the intra particle diffusion model [15].

$$q_t = k_p t^{1/2} + C \text{ -------------------- (7)}$$

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 intra particle diffusion plot is given in the figure 9. The r-values were found to be close to unity, indicating the application of this model. This revealed the presence of the intra-particle diffusion process [16]. The k_p values were calculated by using correlation analysis. The values of intercept (table 3) give an idea about the boundary layer effect. The greater the value of the intercept, the greater is the boundary layer effect.

Table 3. Kinetics and dynamics of adsorption of Coomassie brilliant blue dye on CAC and kaolin

S.No	Parameters	CAC	kaolin
I	Natarajan –Khalaf equation		
	k (min^{-1}.)	0.0769	0.0609
	Correlation coefficient (r)	0.9665	0.9490
II	Lagergren equation		
	k (min^{-1}.)	0.2094	0.0887
	Correlation coefficient (r)	0.9269	0.9812
III	Bhattacharya- Venkobachar equation		
	k (min^{-1}.)	0.2094	0.1809
	Correlation coefficient (r)	0.9832	0.9811
IV	Intra particle diffusion		
	Correlation coefficient (r)	0.9566	0.9872
	Intercept (C)	1.7135	1.1713

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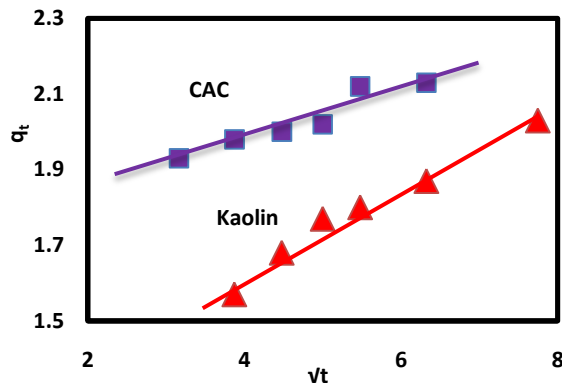*(Scholarly Peer Review Publishing System)*

Figure 9. Intra particle diffusion plot

3.6 Effect of dose of adsorbent

The effect of dose of the adsorption of Coomassie brilliant blue dye on CAC and kaolin were studied by varying the dose of adsorbents CAC and kaolin. The dose of adsorbent 0.6 to 1.4 g L^{-1} of CAC and 6 to 14 g L^{-1} of kaolin were used. The percentage of removal of Coomassie brilliant blue dye by adsorption on CAC and kaolin increases with increase in the dose of CAC and kaolin at the optimum contact time (figures 10 and 11). This may be due to the increase in the availability of the active sites on the surface of the adsorbent CAC and kaolin. The decrease in adsorption density with an increase in the adsorbent dose is mainly because of unsaturation of adsorption sites through the adsorption process [17].
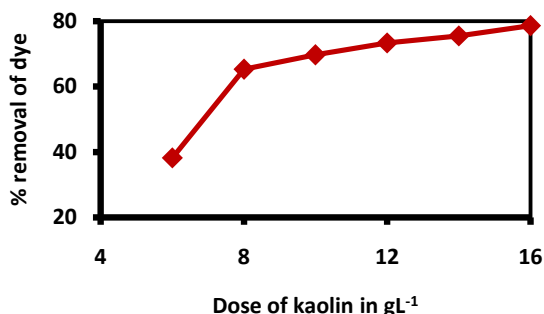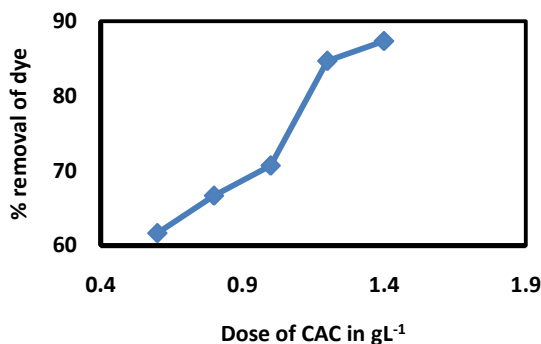

Figure 10. Effect of dose of kaolin

Figure 11. Effect of dose of CAC

3.7 Effect of initial pH

The initial pH of the medium plays a vital role in the adsorption of dye. The percentage removal decreases with increase in pH for adsorption of dye Coomassie brilliant blue on CAC and kaolin (Figure 12). The adsorption of this dye on CAC and kaolin was found to be highly pH dependent.
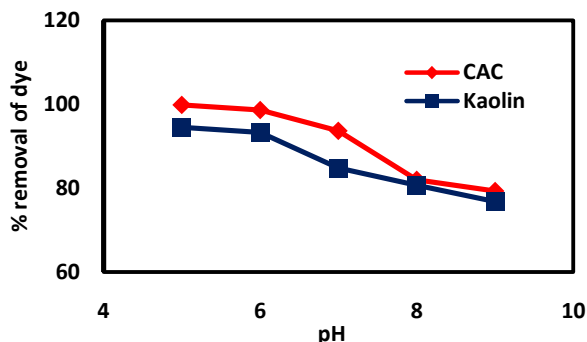
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Figure 12. Effect of pH

The initial pH affects the charge on the surface of the adsorbent CAC, altering its capability to adsorb dye molecule. In addition, the pH also affects the charge and nature of the surface functional groups present on adsorbents. The percentage removal of dye Coomassie brilliant blue decreases with increases in pH. Similar experimental details have been reported [18]. The adsorption maximum was observed at pH 5 (99.9).This is due to the acidic nature of dye Coomassie brilliant blue. Adsorption is greater at lower pH. As the pH decreases, the number of positively charged sites increases and favours the adsorption of Coomassie brilliant blue anion by electrostatic attractions.

4. CONCLUSION

The dye Coomassie brilliant blue is found to adsorb strongly on the surface of CAC and kaolin. The equilibrium adsorption is practically achieved in 30 minutes. The result indicates that intra-particle diffusion process is more important in adsorption process. Langmuir and Freundlich adsorption isotherms were tested and found to be applicable. Mono layer coverage of dye molecules exist on the surface of this system. The adsorption process is found to be first order with intra-particle diffusion as one of the rate determining steps. From this work, it can be concluded that both CAC and kaolin can be used as adsorbents for the removal of colour from wastewater in general and for the removal Coomassie brilliant blue dye in particular.

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