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Research Article

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Kinetics of adsorption of Methylene blue dye onto commercial activated carbon

S. Ayya Adhi[a], M. Kiruthiga[b], A. Akash[a], S. Azhahendhiran[a], K. Anitha[a]*
[a]* Department of Chemistry, Poompuhar College (Autonomous), Melaiyur, Tamilnadu, India.
[b] Department of Chemistry, Government College foe women (Autonomous), Kumbakonam, Tamilnadu, India.
*Corresponding Author e- mail id: krhd944@gmail.com@gmail.com

Abstract

The commercial activated carbon (CAC) was used as adsorbent for the adsorption of the adsorption of Methylene blue dye. Batch mode adsorption experiments were carried out for the removal of Methylene blue dye from aqueous solution using CAC. Influence of the parameters such as dose of the adsorbent, agitation time, initial dye concentration, pH of the solution on adsorption were studied. Kinetics of the system was studied with linearised forms of Legergren, Ho and Webber Morris models. The SSE % result revealed that present system followed pseudo second order kinetics equation with the intra particle diffusion as the rate determining step.

Keywords: Adsorption; commercial activated carbon; Kinetics; pH effect; methylene blue dye.

1. Introduction

Water pollution is the contamination of a water body by chemical, physical, radioactive or microbial substances [1]. Widely varied techniques are available to remove contaminants like fine solids, micro-organisms and some dissolved inorganic and organic materials, or environmental persistent pharmaceutical pollutants. The choice of method will depend on the quality of the water being treated, the cost of the treatment process and the quality standards expected of the processed water.[2]

Adsorption using low-cost activated adsorbents has been effectively applied to remove dyes and heavy metals from aqueous solutions. Activated carbon is the most used adsorbent in adsorption columns. There have been attempts by researchers to explore the adsorption potential of non-conventional, naturally-occurring agricultural residues. An extensive literature survey reveals that commercial activated carbon has been widely used in research and industrial processes. With these backgrounds, an idea has been developed to

remove MB dye using commercial activated carbon. [3].

With these background the present investigation is carried out with the following objectives

- To study the kinetic aspects of the adsorption process and intra particle diffusion using different kinetic models such as Legergren, Ho and Weber Morris.

1. **Adsorbent – Commercial Activated Carbon**

2. **Adsorbate - Methylene Blue**: A cationic dye and it has strong tendency to get adsorbed onto activated carbon. The present study may bring light on the efficiency of the prepared waste material CAC activated carbon as an efficient adsorbent.

2. Experimental Methods

2.1 Batch adsorption studies

Equilibrium studies were carried out in a series of Iodine flasks of 250 mL capacity containing the 50 ml adsorbate solution of desired concentration and required amount of adsorbent. Desired pH of the solution was brought by adding Con. HCl or 6N NaOH solution drops. These flasks were agitated in a temperature controlled orbital shaker (Orbit, India) at 180 rpm for the desired contact time. Then the flasks were set aside for few minutes and the filtered in Whatmann filter paper (no.40). First 5 mL was discarded because filter paper may adsorb some adsorbates; next 5 mL was collected for the determination of concentration. Concentrations of the solutions were estimated by spectrometrically using standard procedures. Concentrations of the solutions were suitably diluted and measured using Systronics double beam UV-visible spectrophotometer: 2202. The wavelengths used for the chosen dyes are given in the Table 2.1. [4, 5]

Table 2.1 Wavelength (nm) for dye ions

Adsorbates	Absorption maxima
Methylene Blue dye ions	663nm

Experiments were conducted to find the optimum pH for each adsorbate. Then optimum dose was found by carrying out the experiment having the optimum solution pH. Next experiments were conducted with dose of CAC ranging from 10 to 100 mg/50 mL with the lower initial concentration of adsorbate solutions (say 10 or 20 mg/L). Initial concentrations of adsorbates which give percentage of removal in between 60 and 80 were chosen for further study where the agitation time was 1 h at 305K temperature and at optimum solution pH already fixed. Data obtained from the effect of contact time experiment was fitted into Lagergren's pseudo first order kinetic equation, Ho's pseudo second order kinetic equation. Best suitable kinetic equation was selected using normalized standard deviation statistical tool.

Experimental parameters such as initial adsorbate concentration, solution pH, carbon dosage and temperatures adopted in this present wok were listed in the Table 2.2.[6].

Table 2.2 Experimental parameters

Time (min)	5 to 180
pH	2, 4, 6, 8 & 10
Concentration (mg/L)	75, 100, 125 & 150
Adsorbent dose (mg/50 mL)	10 to 100
Temperature (K)	305, 315. 325 & 335

Range of pH of the dye solutions were decided depending upon the color change of dye with respect to pH of the solution. Initial concentration range for dye solutions was 10 to 40 mg/L.

2.2 Data processing tools:

2.2.1 Pseudo-first-order model

The pseudo first order adsorption kinetic can be described by the equation as below suggested by Legergren.[7, 8]

$$\log (q_e - q_t) = \log q_e - k_1 / 2.303 \times t \quad \ldots\ldots\ldots\ldots 1$$

Where q_e and q_t are the amount of adsorbate adsorbed (mg/g) at equilibrium and at time t (min) respectively and k_1 is the pseudo first order rate constant of adsorption (min^{-1}). The plot is drawn between $\log (q_e - q_t)$ versus t to get a straight line. The values k_1 and calculated q_e can be obtained from the slope and intercepts of the straight line respectively.

2.2.2 Pseudo-second-order model

The pseudo second order adsorption kinetic equation is given below as suggested by Ho.[9]

$$t/q_t = 1/h + 1/q_e\, t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where $h = k_2 q_e^2$ ($mg\ g^{-1}\ min^{-1}$)can be regarded as the initial adsorption rate as $t \rightarrow 0$ and k_2 is the pseudo first order rate constant of adsorption ($g\ mg^{-1}\ min^{-1}$). The plot is drawn between t/q_t versus t to get a straight line. The values k_2 and h can be obtained from the slope and intercepts of the straight line respectively.

2.2.3 Intra-particle diffusion

The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting the experimental data in an intra-particle diffusion kinetic model. According to Weber and Morris, an intra-particle diffusion coefficient k_p is defined by the equation:

$$q_t = k_p\, t^{0.5} + C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

Where k_p ($mg/g/min^{0.5}$) is the intra particle diffusion rate constant and C is the thickness of the boundary film. Weber and Morris plot is drawn between q_t and $t^{0.5}$ to understand the intra particle diffusion. The k_p and C values were obtained from the slope and intercept of the linear portions of the curves. [10]

2.2.4 Test for kinetics models

Best fitting kinetic model for a system can be determined by using the statistical tool called Mean of sum of error squares (SSE). This can be evaluated by the following formula.

$$MSSE = \sqrt{\sum[(q_e)_{exp} - (q_e)_{cal}]^2 / N} \quad \ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where N is the number of data points, $(q_e)_{exp}$ is the experimental q_e and $(q_e)_{cal}$ is the calculated q_e.

3. Results and Discussion

3.1 Effect of adsorbent dosage

Adsorbent dosage is one of the important parameters in adsorption processes because amount of adsorbate adsorbed vary with the dosage of an adsorbent for a given in initial concentration of the adsorbate under a given set

of operating conditions. Figure 3.1 showed the effect of adsorbent dosage on adsorption of MB dye ions. As can be seen in this figure, increase of dosage increases the percentage of removal of adsorbate from the solution. The percentage of removal increased from 32.10 to 99.80% for MB dye ions, for the increase of dosage of 10mg / 50Ml.

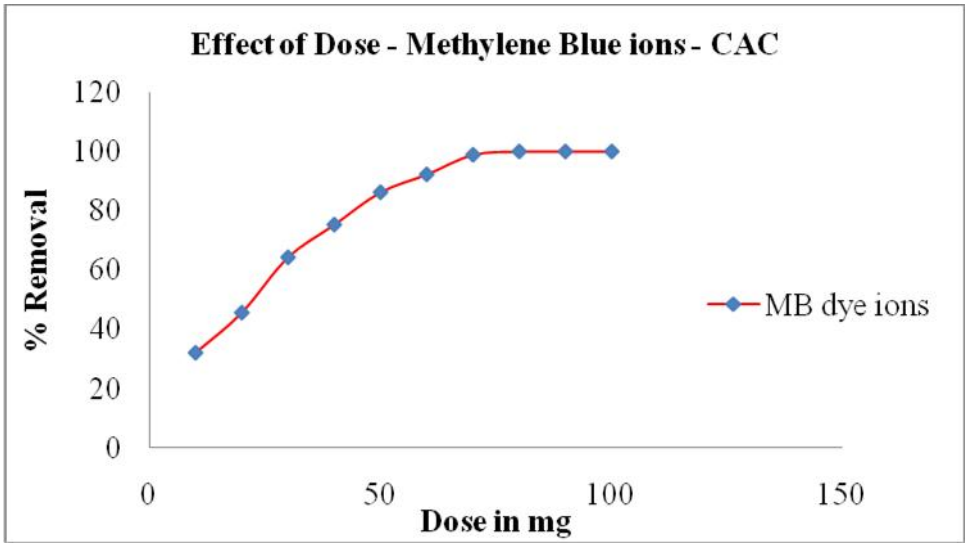

Figure 3.1 Table – 3.1Effect of dose for Methylene Blue ions onto CAC (CT = 60 min)

3.2 Effect of contact time

The contact time was evaluated as one of the most important factors affecting adsorption efficiency. The effect of contact time on the percentage removal from aqueous solution was studied by taking 75, 100, 125 and 150 mg/L of MB dye ion solutions as initial concentrations [11].

At the initial stage, the ratio of surface area of the adsorbent to the amount of solute in liquid phase is high and hence the concentration driving force makes soluteto rush towards the adsorbent surface. As the time increases the above ratio begins to decrease due to adsorption and hence the rate of adsorption becomes slow.

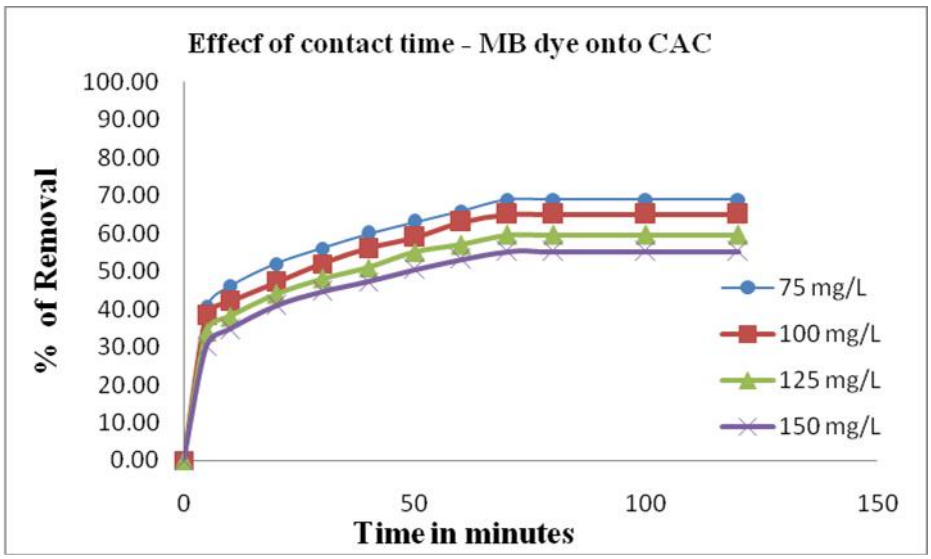

Figure 3.2

3.3 Effect of pH

The pH of the adsorbate solutions has been identified as the most important parameter governing sorption of adsorbates on different adsorbents. This is partly due to the fact that hydrogen ions themselves are a strong competing sorbate and partly to the fact that the influence on the chemical speciation of adsorbates. The effect pH of solution was studied by taking pH of the adsorbate solution from 2 to 12.

Figure 3.3 shows the effect of initial pH of the dye solution on the removal of MB dye ions. The percentage of removal was found to increase as the pH of the solution increased. Basically, Methylene blue and other cationic dyes produce an intense molecular cation (C^+) in neutral and alkali medium and reduced ions (CH^+) in acidic medium. At lower pH, positively charged surface of the adsorbent render electrostatic repulsion towards dye cations. [12]

Hence dye removal from the solution was low at lower pH, when the pH of the solution increased, the positive charge on the surface of the adsorbent decreased. Further the competition with the H^+ ion for the adsorbent cite also decreased as the H^+ ion concentration decreased with the rise of pH of the solution and hence the percentage adsorption increases with an increase of pH solution. At the solutionpH >pH_{ZPC}, the adsorbent surface was negatively charged and favor's an uptake of cationic dyes due to the increased electrostatic force of attraction. At pH 7, surface of adsorbent was negatively charged to its maximum extent. Further an increase in pH did not increase surface charge intensity as well as adsorption capability. Therefore, pH 7 was used for adsorption studies.

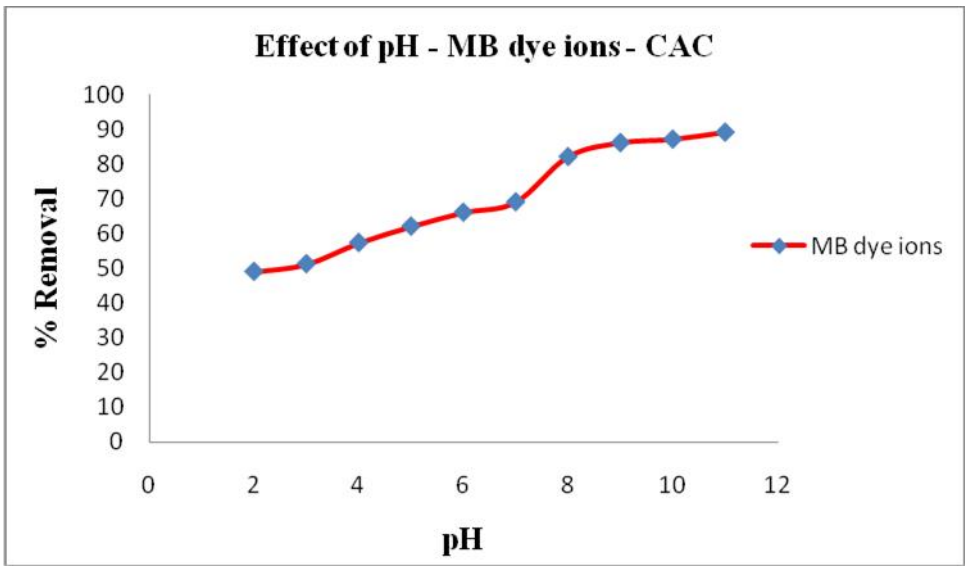

Figure 3.3

3.4 Kinetic study

3.4.1 Kinetic study on Methylene Blue dye ions adsorption

The plots drawn for the pseudo first order kinetic were shown in figure 3.4 and the constants obtained from pseudo first order were given in table 3.1. The pseudo first order rate constant k_1 and the calculated adsorption capacity $q_{e(cal)}$ from pseudo first order kinetic model were given in table 3.1. The plots drawn for the pseudo second order kinetic were shown in figure 3.5 and the pseudo second order rate constant k_2 and the calculated adsorption capacity $q_{e(cal)}$ from pseudo second order kinetic model were given in table 3.2. [13]

Table –3.1 Pseudo first order Kinetics results for the adsorption of MB dye ions onto CAC [pH = 7; Dose = 30 mg/ 50 mL; Contact time = 120 min; Temp=303K]

Concentration (mg/L)	Pseudo First Order Kinetics					
	$k_1 \times 10^{-2}$ (min^{-1})	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	Δq_e	R^2	MSSE
75	0.0359	44.48	51.75	07.26	0.9788	18.98
100	0.0348	39.78	65.00	25.21	0.9936	
125	0.0336	32.86	74.50	41.63	0.9951	
150	0.0327	25.15	82.95	57.79	0.9924	

Table –3.2 Pseudo second order Kinetics results for the adsorption of MB dye ions onto CAC [pH = 7; Dose = 30 mg/ 50 mL; Contact time = 120 min; Temp=303K]

Concentration (mg/L)	Pseudo Second Order Kinetics					
	$k_2 \times 10^{-3}$ (g/mg.min)	$q_{e(cal)}$ (mg/g)	Δq_e	h	R^2	MSSE
75	0.0035	54.05	2.30	10.34	0.9959	1.65
100	0.0026	68.03	3.02	12.06	0.9949	
125	0.0023	78.13	3.62	13.91	0.9954	
150	0.0020	86.96	4.00	15.08	0.9954	

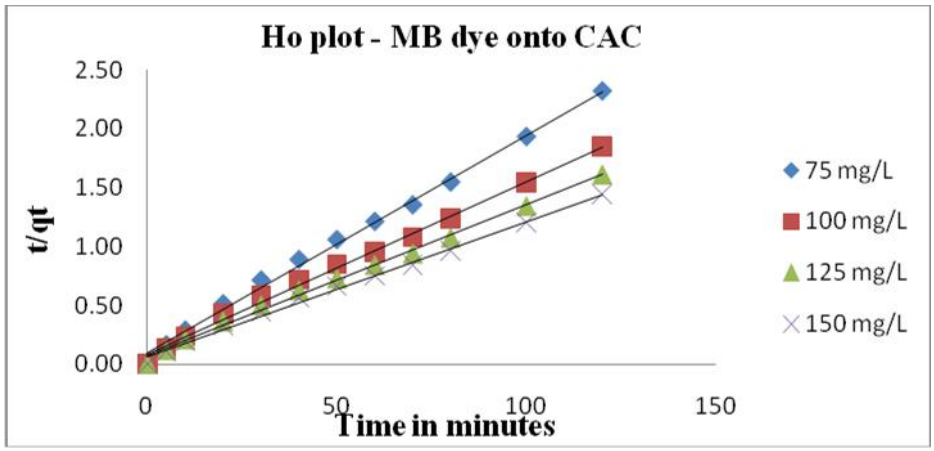

Figure: 3.4

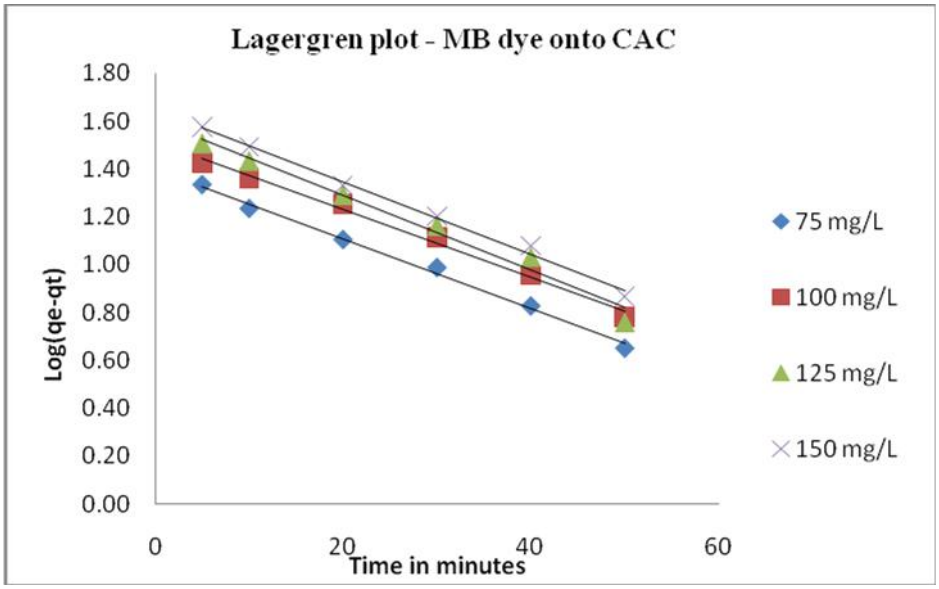

Figure 3.5

The values of regression coefficient (R^2) of the curves for pseudo first order kinetic model ranged from 0.9788 to 0.9951, whereas the values for pseudo second order model were ranged from 0.9949 to 0.9959. This also indicates that the best fitted in pseudo second order kinetic model.

The values of pseudo first order rate constant k_1 ranged from 0.0327 to 0.0359 and pseudo second order rate constant $k_2$values ranged from 0.0020 to 0.0035. The pseudo second order initial sorption rate, 'h', increases directly with an increase of initial MB dye concentration at 303K temperature (10.34 – 15.08 mg/g.min^{-1}).

The difference between the calculated adsorption capacity $q_{e\ (cal)}$ obtained from pseudo first order equation and the experimental adsorption capacity $q_{e\ (exp)}$ were found to be large. Whereas the difference between the calculated adsorption capacity $q_{e\ (cal)}$ obtained from pseudo second order equation and the experimental adsorption capacity $q_{e\ (exp)}$ were found to be small. When compared to pseudo first order kinetic data. It is shown in the table 3.3.

Table –3.3 Pseudo first and second order Kinetics Δq_e results
[pH = 7; Dose = 30 mg/ 50 mL; Contact time = 120 min; Temp=303K]

Initial concentration C_i (mg/L)	Δq_e	
	Pseudo first order	Pseudo second order
75	07.26	2.30
100	25.21	3.02
125	41.63	3.62
150	57.79	4.00

Best fitting kinetic model is tested with statistical tool mean of sum of error squares (MSSE). The MSSE of pseudo first order kinetic model is 18.98 whereas second order model it is 1.65. The lower value for second order kinetic model reflect the suitability of second order kinetic rather than fist order kinetic for the MB dye ions – CAC adsorption system.

3.4.2 Intra particle diffusion

The plots for intra particle diffusion kinetic model were drawn between mass of adsorbate adsorbed per unit mass of adsorbent (q_t) versus $t^{0.5}$. The K_p values were found to increase with an increase of MB dye ions concentration that reveals the rate of adsorption governed by the diffusion of adsorbed MB dye ions within the pores of the adsorbent. Present results were showed that pore diffusion limits the overall rate of MB dye ions adsorption.

Table –3.4 Intra Particle Diffusion results - adsorption ofMB dye on CAC [pH = 7; Dose = 30 mg/ 50 mL; Contact time = 120 min; Temp=303K]

Concentration (mg/L)	Intra Particle Diffusion	
	k_p (mg/g.min)	R^2
75	3.2082	0.9988
100	4.6411	0.9980
125	5.1843	0.9932
150	5.3380	0.9974

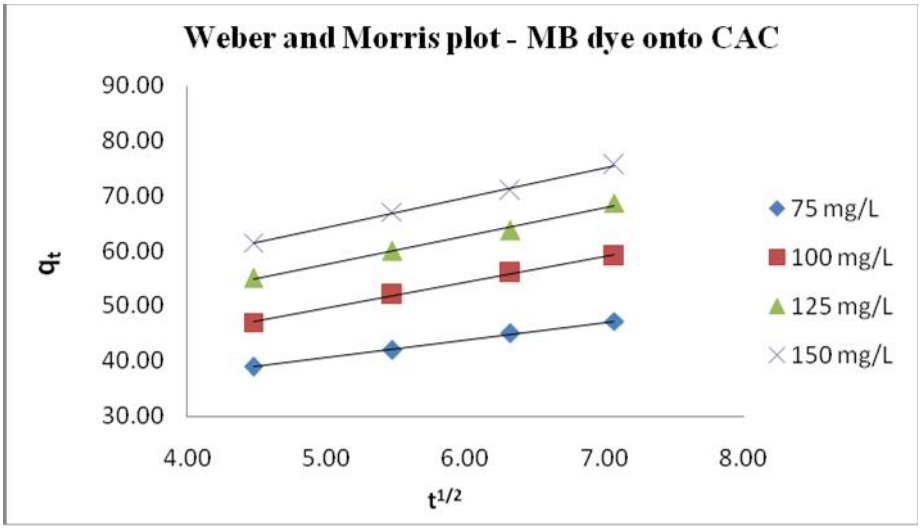

Figure 3.6

4. Summary and Conclusion

The Adsorption potential of CAC was investigated with cationic dye Methylene blue (MB) from aqueous solution. A detailed investigation on the adsorption of chosen adsorbates with respect to kinetic aspects was carried out under batch equilibrium method. The different parameters related to the adsorption study such as effect of solution pH, adsorbent dose and contact time, initial concentration of adsorbate and temperature were determined to establish the adsorption behavior of adsorbent CAC for the chosen adsorbate. Optimum pH selected for the adsorption of Methylene Blue dye was 7. Adsorption kinetics was studied by using linear forms of the pseudo-first-order (Lagergren equation), pseudo second order (Ho equation) and intraparticle diffusion (Weber Morris equation) kinetic models. Pseudo-first-order rate constant k1 and pseudo-second-order rate constant k2 were determined for different initial concentrations. Deviation of the qe(pr) values from the quantity of adsorption determined experimentally ‘qe(exp)’ for both pseudo first and pseudo second order models for different initial concentrations were evaluated with a statistical tool “Mean of Sum of Squared Error” (MSSE). Lower MSSE value means lower deviation. The kinetic model which has the low deviation is suitable model to describe the kinetic aspects. The results indicated that all the chosen adsorptions carried out on CAC followed pseudo second order kinetics.

The intraparticle diffusion rate constants (kp mg/g/min0.5) were obtained from the Weber Morris plots (plot of 'qt' versus 't0.5') had multi linear portions, which informed more number of steps involved in the sorption process. The increase of 'kp' values with a rise in initial concentration showed that pore diffusion was the rate controlling step in each adsorption process studied.

On the basis of the above investigations, it can be concluded that the adsorbents Commercial Activated Carbon (CAC) have high potential to remove Methylene blue dye ions. Performance of CAC was found to be better.

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