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Preparation of activated carbon from *shorea roxburghii* extracts waste and its application in methylene blue removal

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ABSTRACT

A cost effective activated carbon obtained from *shorea roxburghii* for the removal of methylene blue, from aqueous solutions at various contact times, pHs and temperatures was investigated. The activated carbon was characterized for their surface morphology by SEM. From the SEM analysis, it can be concluded that, the activated carbon has lesser number of impurity and highly porous in nature. Evaluation of adsorption of MB was studied using different concentrations of adsorbent, pHs and different times. Adsorption of methylene blue on activated carbon decreases with increase of temperature. The adsorption isotherms were verified with the models of Langmuir and Freundlich isotherms. The best fitting adsorption isotherm was the Langmuir isotherm which shows that dyes form a monolayer over the surface. From the rates of adsorption, it follows the pseudo-second order kinetics with good correlation. As prepared activated carbon would be potential material for the water and wastewater treatment.

Keywords: Methylene blue; dye removal; activated carbon; *shorea roxburghii*; adsorption.

1. INTRODUCTION

There is an increasing development of a number of industries using different dyes, leading to the growth of toxic pollutants in the environment. Dyes are deliberated to be hazardous pollutants and are released to the environment in large quantities from the textile, paper and pulp, tannery, and paint industries[1,2]. These dyes are considered to be hazardous, have low biodegradability, and can disturb the human health as well as the marine life cycle. Owing to its extensive usage in the textile industries, methylene blue (MB) is one of the basic (cationic) dyes that is often widely used in the industries[3]. Methylene blue (MB) is a cationic dye which utilized in large scale amount in the textile, dyeing leather, cotton industries. But when discharge into the nearby environment without proper management, particularly in developing countries. As result, it can cause sickness, high blood pressure, skin decease, cancer and many allergic reactions to the humans.

Several studies have been conducted to inspect various methods for the MB removal such as electrocoagulation[4, 5], ozonation[6], electrolysis[7, 8], phytoremediation[9, 10], photocatalyst[11, 12] and adsorption[13-15]. Moreover, chemical methods are not effective for dye removal due to the low biodegradability of the dye itself. Among advanced treatment methods, adsorption has been found to be good treatment technology for dye removal[16, 17]. Essentially, adsorption treatment technology is simple, cost effective, comparatively ease of operation, and yield high efficiency, and environmentally friendly. Some adsorption studies exploited using clays, fly ash, activated carbon, and hydrogel for the dye removal[18-20]. Moreover, commercial activated carbon is universal adsorbent but very expensive to be used in established methods. Hence, searching for low cost, efficient, high carbon content and locally available precursor materials are still under investigation[21].

Alternatively, phytoremediation is a development that uses different kinds of plants to remove contaminants, for example, a study conducted by Imron et al.[22] showed successful phytoremediation of MB using duckweed (Lemna

minor). So, the production of activated carbon from wastes has economically low-cost and environmental implications[23]. It transforms unwanted, low-value waste materials converted into more advantageous and valuable materials. Activated carbon is the most commonly utilized adsorbent for colour removal[24]. It is also used for the purification and removal of toxic organics and heavy metal ions[25]. In over-all, plants consist of cellulose, hemicellulose, and pectin; they have different functional groups such as hydroxyl, carboxyl, and carbonyl. Advantage of this different the functional groups of these plants interrelate well with the functional groups of dyes, leading to the binding of dyes to the biomass of the plants.

Thus, researches are now tending towards the development of new low-cost adsorbent from various non-conventional waste materials from industries and agriculture, having equivalent potential as that of commercial activated carbon. Though a number of studies have been made in this line, no investigation was made to explore the possibility of usage of plant extract waste, as the precursor for activated carbon preparation. Thus, in the present work, an attempt has been made to prepare a low-cost adsorbent from stem bark of Shorea Roxburghii plant extract waste by carbonizing it through chemical activation method. Shorea Roxburghii plant has no use after the extraction from the stem bark and is thus inexpensive and readily available and being a market waste, causes disposal problem vis-à-vis environmental pollution. So the removal of MB, using activated carbon produced from Shorea Roxburghii plant extract waste by carbonizing with chemical activation methods were investigated and compared. The isotherms and kinetics data, as well as the diffusion parameters, were also evaluated. The activation energy, Gibbs free energy, enthalpy, and entropy of the adsorption process were also evaluated.

2. MATERIALS And METHODS

2.1. Chemicals

Sodium hydroxide, hydrochloric acid, methylene blue dye and acetic acid were analytical grade chemicals which were obtained from MERCK and all chemicals were used as such without any further purification. All the solutions were made up of by using doubly distilled water.

2.2. Plant collection

Stem bark of *Shorea Roxburghii* plant was collected from Alagiri Hills, Madurai, which is belongs to Tamil Nadu state, India. The plant waste was washed exhaustively with tap water to remove the dirt and was then dried in the absence of sun light for three days under the Sun.

2.3. Preparation and activation of carbon (adsorbent)

After plant material was dried in the absence of sunlight then finely powdered, and extracted by the help of organic solvents such as ethyl acetate and methanol, remaining solid materials were placed in Millipore water then boiled for 1h to remove organic and water soluble matters. Finally raw extracted plant waste material (REPWM) was filtered and dried at 110^{o}C in an electric oven, and used as adsorbent for further study. REPWM was used as precursor for the preparation of activated carbon (AEPWM). REPWM was carbonized in muffle furnace at 350^{o}C for 1 h grained to powder and activated in a muffle furnace at 525^{o}C for 3 h.

2.4. Preparation of dye solution

The stock solution 1000 ml was prepared by dissolving 1g of dye in one litre double distilled water in a standard measuring flask; The working solution of desired concentrations were prepared by successive dilution of the stock solution.

The absorbance of the dye solutions were measured by using ELICO UV-Visible spectrophotometer. Adsorption studies were done at various parameters (pH, concentration, temperature).

2.5. Effect of contact time

30 ml of dye solution with dye concentration 30 mg/l was taken in a conical flask with 0.1g of adsorbent and mixture was stirred in a magnetic stirrer. The samples were withdrawn from the flask at predetermined time intervals and the dye solution was separated from the adsorbent by centrifuge. Dye concentration was estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λmax using a spectrophotometer. The dye concentration was measured after 10-150 min until equilibrium was reached.

2.6. Adsorbent concentration

30 ml of dye solution was prepared in 5 different beakers with dye concentration 30mg/l and adsorbent concentration (50-120 mg of activated carbon). The dye concentration readings were taken for after stirring the mixture for every 10 min upto 120 min.

2.7. Dye concentration

30 ml of dye solution with four different dye concentrations (20, 30, 40, 50 mg/l) at pH 9 were prepared in four different beakers. An adsorbent concentration of 0.1g was dipped to all beakers and the solutions were stirred for 120 min and for every 10 min the concentration was noted using UV-Visible spectrophotometer.

2.8. Effect of temperature

30 ml of dye solution of concentration 30 mg/l was kept in heating magnetic stirrer for different temperatures (30-50°C). An adsorbent concentration of 0.10 mg was mixed to all beakers and the solutions were stirred for 120 min and for every 10 min the concentration was noted from the UV-Visible spectrophotometer.

2.9. Effect of pH

30 ml of dye solution was prepared in five different beakers and five different pHs (3, 5, 7, 9, and 12). Then the dye concentration readings were noted after stirring the mixture for every 10 min upto 120 min.

2.10. Adsorption isotherms

The adsorption isotherm is substantial in adsorption studies which describes the adsorbate will interact with the adsorbent and the adsorbent's adsorption capacity[26-28]. The experimental adsorption data were verified using the Langmuir[29], Freundlich[30] and Langmuir-Freundlich isotherm[31] non-linear equations. Isotherm studies were carried out to determine the adsorption ability and amount by adding various concentrations of adsorbate and shaking the reaction mixture for the equilibrium time.

3. RESULTS AND DISCUSSION

Using activated carbon, adsorption studies were carried out for the removal of methylene blue dye. In this work, influence of pH of the methylene blue dye, temperature of the system, concentration of the dye and adsorbent and contact time were studied using activated carbon prepared from plant *shorea roxburghii* as an adsorbent.

3.1. Surface morphology

The SEM technique was used to observe the surface physical morphology of the prepared activated carbon. Fig. 1a and b presents the micrographs of extracted *shorea roxburghii* employed as the raw material and the prepared activated carbon. The material presents a surface morphology in the arrangement of particles, feasibly with a short specific surface area. Nevertheless, after activation, the condensed structure of the sample turned to be brittle and spongy like a surface.

For the activated carbon prepared under the optimum conditions (Fig.1), its surface is smooth and different from the rough surface of the raw *shorea roxburghii*. All of the pores observed by SEM are macropores. Hence, that surface will be suitable for the adsorption of the dye molecules and hence suitable for the catalytic applications.

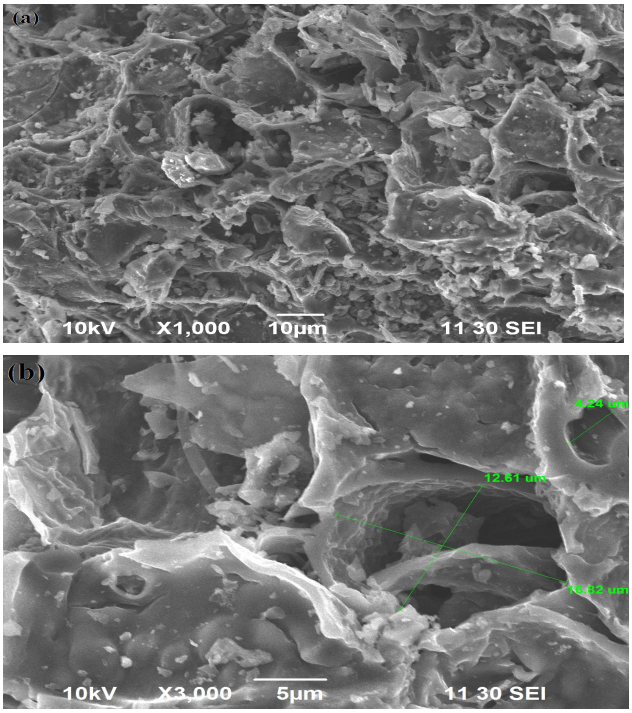

Figure - 1: SEM image of activated carbon formed from *shorea Roxburghii* (a) REPWM (b) activated carbon.

3.2. Adsorption studies

3.2.1. Effect of adsorbent (activated carbon)

In order to optimize the conditions for getting better adsorbent dosage for adsorption, adsorption was carried out with various amount of activated carbon. Fig.2 shows the effect of concentration of adsorbent (activated carbon) prepared from extracted waste plant *shorea roxburghii* on percentage of removal of methylene blue dye.

From the Fig.2, we can see that the optimized adsorbent for the dye adsorption is 0.1 g/l. The figure shows that, the adsorption increases with increase of activated carbon dosage, to certain extent upto 0.1 g/l and then it decreases. This may be explained as follows, generally, activated carbon consisting of uniform pores. It is obvious that, as the number of active sites for adsorption of methylene blue increases results in an increase in removal efficiency. So 0.1 g/l activated carbon has higher % of adsorption. The decrease in adsorption capacity at very high adsorbent could be ascribed to the fact that, some of the adsorption sites remained unsaturated during the process.

3.2.2. Effect of initial pH of the dye

The pH of the solution plays a major role in determining the amount of methylene blue adsorbed on the activated carbon. The effect of initial pH on methylene blue removal ratio was

investigated by varying the pH from 3 to 9. The effect of pH on the adsorption of methylene blue by using activated carbon is shown in Fig.3. From the figure, it can be seen that maximum dye removal was observed when the pH of the solution is 5 and on further increase of pH, the dye removal efficiency of the adsorbent (activated carbon) decreases. The adsorption of these negatively charged dye groups onto the adsorbent surface is primarily influenced by the surface charge of the adsorbent which in turn is influenced by solution of pH. The outcomes displayed that availability of positively charged groups at the adsorbent surface which was necessary for the adsorbing acidic dyes to progress which can be seen at pH 5, is almost unlikely as there is a net positive due to the presence of H_3O^+ charge in the adsorption system. Thus, as the pH decreased, more positively charged surface was available thus facilitating greater dye removal. We can see that the trend is increasing with decreasing pH.

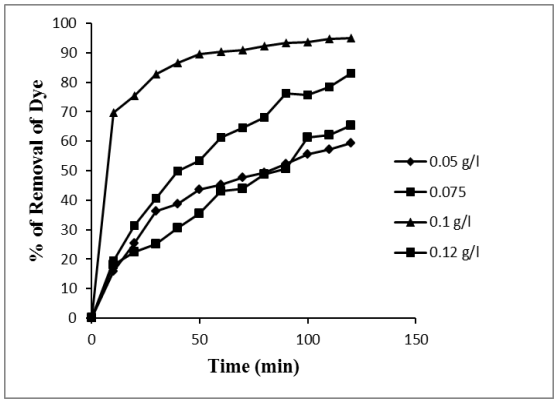

Figure – 2: Effect of various adsorbents (activated carbon) on % of removal of dye.

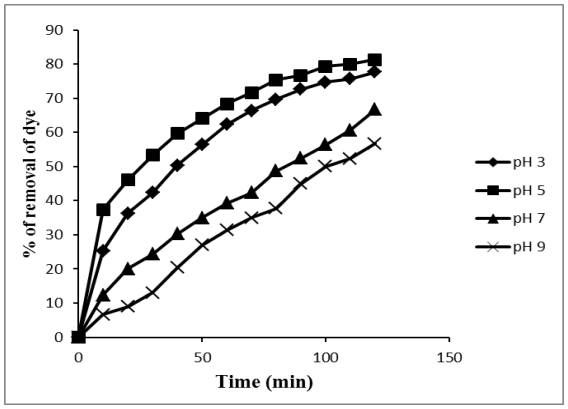

Figure - 3: Effect of pH on % of removal of dye by activated carbon.

3.2.3. Effect of concentration of methylene blue

In order to study the effect of concentration of methylene blue dye on the rate of adsorption on activated carbon, the experiments were carried out at different initial dye concentrations of methylene blue (20-50 mg/l). Fig.4 shows the effect of the initial dye concentration on % of removal of dye adsorption on activated carbon. The figure reveals that, the percentage of removal of dye increases with increase in dye concentration upto 30 mg/l. Further increase in dye concentration, % of dye adsorption decreases. It means that, the adsorption is mainly dependent on the initial concentration of dyes. Due to its lower concentration, the percentage of the initial number of dye molecules to the vacant surface area was quite low, subsequently, the insignificant adsorption become independent on the initial concentration. However, at high concentration, the suitable sites of adsorption becomes fewer and hence, the percentage removal of dye dependent upon the initial concentration[32].

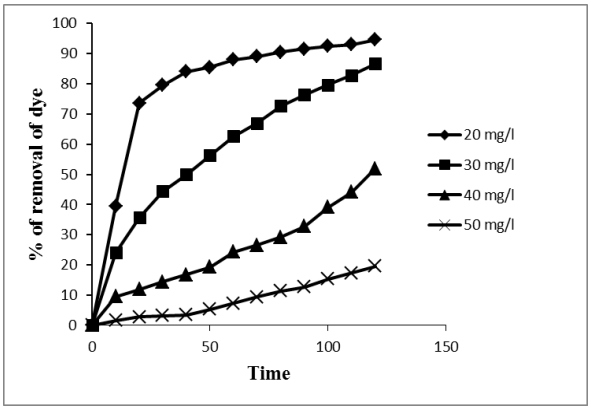

Figure - 4: Effect of dye concentration on % of removal of dye by activated carbon.

3.2.4. Effect of time

In order to study the effect of contact time on the % of removal of dye, the adsorption studies were carried out at constant concentrations of adsorbent (Activated carbon), adsorbate (dye), temperature and pH of the dye solution for various contact time ranging from 0-120 min at various temperature. In all the cases, the removal of adsorption increases with increase of contact time upto 120 minutes beyond that of decreases. This is because, as contact time increases, the number of dye molecules incorporated into the pores of activated carbon increases and hence the % of removal increased. But after 120 minutes, the entire pores of the activated carbon are completely occupied and hence there is no drastic increase in removal.

3.2.5. Effect of Temperature

The rate of the removal of methylene blue dye was studied with initial concentration of 30 mg/l at pH 5 at various temperatures 30, 40 and 50°C. The dye removal efficiency of activated carbon at different temperatures has been shown in the Fig. 5. The percentage of removal increases

with temperature upto 40°C. The optimum temperature for the removal of methylene blue was found to be 40°C and beyond that, there is no remarkable change in the dye removal efficiency of the adsorbent. Also increase in temperature, sometimes leads to desorption of dye molecules, there may be decrease in removal of dye. A similar finding was reported previously by Wong et al[33].

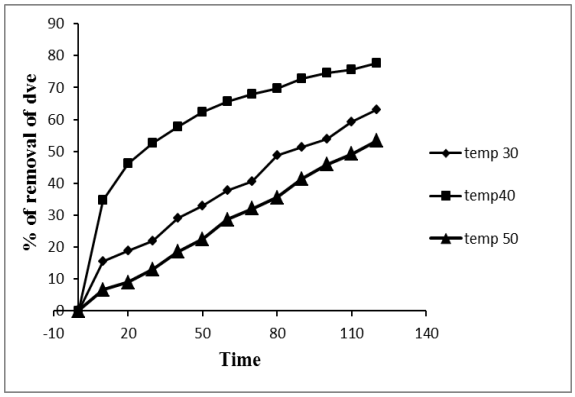

Figure – 5: Outcome of temperature on methylene blue adsorption on activated carbon.

3.3. Adsorption Isotherm

The relationship between the amount of methylene blue adsorbed and the methylene blue concentration remaining in solution is described by an isotherm. Usually adsorption was labelled through isotherms, viz., the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature.

The quantity adsorbed was approximately each time alleviated by the mass of the adsorbent to consent comparison of different materials. The information about the capacity of the adsorbent was provided by equilibrium studies on adsorption. Also, an adsorption isotherm is categorized by definite constant values that prompt the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. The two most common isotherm types for labelling this type of system are the Langmuir and Freundlich isotherms.

The valves of the constants of the two isotherms have been tabulated (table 1). However better fit is indicated using Langmuir adsorption isotherm model. This shows that the methylene blue dye forms a monolayer over the adsorbent surface. Fig. 6 and 7 shows the freundlich and Langmuir adsorption isotherms for the adsorption of methylene blue dye on the activated carbon

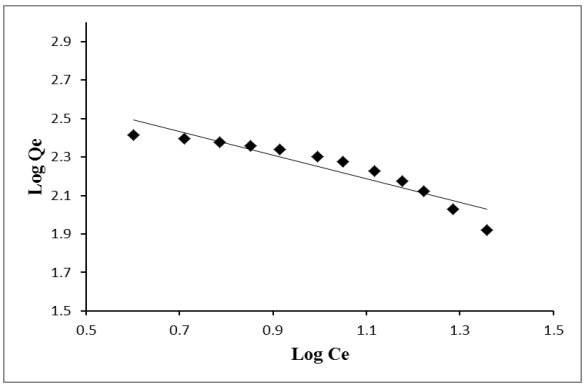

Figure – 6: Freundlich adsorption isotherm for adsorption of methylene blue on activated carbon

The R^2 value for activated carbon was 0.9975. The R^2 value is very close to 1 which indicates that, the adsorption of dye on adsorbent obeys the Langmuir adsorption isotherm. The plot of log Qe Vs log Ce gave a straight (Fig. 6 & 7) with the intercept K_F and the slope 1/n. The R^2 value for activated carbon was 0.8787. The R^2 value was not closely with 1 indicating that, the adsorption disobeys the Freundlich adsorption isotherm[34].

Table – 1: Langmuir and Freundlich adsorption isotherm parameters for the adsorption of methylene blue on AAO

Langmuir isotherm				**Freundlich isotherm**			
K_L	R^2	$1/n_L$	n_L	K_F	R^2	$1/n_F$	n_F
1.647 X 10^{-2}	0.9975	0.0831	12.0336	2.8625	0.8787	0.6139	1.63

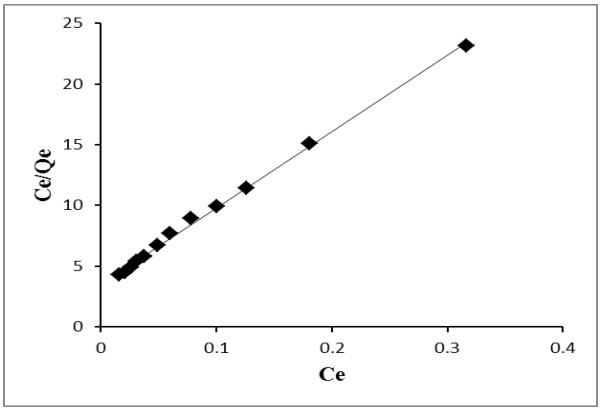

Figure - 7: Langmuir adsorption isotherm for adsorption of methylene blue on Activated carbon.

3.5. Kinetics studies

Generally adsorption capacity was reliant on time and it reaches the equilibrium after an optimal time. Equilibrium process be subject to

Table - 2: Kinetic statistics for the adsorption of methylene blue on activated carbon

Dye Conc (g/l)	Pseudo first order			Pseudo second order		
	q_e	K_1	R^2	q_e	K_1	R^2
20	7.169242	0.031551	0.9667	1.052954	0.011285	0.9969
30	11.76937	0.026024	0.9579	1.14855	0.006448	0.9835
40	10.4458	0.012667	0.9321	1.264529	0.011285	0.9894
50	8.063115	0.013818	0.9469	1.677157	0.010133	0.9696

the initial dye concentration and this process is also directly correlated with time. In the present study, the adsorption of methylene blue reached equilibrium in 120 min for all initial dye concentration studied. In order to characterize the kinetics of reactions, two kinetic models namely pseudo first order and pseudo second order were used to fit the experimental data.

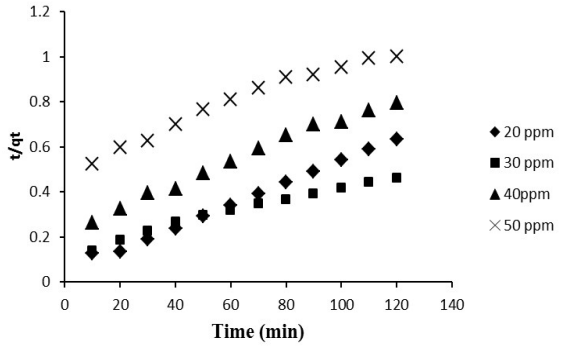

Figure - 8: Pseudo first order adsorption kinetic plots for the adsorption of methylene blue on activated carbon.

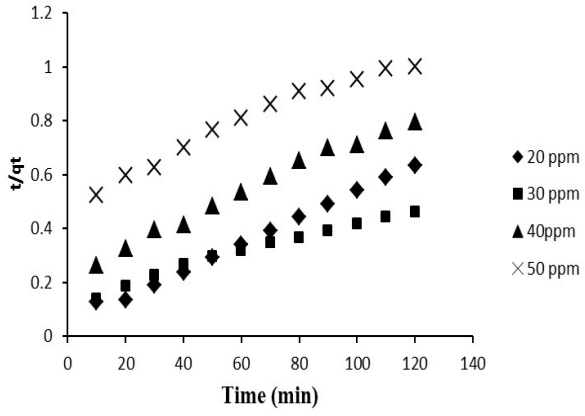

Figure – 9: Pseudo second order adsorption kinetics plots for the adsorption of methylene blue on activated carbon

Both the pseudo first order and pseudo second order kinetics were tested for the adsorption of methylene blue onto activated carbon (fig.8 & 9). The best-fit model was determined based on the linear regression correlation coefficient valves. The values of correlation coefficient for the application of the pseudo-second-order model indicates that this model fits the experimental data more accurately than the pseudo first-order model. Hence the adsorption of methylene blue on activated carbon follows pseudo second order kinetics.

4. CONCLUSION

This study explained the removal of MB using activated carbon which was prepared from extracted waste of *Shorea Roxburghii* plant by physical activation method. The activated carbon was characterized for their surface morphology by SEM. From the SEM analysis, it can be concluded that, the activated carbon has lesser number of impurity and highly porous in nature. The results are summarized as follows, the maximum time for removal of methylene blue dye was determined to be 120 min for 0.1 g/l of adsorbent. The removal of methylene blue was maximum at the pH 5 and the concentration of the adsorbate was 30 mg/l. Adsorption of methylene blue on activated carbon decreases with increase of temperature. From the results, the best fiited adsorption isotherm was the Langmuir isotherm. This shows that dyes form a monolayer over the surface. The rates of adsorption were clearly indicated the pseudo-second order kinetics to a good correlation. The equilibrium contact time and equilibrium concentrations have been obtained from the kinetic data and using Langmuir adsorption isotherms parameters. It is observed from the experiments that about 90-100 % removal is possible at lower concentration ranges.

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