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Removal of Methylene blue Dye by Adsorption onto Activated Carbon from *Adenanthera pavonina L* Seeds

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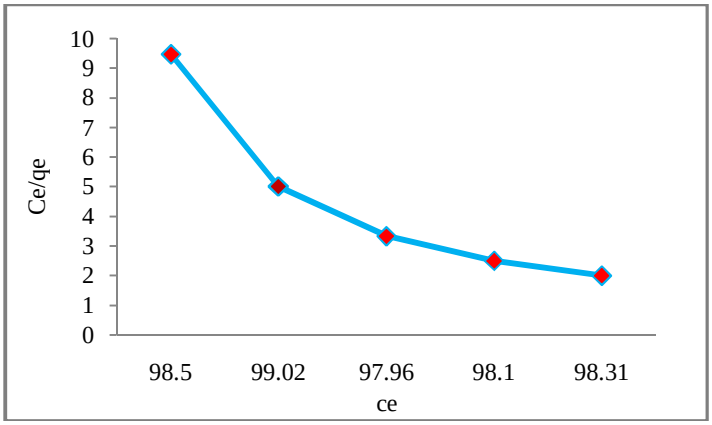
ABSTRACT

Activated carbon has been extensively used as an active adsorbent for removing impurities from the water stream. Preparation of activated carbon using agricultural by-products is ecologically friendly and can significantly contribute to the virtuous cycle of natural polymers. In this study, removal of Methylene blue from aqueous solutions is studied using an Adenanthera pavonina L seeds sample as a low-cost adsorbent. The effects of pH, contact time and dye concentration is taken into consideration. The adsorption kinetics results are adjusted to best fit the pseudo-second-order model. The experimental data are analyzed by Langmuir isotherms and Freundlich isotherms, revealing that the maximum adsorption capacity of methylene blue on this Adenanthera pavonina activated carbon sample equals 49.55 mg g^{-1} at 60 min. From these results, it can be considered that the Adenanthera pavonina activated carbon sample tested herein is effective in the removal of methylene blue from aqueous solutions and moreover may be used as an alternative to high-cost commercial adsorbents.

Graphical Abstract



Langmuir adsorption isotherm of methylene blue into *Adenanthera pavonina* activated carbon.

Keywords: Activated carbon, *Adenanthera pavonina L* seeds, Batch adsorption, Methylene blue, Synthetic dyes.

INTRODUCTION

Synthetic dyes have been gradually developed to impart favourite colours in advanced and traditional industries, including leather tanning, plastics, pharmaceutical, textile, dye manufacturing, paper, food processing and cosmetics industries [**1, 2**]. Their presence in water bodies decreases light penetration, and this subsequently thwarts the aqueous flora photosynthesis [**2**]. The textile industry is the primary source of dyes and creates colored wastewater that is capable of producing severe water pollution. According to Allègre *et al*. [**3**], dying 1 kg of cotton with reactive dyes needs an average of 70–150 L water, 0.6 kg NaCl and 40 g reactive dye. >80,000 metric tons of reactive dyes are produced and consumed each year, but up to 20%–30% of these applied dyes (approximately 2g L^{-1}) is not fixed to the fabric and thus contributes to the coloration and toxicity of the effluent. Such wastewater is commonly associated with a high pH (10−11) and temperature (50°–70°C). Colored dye effluents are generally considered to be toxic to the animal and plant life of a particular region and habitat [**4**].

Methylene blue, a basic dye, was used primarily for dyeing of leather, paper, silk, plastics, and cotton mordant with tannin, besides for the manufacture of ink and copying paper in the office supplies industry. The expulsion of these dyes in the environment is perturbing for both aesthetical and toxicological causes as dyes impede light penetration, damage the quality of the receiving streams and are poisonous to food chain organisms [**5**]. However, it can cause burns and permanent injury to the eyes of both humans and animals. Inhalation may cause difficult or rapid breathing in a short period, while its ingestion through the mouth can cause nausea and burning sensation, sweating, hemoglobinuria, vomiting and sweating [**6**]. Subsequently, dyes have complex aromatic and synthetic origin molecular structures; they are inert and challenging to biodegrade when discharged into waste streams. This aspect has always been overlooked in their discharge [**7**]. To evade these AE (Adverse Effects), the usage of methylene blue in food-producing animals is not allowed in the European Union. Furthermore, Japan has set a maximum residue limit of 10 μg kg^{-1} for the use of methylene blue in aquatic products. Therefore, effluent treatment for removing these dyes is critical [**1**].

The removal of synthetic dyes is of high anxiety, since some dyes and their degradation products may be toxic and carcinogens and, subsequently, their therapy cannot be based on biodegradation alone [**8**]. To degrade or remove the exposed dyestuff in the hyper sphere, several remediation methods are employed based on biological, physical and chemical dye elimination mechanisms [**9, 10**].

Many physicochemical techniques have been tested, but only that of batch adsorption is deliberated to be superior to other methods. This is attributed to its easy availability, high efficiency, biodegradability, low cost, the simplicity of design, easy operation and capability to treat dyes in more concentrated forms [**11, 12**]. For removal of methylene blue dye, various adsorbents like synthetic or natural polymers and carbon-based materials (carbon nanotubes, activated carbon and graphene) have been actively examined [**13, 14**]. Among these adsorbents, activated carbon has been extensively used for the removal of inorganic and organic contaminants present in aqueous solution and aquatic environments because of its well-developed porous structure and the presence of a wide spectrum of surface functional groups [**15**].

Commercially obtainable activated carbons are commonly derived from natural resources, for example, coal or wood and still deliberated expensive. This has led to the search for inexpensive alternates. Therefore, low-cost activated carbon based on solid farming wastes has been examined for a long time. Farming waste materials and by products used for the synthesis of activated carbons contain cassava peel, jute fiber, rice husks, date pits, nutshells, plum kernels, bagasse, palm-tree cobs, olive stones and fruit stones, peach stones, orange peel carbon, rattan sawdust, oil palm shell and Egyptian rice hull [**8**]. The present investigation reports the results of removal of methylene blue dye from aqueous solution by adsorption onto activated carbon prepared from *Adenanthera pavonina L* seeds.

Adenanthera pavonina L (red sandalwood tree) is an attractive medium to large size tree, ranges from 18 to 45 feet in height, belong to family Leguminosae (Bean family). Usual weight of single seed is 0.27 g. The high digestibility of *A. pavonina* seed has been recognized because of the presence of good quality fat and protein. *A. pavonina* was cultivated as valuable agro forestry genus venerated for the production of fuel wood. Traditionally some plant parts were used in the traditional medicines, e.g., the ethanol extract of *A. pavonina* leaves were used as an anti-inflammatory [**16**]. The objective of the present work is to examine the effectiveness of the extracted (*Adenanthera pavonina L*. seeds) activated carbon in removing methylene blue from aqueous solution. The kinetic data and equilibrium data of adsorption studies were processed to understand the adsorption mechanism of the dye molecules onto the *Adenanthera pavonina* L. seed activated carbon.

MATERIALS AND METHODS

Materials: Methylene blue (tetramethylthionine chloride, Fig.1; CAS Number: 122965-43-9; Color Index number CI-52015), was selected as adsorbate and not purified before use. The methylene blue molecular properties are: molar mass (319.85 g mol^{-1}), molar volume (241.9 cm^3 mol^{-1}), width (14.3 Å), depth (6.1 Å), thickness (4 Å), and molecular diameter (0.8 nm), according to the assessments showed by Pelekani and Snoeyink [**17**].

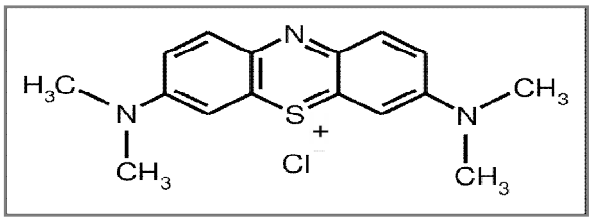


Figure 1. The chemical structure of methylene blue.

The wavelength value of the dye was determined by plotting a graph between absorbance of the dye solution at different wavelengths (Fig. 2). Since the maximum absorbance was obtained at 680 nm, it was taken as the Λ_{max} value of the dye.

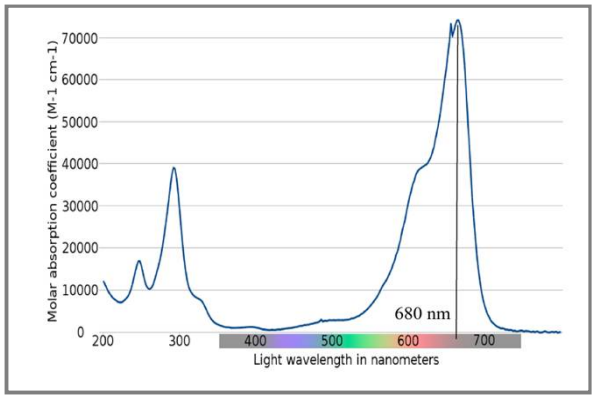


Figure 2. Calibration curve of methylene blue.

Preparation of adsorbents (Activated carbon): The *Adenanthera pavonina L* plant was collected from Don Bosco College, Dharmapuri District, Tamilnadu, India. The seed of the plant was removed while they were washed numerous times with water then washed with distilled water. They were broken into small pieces, dried in sunlight until the moisture content was evaporated. The dried materials were then used for the preparation of activated carbon using the chemical activated method.

The material to be carbonized was soaked with concentrated sulphuric acid (H_2SO_4) solution were analytical reagent grade (SDFCL India) for 24 h. After the impregnation process, the liquid portions decanted off and dried at 360°C. The dried mass was subjected to carbonization process at 900°C in a muffle furnace. The carbonized sample was washed well with double H_2O many times until its pH becomes neutral. The neutralized sample was dried and powdered well. This was sieved to a size 300µ size mesh, and the collected sieved sample was again thermally activated by placing it in the Air Oven at 360°C for about 30 min. The activated sample was allowed to cool down naturally after the dwell times had been attained and stored airtight plastic container. This process yielded a carbon sample which is named as *Adenanthera pavonina* activated carbon. This standard size of carbon sample was used throughout the study.

Analysis of methylene blue concentration: Methylene Blue ($C_{16}H_{18}C_lN_3S{\cdot}2H_2O$) was selected as the adsorbate species. The dye stock solutions were prepared by dissolving accurately weighted dye powder in Milli-Q water at a concentration of 0.1 mg L^{-1}. The experimental solutions were derived by diluting the dye stock solutions in precise proportions to different initial concentrations (20 to 100 mg L^{-1}). The pH of these solutions was adjusted to the preferred value by adding a small quantity of 0.1 mol L^{-1} NaOH and/or 0.1 mol L^{-1} HCl. The concentration of methylene blue in the supernatant solution before and after adsorption was determined using a UV spectrophotometer at 680 nm. The calibration curve was highly reproducible and linear over the concentration range targeted by this work (i.e., from 0 to 100 mg L^{-1}). All the experimentations were carried out in triplicate, with all data being considered and the mean values are taken to signify the result.

Adsorption studies: Batch adsorption experiments were executed in a set of Erlenmeyer flasks (250 mL), each of which contained 50 mL of different methylene blue concentrations (0–100 mg L^{-1}) together with 0.1 mg of adsorbent. An orbital shaker (Labwit ZWY-304) was introduced at a preferred pH and temperature. To reach steady-state adsorption, a time contact equal to 60 min was set for all experiments. After 60 min, the dispersion was filtrated with Millipore 0.45µm (Millex syringe filter units) and the filtrate was analyzed by UV/visible spectrophotometry at λ= 680 nm.

Equilibrium experimentations were conducted for different times, while the pH was progressively adjusted by adding small amounts of diluted NaOH or HCl solutions (0.1 mol L^{-1}). The following equation calculated the adsorbed amount of methylene blue at equilibrium:

$$q_e = (C_0 - C_e)\, xV/M$$

Where q_e (mg g^{-1}) represents the equilibrium adsorption capability of methylene blue adsorbed per gram of the *Adenanthera pavonina* active carbon, C_0, and C_e (mg L^{-1}) the initial and equilibrium methylene blue concentrations respectively, V the volume of the methylene blue solution (L), and m the *Adenanthera pavonina* activated carbon mass (g). Each experiment was executed at least in duplicate under equal conditions. Two separate tests exhibited that the standard deviation of the measurement equalled ± 2.0%. The adsorption percentage (% removal) of methylene blue from aqueous solution can be calculated as follows:

$$\text{Removal percentage} = 100\ x\ (C_0 - C_e)/C_0$$

Adsorption experiments: Methylene blue solution was used as the model adsorbate, and the adsorption experiments were conducted in a series of 250 mL conical flask. Assured amount of adsorbate was put into the conical flask. The adsorbent material was introduced to adsorbate aqueous before putting them in the constant temperature incubator shaker. It was confirmed that the conical flask did not adsorb the methylene blue. The methylene blue concentration was measured by an UV-Visible spectrophotometer (UV-1100, Mapada) and 5B-3(C) ammonia nitrogen detector (Lian-Hua Tech Co., Ltd.) at 680 nm. The amount of methylene blue adsorbed onto adsorbent (qt, mg g^{-1}) at any time t (min, a specific contact time) was calculated by:

$$q_t = \frac{(C_0 - C_t) \times V}{M}$$

Where C_0 (mg L^{-1}), C_t (mg L^{-1}), V (L) and M (g) were the initial concentration of methylene blue, the concentration of methylene blue at t (min), the volume of methylene blue solution, and the mass of adsorbent respectively.

The adsorption capacity (q_e, mg g^{-1}) was determined as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{M}$$

Where C_e (mg L^{-1}) was the equilibrium concentration of methylene blue.

We performed the same experiment at least in triplicate for each run and the standard error was <5%.

Error analysis: Each experiment or analysis was at least duplicated, often triplicated, in all figures, the size of symbols includes the standard deviation from experimental data (3% to 5%). The unknown constants in the model equations for isotherm and kinetics investigation were attained using nonlinear least-squares (NLLS) data processing with the Origin 8.0 software at the 95% confidence level. In this single-component isotherm investigation, the optimization technique needs an error function to be described to evaluate the fit of the isotherm equation to the experimental equilibrium data. In this study, the linear coefficient of determination (R^2), the non-linear Chi-square test (χ^2) and the root mean square error (RMSE) statistical tests were all performed for both the isotherm and kinetics models. The corresponding mathematical equations are then:

$$x^2 = \sum (q_{e.\exp} - q_{e.calc})^2 / q_{e.calc}$$

$$RMSE = \left[\sum (q_{e.\exp} - q_{e.calc})^2 / n\right]^{1/2}$$

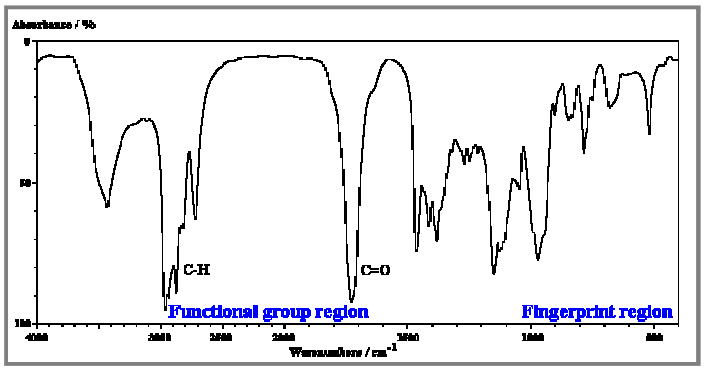


Figure 3. FTIR spectrum of *Adenanthera pavonina* active carbon.

Where $q_{e,exp}$ (mg·g^{-1}) is the experimental data of the equilibrium capacity, and $q_{e,\ calc}$ (mg·g^{-1}) the equilibrium capability attained from model calculations. If the model data are similar to the experimental data, then χ^2 will be a smaller number; if they differ, χ^2 will be a higher one. It is necessary therefore to analyze the data using the non-linear Chi-square test to confirm the best-fit isotherm for this adsorption system [**18**].

RESULTS AND DISCUSSION

Effect of initial dye concentration: Adsorption of the methylene blue dye on activated carbon for the sample *Adenanthera pavonina* activated carbon studied at a different initial concentration from 20 to 100 mg L^{-1} of methylene blue at 25°C. Study of results represented in table 1-5 shows the presence of

relation among the concentration of dye and the available binding sites on the adsorbent surface, and it shows high removal of dye concentration in the start of the adsorption process, then the dye removal decreases due to the completion of the available sites. The removal of the initial concentration of dye decreases with the increases of its concentration. The amount of methylene blue adsorbed at equilibrium (qe) increase (0.1 mg L^{-1}) for *Adenanthera pavonina* activated carbon adsorbents. This may be attributed to the fact that the increase of the initial concentration of the adsorbate signifies a

Table 1. Adsorption concentration of methylene blue dye (20 mg L^{-1}) volume 50 mL and weight of adsorbent (0.1 mg) at various time interval (Initial intensity = 1.04)

S.No	Time (min)	C_0 (mg L^{-1})	C_e (mg L^{-1})	% Removal of Methylene blue	Amount adsorbed
1.	10	20	0.68	99.60	9.660
2.	20	20	0.63	99.85	9.685
3.	30	20	0.59	99.05	9.705
4.	40	20	0.54	99.30	9.730
5.	50	20	1.40	98.00	9.800

Table 2. Adsorption concentration of Methylene blue dye (40 mg L^{-1}) volume 50 mL and weight of adsorbent (0.1 mg) at various time intervals (Initial intensity = 1.15)

S.No	Time (min)	C_0 (mg L^{-1})	C_e (mg L^{-1})	% Removal of Methylene blue	Amount Adsorbed
1.	10	40	0.79	98.02	19.605
2.	20	40	0.72	98.20	19.640
3.	30	40	0.63	98.42	19.685
4.	40	40	0.42	98.90	19.790
5.	50	40	0.39	99.02	19.805

Table 3. Adsorption concentration of Methylene blue dye (60 mg L^{-1}) volume 50 mL and weight of adsorbent (0.1 mg) at various time intervals (Initial intensity = 1.69)

S.No	Time (min)	C_0 (mg L^{-1})	C_e (mg L^{-1})	% Removal of Methylene blue	Amount Adsorbed
1.	10	60	1.22	97.96	29.390
2.	20	60	1.22	97.96	29.390
3.	30	60	1.22	97.96	29.390
4.	40	60	1.04	98.26	29.480
5.	50	60	1.22	97.96	29.390

Table 4. Adsorption concentration of Methylene blue dye (80 mg L^{-1}) volume 50 mL and weight of adsorbent (0.1 mg) at various time interval (Initial intensity =2.00)

S.No	Time (min)	C_0 (mg L^{-1})	C_e (mg L^{-1})	% Removal of Methylene blue	Amount Adsorbed
1.	10	80	1.39	98.26	39.305
2.	20	80	1. 39	98.26	39.305
3.	30	80	1. 39	98.26	39.305
4.	40	80	1.42	98.22	39.290
5.	50	80	1.52	98.10	39.240

driving force to overcome the mass transfer resistance of dye among the solid and aqueous phases. Similar observations were described for adsorption of dyes representing that the adsorbent has a net positive charge on its surface [**19, 20**].The increase in initial dye concentration will cause an increase in the loading capability of the adsorbent, and this may be due to the high driving force for mass transfer at a high initial dye concentration [**21**]. Though, a further increase in dye concentration, don't affect the adsorption yield. This will be attributed to the saturation of adsorption sites on the adsorbent surface [**22**].

Table 5. Adsorption concentration of Methylene blue dye (100 mg L^{-1}) volume 50 mL

and eight of adsorbent (0.1 mg) at various time intervals(Initial intensity = 2.00)

S.No	Time (min)	C_0 (mg L^{-1})	C_e (mg L^{-1})	% Removal of Methylene blue	Amount Adsorbed
1.	10	100	1. 62	96.62	49.55
2.	20	100	1. 62	96. 62	49.55
3.	30	100	1. 62	96. 62	49.55
4.	40	100	1. 62	96. 62	49.55
5.	50	100	1.69	98. 31	49.15

Effect of contact time on methylene blue removal: The adsorption dynamics of the methylene blue solution/*Adenanthera pavonina* activated carbon system strongly depend on the contact time. A contact time optimization for the above system was therefore carried out in batch mode. The extent of methylene blue removal by *Adenanthera pavonina* activated carbon at different shaking times up to 60 min, while imposing a constant settling time, is shown in table 6. Methylene blue adsorption reached a maximum after a concise time of equilibrium, thus signifying an almost instantaneous removal of methylene blue from aqueous solution. From these data, we selected a contact time of 60 min for all adsorption experiments. The result recommends that adsorption takes place quickly at the initial stage on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate-determining step [**23, 24**]. Furthermore, the fast adsorption at the initial stage may be since a large number of surface sites are available for adsorption, but after a lapse of time, the residual surface sites are challenging to be occupied. This is due to the repulsion among the solute molecules of the bulk and solid phases, thus, taking a long time to reach equilibrium [**25**].

Table 6. Adsorption of Methylene blue dye at different concentration of volume 50 mL and weight of adsorbent (0.1 mg) at Standard time intervals (60 min)

S.No	C_0 (mg L^{-1})	C_e (mg L^{-1})	% Removal of Methylene blue	Amount Adsorbed
1.	20	0.40	98.00	9.800
2.	40	0.39	99.02	19.805
3.	60	1.12	98.13	29.390
4.	80	1.52	98.10	39.240
5.	100	1.69	98.31	49.550

Adsorption Isotherm: The adsorption isotherm specifies how the adsorption molecules distribute among the solid and liquid phase when the adsorption process reaches an equilibrium state. The analysis of equilibrium adsorption data, by fitting them to various isotherm models, is a vital step to find the appropriate model that can be utilized for design purpose [**26**]. Adsorption isotherm investigation was carried out on two well-known isotherms, Freundlich and Langmuir. The applicability of the isotherm equation was likened by judging the correlation coefficients R^2.

Langmuir Model: The adsorption isotherm is generally used the designing adsorption system. For that, we use the leaner equation of Freundlich and Langmuir. The leaner equation of Langmuir is given below.

$$C_e / Q_e = (C_e / Q_0) + (1 + / Q_0 b)$$

Where Ce is the equilibrium concentration of the adsorbent (mg L^{-1}), qe is the amount acerbate adsorbed per unit mass of adsorbent (mg g^{-1}), Qo and $b_L$are constant related to monolayer adsorption capacity of adsorption (L mg^{-1}).

When C_e/Q_o was plotted against C_e straight line with slope $1/Q_o$ was obtained, indicating that the adsorption of the methylene blue onto *Adenanthera pavonina* activated carbon follows the Langmuir isotherm. The Langmuir constant “b” and “Q_o" were calculated from this isotherm, and their values

are specified in table 7. Conformity of the experimental data to Langmuir isotherm model indicates the homogenous nature of *Adenanthera pavonina* activated carbon similar observations were reported on the adsorption of Cd onto *Adenanthera pavonina* seeds [7]. The essential characteristics of the Langmuir isotherm can be expressed concerning a dimensionless equilibrium parameter (R_L) [27].

Table 7. Langmuir Adsorption Isotherm

S.No	C_0 (mg L^{-1})	C_e (mg L^{-1})	$q_e = \frac{Co-Ce}{m} \times V$	Ce/q_e (mg L^{-1})
1.	10	98.50	10.40	9.47
2.	20	99.02	19.80	5.00
3.	30	97.96	29.39	3.33
4.	40	98.10	39.24	2.5
5.	50	98.31	49.15	2.00

Plotting Ce/q_e against Ce gave a straight line with slope 1/Qo and intercepted with b indicating the adsorption of methylene blue (Figure 4).

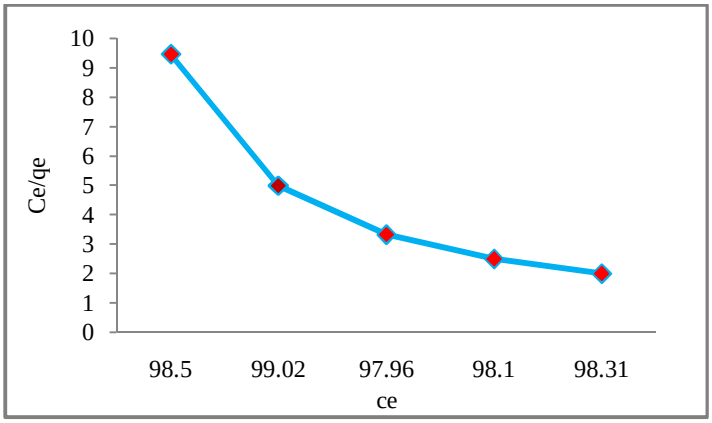


Figure 4. Langmuir adsorption isotherm of methylene blue into *Adenanthera pavonina* activated carbon.

The Langmuir isotherm fits the experimental data is very well may because of homogenous distribution of active sites into the surface since the Langmuir model assume the surface in homogenous, the Langmuir adsorption if methylene blue into *Adenanthera pavonina* activated carbon.

Freundlich Isotherm: This model can be useful to reversible multilayer and non-ideal adsorption system on heterogeneous surfaces. The linearized form of Freundlich equation was given by

$$\log q_e = 1/n \log C_e + \log K_f$$

Where K_f is measuring the adsorption capacity (mg g^{-1}), n is adsorption intensity and is calculated from intercept and slope of a linear plot of log qe Vs log Ce.

K_f can be described as the distribution or adsorption coefficient and signifies the quantity of methylene blue onto SALCS for a unit equilibrium concentration. The slope 1/n ranging amid 0 and 1 is a measure of surface heterogeneity or absorption intensity, becoming more heterogeneous as its, value gets closer to 0 [28]. Value of 1/n <1 shows a standard Langmuir isotherm while >1 is suggestive of cooperative adsorption [29]. The plot of log q_e Vs Log C_e gives straight lines with slope "1/n" (Figure 5), which displays that the adsorption of methylene blue also follows the Freundlich isotherm. Therefore, Freundlich constants (K_f and n) were calculated and recorded in table 8.

The calculated n values showed that at average temperature, the dye adsorption due to the physical force. It was evident that the slop (1/n) decreased as the intensity of adsorption.

Table 8. Freundlich Adsorption Isotherm

S.No	C_0 (mg L^{-1})	C_e (mg L^{-1})	$q_e = \frac{Co-Ce}{m} \times V$	log C_e (mg L^{-1})	log q_e
1.	10	98.50	10.40	1.9934	1.0170
2.	20	99.02	19.80	1.9957	1.2966
3.	30	97.96	29.39	1.9910	1.4681
4.	40	98.10	39.24	1.9916	1.5937
5.	50	98.31	49.15	1.9925	1.6915

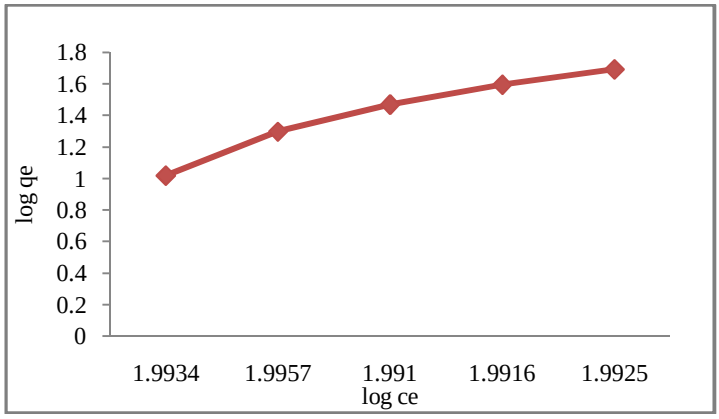


Figure 5. Freundlich adsorption isotherm of methylene blue into *Adenanthera pavonina* activated carbon.

APPLICATION

So these adsorbents can be used for wastewater contaminated with reactive dye on a bulk scale.

CONCLUSION

The selected *Adenanthera pavonina* activated carbon sample proved to be an effective adsorbent for the removal of methylene blue from aqueous solution. The percentage of adsorption was decreased at an increased initial concentration of methylene blue solutions. At an initial dye concentration of 20-100 mg L^{-1}, the percentage of adsorption decreased from about 98% to 68%. The adsorption equilibrium was achieved within times of<60min. The pseudo-second-order model equation well defined the adsorption kinetics. An adsorption isotherm was fitted by the Langmuir and Freundlich model, with the maximum adsorption capacity of methylene blue on *Adenanthera pavonina* activated carbon was calculated at 49.55 mg g^{-1} at 60min. These results also conclude that the adsorption capacity is dependent on the pH solution, initial concentration, contact time, and adsorbent dosage. Our results, therefore, indicate that an *Adenanthera pavonina L* seed sample, like the *Adenanthera pavonina* activated carbon used in this work, can be successfully utilized for the adsorption of Methylene Blue dye from aqueous solutions.

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