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Research Paper

Equilibrium Isotherm, Kinetic and Thermodynamic Study on Removal of Methylene Blue Dye from Aqueous Solution by using Corn cob Activated Carbon

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Abstract: *The adsorption performance of corn cob based activated carbon (CCAC), for adsorptive removal of methylene blue dye from aqueous solution, has been investigated by batch experiments. Batch studies have been performed to describe the impact of parameters such as pH, adsorbent dose, initial dye concentration, temperature and contact time on the removal of the dye. The maximum removal percentage (approximately 99%) was observed when used 2.5 g L^{-1} of CCAC, 200 mg L^{-1} of initial MB concentration at initial pH 6.97, and contact time of 90 min. The experimental data were analysed by the Langmuir and Freundlich isotherm models. The monolayer adsorption capacity of CCAC was found to be 119.04 mg g^{-1} by using Langmuir isotherm model. The calculation of the thermodynamic parameters such as Gibbs free energy, entropy and enthalpy changes of the on- going adsorption process indicated the feasibility and endothermic nature of MB adsorption. Pseudo- first- and second- order kinetic models have been applied to the experimental data and pseudo- second- order kinetics was found to describe the adsorption of the dye (methylene blue) on the adsorbent.*

Keywords: Adsorption, Methylene blue, Corn cob activated carbon, Adsorption isotherms, Kinetics, Thermodynamics.

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Introduction

Dyes and pigments can be considered as one of the most dangerous contaminants among the different pollutants released to the environment from a variety of industrial applications. Because they have mutagenic, teratogenic and carcinogenic effects and cause many health disorders to human beings such as dysfunction of the kidney, reproductive system, liver, brain and central nervous system even present at low concentrations[1]. Because of these, the removal of dyes from water and wastewater is an extremely important application.

Cationic dyes, such as MB, were used initially for dyeing of silk, leather, plastics, paper, and cotton as well as for the production of ink and copying paper in the office supplies industry[2]. Such extensive use of dyes often poses problems in the form of colored wastewater that require pretreatment for color removal prior to disposal into receiving water bodies or publicly owned treatment works [3].

There are several methods available for color removal from water and wastewater such as oxidative degradation, photo degradation, electrocoagulation and biochemical degradation have been exploited, but these methods possess drawbacks due to their inapplicability to large scale units along with both energy and chemical intensiveness. Adsorption is a well- known and superior technique for dye and organic removal because of its easy operation, cost-effectiveness, insensitivity to toxic substances, ability to treat concentrated forms of the dyes, and the possibility of reusing the spent adsorbent via regeneration. In the process of adsorption, a solid adsorbent is employed in order to attract the dye component and finally leading to its removal from the water by the formation of physical and chemical bonds [4]. Recently, various low

cost activated carbons derived from agricultural wastes such as palm shell [5], rattan [6] and mangosteen peel [7] have been investigated intensively for dyes removal from aqueous solution. Corn is widely cultivated throughout the world, and a greater weight of corn is produced each year than any other grain. So the present study undertaken to evaluate the efficiency of an activated carbon as an adsorbent prepared from corn cob, agricultural waste, for the removal of the dye methylene blue from aqueous solution. In order to design adsorption treatment systems, knowledge of kinetic models, thermodynamics and isotherm studies is essential.

Material and Methods

Materials

All the reagents and chemicals used in the study were of analytical reagent grade. Methylene Blue dye (C.I. 52015, $C_{16}H_{18}N_3SCl$, mol. wt. 319.85, IUPAC name 3,7-bis(Dimethylamino)-phenothiazine-5-ium chloride (aq. Solubility 40 g L^{-1}) with the chemical structure (Figure 1) was procured from M/s Merck, India. The stock solutions of the dye were prepared by dissolving the desired amount of dye in double distilled water. pH of the test solution was adjusted using reagent grade dilute hydrochloric acid and sodium hydroxide.

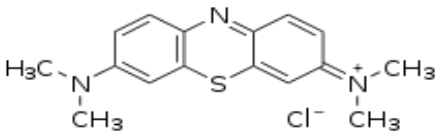


Figure 1: Chemical structure of Methylene Blue dye in neutral medium

Material Development

Corn cob was obtained from the local market in Lucknow, India. Corn cob was firstly washed with water and subsequently dried at 105ºC for 24 h to remove the moisture content. The dried corn cob was crushed and sieved to the size of 1-2 mm. Carbonization procedure was carried out at 700ºC for 2 h under purified nitrogen (99.99%) flow of 150 mL min^{-1} [8]. The char produced was mixed with Na_2CO_3 pellets in 1:1. Deionised water was added to dissolve all the Na_2CO_3 pellets. The mixture was then dehydrated in an oven at 110ºC for 24 h to remove moisture.

After dehydration, the sample was placed in oven for activation step. Once the final activation temperature (758°C) was reached, the gas flow was switched from nitrogen to CO_2 at flow rate of 150 mL min^{-1} for different period of time. The sample was then cooled to room temperature under nitrogen flow. Then the sample was dried in an oven at 110°C for 6 h. The product was sieved to the desired particle size and finally, stored in vacuum desiccators until required. The developed carbon was designated as the corn cob activated carbon (CCAC).

Adsorbent Characterization

The chemical constituents of the prepared corn cob activated carbon were determined following the methods reported elsewhere [9]. The elemental analysis was performed using the Elemental Analyser model Vario EL- III (Hanau, Germany). The multipoint BET specific surface area (S_{BET}), pore volume (micropore volume, V_{mi}; and total pore volume, V_T), and pore size distribution of the prepared CCAC were determined by N_2- physiosorption using the surface area analyser model Autosorb- 1C (Quantachrome, USA).

Scanning electron microscopy (SEM) was used to examine the surface topography of the developed corn cob activated carbon using the SEM model LEO 430 (Cambridge, England) [10]. The identification of various forms of different constituents in CCAC was performed with the help of IR spectra [11]. The IR spectrum was recorded using the Perkin- Elmer FTIR model RX1 (USA) in the range 4000- 450 cm^{-1}. The pH measurements were made using a pH meter (Model 744, Metrohm, Switzerland).

Absorbance measurements were made on a Perkin Elmer UV- visible spectrophotometer model Lamda- 35. Absorbance values were recorded at the wavelength for maximum absorbance (λ_{max}), i.e. 663 nm for the MB dye.

Adsorption studies

To study the effect of parameters like adsorbent dosage, pH, initial concentration and time for the removal of the dye, batch experiments were carried out at three different temperatures, 20, 35 and 50°C. For each experimental run, 25 ml of dye solution of known concentration, pH and 0.4 g of adsorbent L^{-1} was taken in a 250 ml conical flask. The mixture was agitated in an orbital shaker (Orbitek, Scigenies Biotech, India) at a constant speed of 120 rpm. The samples were centrifuged for 2 min and analysed for the residual dye concentration by measuring absorbance at λ_{max} using UV-vis spectrophotometer (Perkin-Elmer Spectrophotometer model Lamda- 35). The effect of pH on dye removal was studied over a pH range of 3-9. The pH of the solution was controlled by the addition of dilute HCl or NaOH solutions. The amount of adsorbent used was varied in the flasks having equal volume of dye solution of the same concentration. The adsorbent dosage varied from 0.4 to 2.5 g L^{-1}. After 1.5 h, the samples were collected and analysed in a spectrophotometer. Solutions of various concentrations ranging from 80 to 200 ppm were prepared in a separate 250 ml conical flasks. The standardized adsorbent dosage was transferred into each of the

conical flasks. After a period of 1.5 h, the aqueous phase was analysed for the residual concentration of dye using UV-vis spectrophotometer. The absorbance measured was then converted to concentration. The percentage of removal was assessed using the following equation:

$$\frac{C_i - C_o}{C_i} \times 100$$

where C_i is the initial dye concentration and C_o is the final dye concentration after adsorption. Duplicate experiments were performed in parallel to check the results. The result showed that the error was within 2%.

The kinetics of adsorption was determined by analyzing the adsorptive removal of the dye from aqueous solution at different time intervals. For adsorption isotherms, MB dye solution of different concentrations was agitated with a known amount of adsorbent till equilibrium was achieved. The samples were collected at regular time intervals and the residual concentration of dye in the aqueous phase was analysed after centrifuging.

Results and Discussion

Characterization of adsorbent

The chemical composition and surface properties of the developed corn cob activated carbon are presented in Table 1.

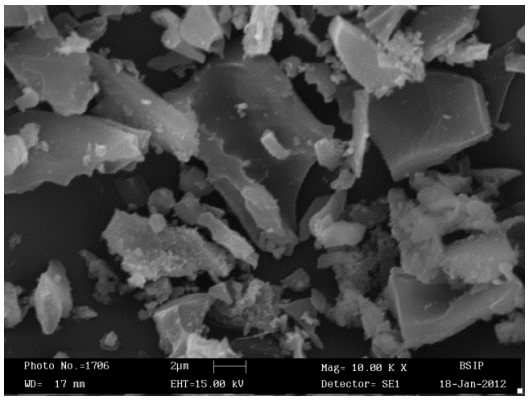
Table 1: Composition and surface properties of the corn cob activated carbon

C (%)	H (%)	N (%)	S_{BET} (m^2g^{-1})	V_T (cm^3g^{-1})	pH_{zpc}
56.65	0.01	0.1	498.02	0.2880	7

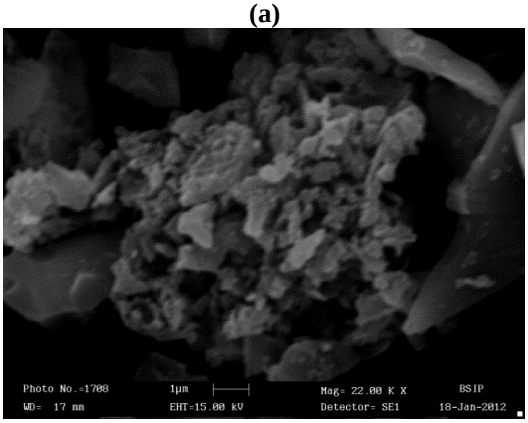
S_{BET} : Surface area, V_T : Total pore volume

In the present study, scanning electron microscopic (SEM) photograph of the adsorbent revealed the surface texture, porosity and fibrous structure of the developed activated carbon (Figure 2a and 2b). The coarse and rough morphology of an activated carbon could provide more reactive sites than the smooth morphology, and thereby, was in favour of the sorption of dye from aqueous solution.

Different constituents in developed activated carbon were identified with the help of IR spectra [11]. The IR spectrum of the developed adsorbent (figure not shown due to brevity) showed weak and broad peaks in the region of 3420-525 cm^{-1}. FTIR spectra shows peak at 3420 cm^{-1} due to presence of O-H and N-H stretching vibration, while peak at the 2921 cm^{-1} is attributed to the C-H group of alkyl chain. The 1559-1018 cm^{-1} band was assigned to the C-O stretching and O-H bending modes such as phenolic and carboxylic acids. The spectral analysis shows the heterogeneous nature of the corn-cob activated carbon surface.



(a)



(b)

Figure 2: Scanning Electron Micrograph (SEM) of activated carbon

Adsorption studies

Effect of pH

The initial pH of the dye solution is an important parameter, which controls the adsorption process, particularly the adsorption capacity. pH of the solution changes due to (1) the surface charge of the adsorbent, (2) the degree of ionization of the adsorptive molecule and (3) extent of dissociation of functional groups on the active sites of the adsorbent [12].

The adsorption of MB onto the CCAC as a function of pH was investigated at the initial dye concentration of 200 mg L^{-1} and the contact time of 90 min. Solutions of NaOH and HCl were employed to adjust the pH of the test solutions. In the case of adsorption of MB, a pH range of 2- 9 was selected. There is an increase in adsorption capacity with increasing pH values, which is due to neutralization of the negative charge at the surface of the adsorbent by the positively charged dye molecule. Hence, there is a lower adsorption capacity at lower pH values, and adsorption capacity slight increases with increasing pH values. Basic conditions

favour adsorption of dye; thus pH 9 was considered as optimum pH for the adsorption of the dye.

Effect of adsorbent dose

The adsorbent dose is an important parameter in the adsorption studies because it determines the capacity of the adsorbent for a given initial concentration of dye solution. It was observed that the adsorption capacity increased rapidly with the increase in the adsorbent dose till 2.5 g L^{-1} and after the critical dose, the adsorption capacity reached almost a constant value. This can be attributed to the increase in the adsorbent surface area and availability of more active adsorption sites on the CCAC surface with increasing the dosage of the adsorbent. On the other hand, the adsorbed amount of dye per unit mass of the adsorbent decreased with the increase in the adsorbent dosage, as a result of aggregation of the adsorbent particles.

Effect of initial dye concentration

The effect of initial MB concentration on the efficiency of its adsorption onto CCAC was investigated in the initial concentration range of 80- 200 g L^{-1}. By increasing the initial dye concentration, the adsorption capacity decreased. The decrease in the adsorption capacity is probably due to the saturation of the active binding sites on the CCAC surface at higher concentrations. On the other hand, by increasing the initial dye concentration the actual amount of dye adsorbed per unit mass of the CCAC increased. The higher initial concentration of MB provides an important driving force to overcome the mass transfer resistance for MB transfer between the solution and the surface of the CCAC [13].

Effect of temperature

The temperature influence is an important controlling factor in the real applications of the proposed adsorptive dye removal process since most of the textile dye effluents are produced at relatively high temperatures. In order to determine whether the ongoing MB adsorption process was endothermic or exothermic in nature, a set of similar experiments were carried out in the temperature ranges of 20- 60°C. The results showed that the adsorption amount of MB dye onto CCAC increased with an increase in temperature indicating that the process is endothermic in nature. The increase in the adsorption capacity of CCAC with temperature may be results of the increase in the mobility of dye molecules and also increase in the number of available active surface sites on the CCAC for adsorption as a result of pore enlargement.

Effect of contact time

The adsorption of MB dye onto CCAC was studied as a function of contact time in order to decide the sufficient equilibrium time. For this, it was observed that the adsorption rate of the dye increase with an increase in time and almost 90 min. of time was required to bring complete saturation of the active sites of the adsorbent.

Adsorption isotherms

The equilibrium distribution of dyes in the solution is important factor to determine the maximum of sorption capability. Adsorption mechanisms of a sorbate and maximum sorption capacities are determined by adsorption isotherms[14-15]. In this work, the experimental data were fitted with two important isotherm models named Langmuir and Freundlich, also isotherm coefficients and correlation coefficient (R^2) were calculated.

Langmuir isotherm

Langmuir isotherm has a wide application in lots of pollutants sorption process. The main assumption of this theory is based on homogeneous and one layer sorption without any interaction among adsorbate molecules. It is thought that adsorbate molecule takes up one site and then another sorption cannot take place there. It also suggests that all the adsorption sites are of equivalent energy. The equation was developed by Irving Langmuir in 1916 [16-17]. The equation is stated as,

$$q_e = \frac{Q_o b C_e}{1 + bC_e} \qquad \text{(non- linear form)}$$

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_o b}\right) + \left(\frac{1}{Q_o}\right) C_e \qquad \text{(linear form)}$$

where, q_e is the amount of solute adsorbed per unit weight of adsorbent (mg g^{-1}), C_e, the equilibrium concentration of solute in the bulk solution (mg L^{-1}), Q_0, the monolayer adsorption capacity (mg g^{-1}), and b is the constant related to the free energy of adsorption/ desorption ($b\alpha\ e^{-\Delta G/RT}$).

High values of b are reflected by the step initial slope of a sorption isotherm and indicate a high affinity for the adsorbate. In terms of implementations, sorbents with the highest possible Q_0 and high b are the most desirable [18].

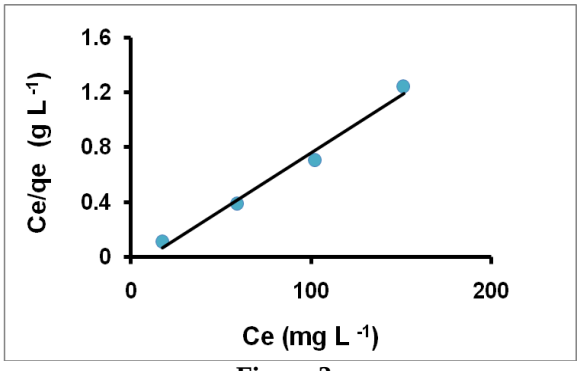


Figure 3a

The graphical presentations for the Langmuir isotherm for the corn cob activated carbon are given in Figure 3a. High R^2 values of the straight lines obtained, confirmed the validity of Langmuir adsorption isotherm for CCAC adsorbent. The Langmuir constants for CCAC adsorbent were calculated and are presented in Table 2.

Freundlich isotherm

Freundlich isotherm supposition is non- uniformity of active sites energy, which means different functional groups adsorbed on surface by different energies. In contrary to Langmuir isotherm sorption can happen in multilayer manner [19-20]. This isotherm is expressed as;

$$q_e = K_F C_e^{1/n} \quad \text{(non- linear form)}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \text{(linear- form)}$$

where, C_e denotes the equilibrium concentration of MB, q_e, its amount adsorbed (g mol^{-1}), and K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively and can be determined by plotting log q_e versus log C_e, which are obtained from linear form of the equation, which are presented in Figure 3b. The Freundlich constants for CCAC adsorbent were calculated and are presented in Table 2.

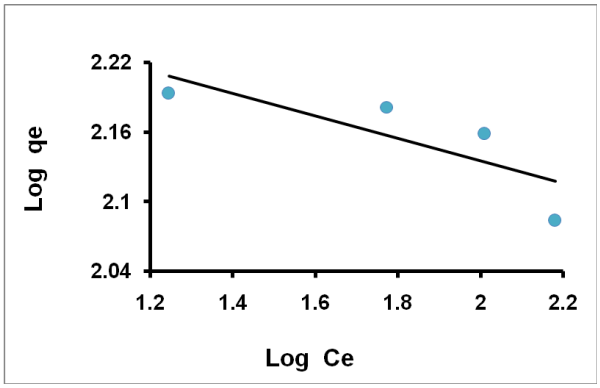


Figure 3b

On comparing the regression coefficients obtained for Langmuir and Freundlich, it can be very well predicted that the Langmuir isotherm is more favoured by the adsorption process. The data presented above clearly show that Langmuir adsorption isotherm graph is better fit than Freundlich adsorption isotherm graph; this indicates that a unilayer adsorption process taking place in the present case is more favourable than a multilayer formation of the adsorbate.

Table 2: Adsorption isotherm parameters of MB adsorption onto corn cob activated carbon

Adsorbent	Freundlich			Langmuir		
CCAC	K (mgg^{-1})	n	R^2	Q (mgg^{-1})	b	R^2
	213.55	10.28	0.64	119.04	0.103	0.9849

Kinetic studies

The kinetic study of the adsorption processes provides useful data regarding the efficiency of adsorption and feasibility of scale up operations. The kinetic data of adsorption can be evaluated using different types of mathematical models as;

Lagergrens first- order kinetics

In order to determine the order of the ongoing adsorption process and also to evaluate the specific rate constants Lagergrens first- order rate equation was employed for the system. Among the different types of mathematical models, it is one of the most widely used Lagergrens' rate equation[21]. The kinetics of the adsorption process was analysed using the pseudo-first- order rate equation as given below;

$$\frac{Dq_1}{d_t} = k_1(q_e - q_t) \quad (1)$$

where q_e and q_t are the concentrations of the dye (mg g^{-1}) at equilibrium and at time, respectively, after the adsorption processes. k_1 is the equilibrium rate constant of pseudo- first order adsorption for dye adsorption. On integration with limits from t = 0 to t and q = 0 to q_t, we have,

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

The values of adsorption rate constant (K_1) for methylene blue adsorption on corn cob activated carbon was determined from the plot of log ($q_e - q_t$) against t. These values are given in Table 3. The experimental data deviated greatly from linearity. This was evidenced by low q_e and low correlation values.

Pseudo- second- order kinetics

Kinetic data were further applied to the pseudo-second- order kinetic model proposed by[13]. The differential equation has the following form:

$$\frac{Dq_1}{dt} = K_2(q_e - q_t)^2 \quad (3)$$

where k_2 is the equilibrium rate constant of pseudo-second- order adsorption (g mg^{-1} min^{-1}). Integrating Eq. (3) for the boundary condition t = 0 to t = q_t gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (4)$$

which is the integrated rate law for a pseudo- second-order reaction. Eq. (4) can be rearranged to obtain a linear form;

The straight- line plots of t/q_t against t have been used to obtain rate parameters. The values of k_2, q_e and correlation coefficients R_2^2 of dye solution under different concentrations were calculated from these plots (Table 3).

Table 3: Kinetic Parameters for the methylene blue removal by Corn-Cob Activated carbon in aqueous solution at different temperature

Temp (°C)	Carbon Dose	$q_{e,exp}$	Pseudo-first order			Pseudo-second order		
	(g L^{-1})	(mg g^{-1})	k_1(h^{-1})	$q_{e,cal}$ (mgg^{-1})	R^2	k_2 (g$mg^{-1}h^{-1}$)	$q_{e,cal}$ (mg g^{-1})	R^2
20	0.4	104.9	1.9276	69.1	0.895	0.0528	112.35	0.989
35	0.4	113.84	2.659	91.8	0.910	0.0536	124.68	0.995
50	0.4	135.42	2.296	108.5	0.952	0.0840	140.85	0.999

The correlation coefficients are closer to unity for pseudo- second- order kinetics than pseudo- first- order kinetics. This suggests that the sorption system can be represented better by the pseudo- second- order model for the adsorption of methylene blue dye by corn cob activated carbon.

Thermodynamics of adsorption

The thermodynamic parameters such as change in standard free energy (ΔG^o), enthalpy (ΔH) and entropy (ΔS) of adsorption were calculated to evaluate the thermodynamic feasibility and spontaneity of the process. The Gibbs free energy change can be obtained from the following equation:

$$\Delta G^0 = RT \ln k_0$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), K_0 is the thermodynamic equilibrium constant, and T is the absolute temperature (K). The thermodynamic parameters are listed in Table 4. The negative ΔG values confirmed the spontaneous nature and feasibility of the adsorption process. The value of enthalpy (ΔH) and entropy (ΔS) changes may be determined from the Van't Hoff equation given below [22]:

$$InK_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

ΔH and ΔS can be obtained from the slope and intercept of the Van't Hoff plot of In k_0 versus 1/T, respectively (Table 4). The positive values of ΔH confirmed the endothermic nature of the adsorption process, the possible explanation for this being displacement of more than one water molecule by the MB dye ions for their adsorption, which in turn results in the endothermicity of the adsorption process, while the positive values of ΔS implied the increased randomness at the solid solution interface during the adsorption of MB dye onto CCAC. Also the positive ΔS value corresponds to an increase in the degree of freedom of the adsorbed species. This is the normal consequence of the physical adsorption phenomenon, which takes place through electrostatic interactions. In order to further support the assertion that the physical adsorption is the predominant mechanism, the value of activation energy was estimated from the slope of the plot using Arrhenius equation [23-24] given in table 4.

Table 4:Thermodynamic parameters for the adsorption of MB by CCAC

Adsorbent	ΔG^0 (Jmol^{-1})			ΔH^0 (Jmol^{-1})	ΔS^0 (Jmol^{-1}k^{-1})	Ea (kJmol^{-1})
	313k	**323k**	**333k**			
CCAC	-131.12	-380.33	-980.90	12.796	41	11.982

Comparison of various adsorbents

The removal of MB by different adsorbents has been studied extensively, and dye adsorption capacities were reported in literatures. Table 5 compares the adsorption capacities of the CCAC obtained in this work with different adsorbents previously used for removal of dyes. It can be seen from Table 5 that the adsorption capacities of the prepared CCAC for MB dye are much higher than that of many other previously reported adsorbents, indicating that the as- prepared CCAC has great potential application in dye removal from aqueous solution.

Table 5: Comparison of the maximum adsorption capacity of MB from various adsorbents

Adsorbents	Adsorption capacity (mg g^{-1})	References
Date pits	80.31	[25]
Tea waste	85.16	[26]
Fly ash	75.52	[27]
Fe (III)/ Cr (III) hydroxide	22.8	[28]
Wood apple shell	95.2	[29]
MMT/ $CoFe_2O_4$ composite	97.75	[30]
Corn cob activated carbon	**160.71**	**This work**

Conclusion

The corn cob based activated carbon has been synthesized and used as an effective adsorbent for the removal of methylene blue dye from aqueous solutions. The batch sorption process was dependent on some experimental parameters such as initial solution pH, initial dye concentration, contact time, adsorbent dosage and temperature. The kinetics and thermodynamics studies were performed for the adsorption of MB dye from aqueous solutions onto CCAC. The isotherm parameters for the Langmuir and Freundlich models were determined and the adsorption isotherm data were fitted well with the Langmuir model. It was observed that the process is thermodynamically feasible, spontaneous and endothermic in nature, and the kinetics of MB adsorption onto CCAC followed by the pseudo- second order model. In the view of these results, it can be concluded that the corn cob activated carbon can be utilized as a low cost and effective adsorbent in removal of MB dye from aqueous solutions.

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