

2014

BioTechnology

An Indian Journal

FULL PAPER

BTAIJ, 10(24), 2014 [16064-16073]

Adsorption of Methylene Blue by activated carbon from capsicum straw

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ABSTRACT

The dyes are known to be toxic, carcinogenic and mutagenic. Their release in the environment can cause non-aesthetic pollution, and moreover, they are not degraded by conventional aerobic wastewater treatment due to their recalcitrance. Therefore, it is necessary to reduce dye concentration in the wastewater. Activated carbon was obtained from capsicum straw by chemical activation using KOH as an activator. Then it was used as an adsorbent for the removal of dye Methylene Blue. The adsorption of dye Methylene Blue by activated carbon was carried out in details. Kinetic adsorption data were analyzed by the pseudo-first-order kinetic model, the pseudo-second-order model and the intraparticle diffusion model. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. The thermodynamics parameters were also calculated.

KEYWORDS

Adsorption; Methylene blue; Activated carbon; Capsicum straw.



INTRODUCTION

Dyes have been extensively used in many industries, such as textile, leather, tanning, paper production, food technology, hair coloring^[1]. The dyes are known to be toxic, carcinogenic and mutagenic. Their release in the environment can cause non-aesthetic pollution, and moreover, they are not degraded by conventional aerobic wastewater treatment due to their recalcitrance^[2]. The present of these colored compounds in wastewater is not only aesthetically displeasing, but also they impede light penetration in the treatment pans, thus upsetting the biological treatment processes within the treatment plant. They also increase the biological oxygen demand (BOD) and cause lack of dissolved oxygen to sustain aquatic life. In addition, many dyes are toxic to some microorganisms, and may cause direct destruction or inhibition of their catalytic capabilities^[3-4]. Therefore, it is necessary to reduce dye concentration in the wastewater before their biological treatment processes.

Many treatment methods have been adopted to remove dyes from wastewater, which can be divided into physical, chemical and biological methods^[5]. Although chemical and biological methods are effective for removing dyes, they require specialized equipment and are usually quite energy intensive. In addition, large amounts of by-products are often generated^[6].

Generally, physical methods which include adsorption, ion exchange, and membrane filtration are effective for removing reactive dyes without producing unwanted by-products^[7]. Adsorption has been used extensively in industrial processes for many purposes of separation and purification. The removal of colored and colorless organic pollutants from industrial wastewater is considered as an important application of adsorption processes using suitable adsorbent. At present, there is growing interest in using low cost, commercially available materials for the adsorption of dyes. A wide variety of materials, such as fly ash, peat, wood, palm-fruit bunch particles, activated carbon from fertilizer waste and activated slag, are being used^[8-11].

Activated carbons are materials having complex porous structures with associated energetic as well as chemical inhomogeneities. Their structural heterogeneity is a result of existence of micropores, mesopores and macropores of different sizes and shapes^[12]. Activated carbon is one of the most important adsorbents from an industrial view of point. The main application of this adsorbent is for separation and purification of gaseous and liquid phase mixtures^[13-15]. However, appropriate properties and cost of adsorbent materials are the key aspects for practical applications when dealing with dye wastewater. One of the ways to decrease the cost of adsorbent production is use of inexpensive precursors such as agricultural by-products and wastes^[16-18]. It was demonstrated that agricultural by-products and various biosorbent materials have promising capacities to remove a variety of pollutants^[19-21].

The aim of this work is to study the ability of the activated carbon obtained from capsicum straw by chemical activation using KOH as an activator to remove dye from aqueous solutions. The equilibrium and kinetic studies have been performed. The importance of obtaining isotherms and kinetics curve lies in developing a model which accurately represents the results obtained and could be used for design purposes.

MATERIALS AND METHODS

Materials

The capsicum straw was obtained from Shaoxing City in Zhejiang Province of P.R. China. The capsicum straw was dried at 105 °C for 12 h, to achieve constant weight, then comminuted and sieved into a uniform size of 120 mesh. The 50 g of the capsicum straw was soaked stillly with 100mL 10% KOH solution in 250 mL Erlenmeyer flasks for 24 h at room temperature. Then, it was dried again at 105 °C for 12 h to constant weight and was carbonized at 700 °C in a muffle furnace for 60 min. The product of 120 mesh activated carbon was thus obtained and then stored for later adsorption experiments.

The dye of Methylene Blue with commercial purity was used without further purification. The chemical structure is shown in Figure 1.

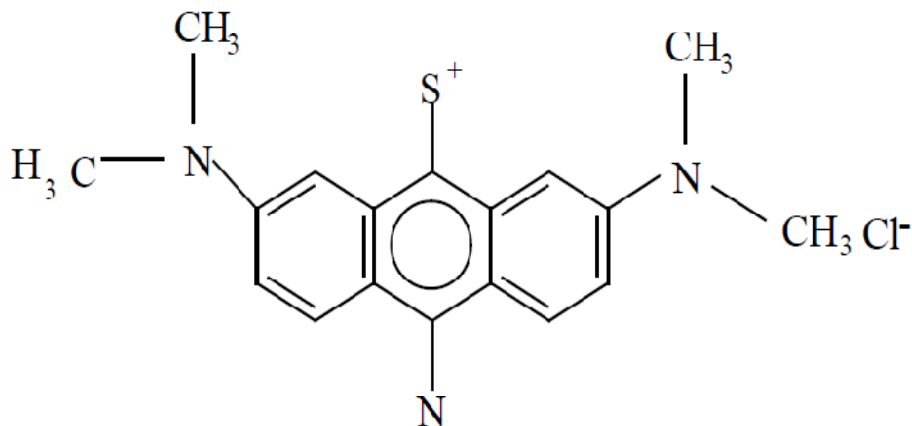


Figure 1: Chemical structures of Methylene Blue

Adsorption experiments

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.10g of activated carbon and 100 mL of dye solutions with various initial concentrations (20mg/L, 30mg/L, 40mg/L and 50mg/L). The initial pH was adjusted to 5.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature (293, 303 and 313K) and 100 rpm. The samples were then filtered and the residual concentration of dye Methylene Blue was analyzed using a UV-1600 spectrophotometer at a wavelength corresponding to the maximum absorbance for dye Methylene Blue.

Analytical methods

The textural characteristics of activated carbon including surface area, pore volume, pore size distribution were determined using standard N₂-adsorption techniques. The surface physical morphology of activated carbon was observed by a scanning electron microscope.

The value of pH was measured with a pH probe according to APHA Standard Method. The concentration of dye Methylene Blue was measured with a UV-1600 spectrophotometer at 665 nm.

The amount of adsorbed dye q_t (mg/g) at different time, was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

where C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of dye Methylene Blue respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Statistical analyses of data

All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All the data were analyzed by the Langmuir and Freundlich adsorption models to test for the effects of temperature and initial dye Methylene Blue concentration. The Kinetic adsorption data were discussed using the pseudo-first-order model and pseudo-second-order model. All error estimates given in the text and error bars in figures are standard deviation of means (mean \pm SD). All statistical significance was noted at $\alpha=0.05$ unless otherwise noted.

RESULTS AND DISCUSSION

Characterization of activated carbon

The surface of the activated carbon was observed using scanning electron microscopy as shown in Figure 2. It can be seen from the micrograph that the activated carbon contains porous structures and presents an adequate morphology for dye Methylene Blue adsorption.

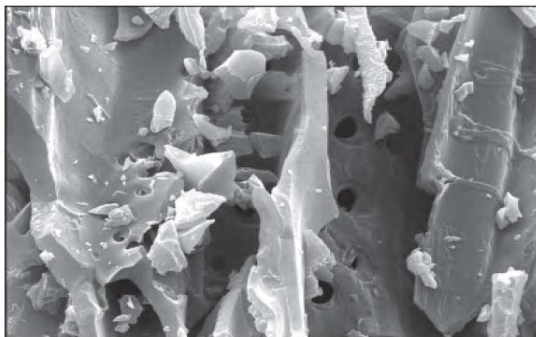


Figure 2: SEM image of activated carbon

The characteristics of activated are obtained from the standard N_2 -adsorption techniques. The BET surface area is $676 \text{ m}^2/\text{g}$, the total pore volume is $0.72 \text{ cm}^3/\text{g}$ and the Nominal pore size is 1.21 nm . In addition, the content of C, N and H in activated carbon was 86.24%, 1.13% and 0.25% respectively. It shows that activated carbon has a large specific surface area.

Adsorption isotherms

The capacity of an adsorbent can be described by its equilibrium sorption isotherm. The Langmuir and Freundlich adsorption models are commonly adopted to investigate the adsorption behavior of materials and the correlation among adsorption parameters. Accordingly, equilibrium data were simulated by the Langmuir^[23] and Freundlich models^[24].

The Langmuir isotherm equation is represented by the following Eq. (2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

Where C_e is the equilibrium concentration of dye Methylene Blue (mg/L), q_e is the amount of dye Methylene Blue adsorbed (mg/g), q_m is the maximum adsorption capacity of dye Methylene Blue (mg/g), and K_L is the Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites.

The Freundlich isotherm equation is described by the following Eq. (3):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

Where K_F and n are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity respectively.

The corresponding values of Langmuir and Freundlich isotherms for dye Methylene Blue adsorption on activated carbon were listed in TABLE 1. The results indicate that the Langmuir isotherm fits better than the Freundlich isotherm. The value of R_L is between 0 and 1, which indicate heterogeneity of the adsorbents and favorable adsorption^[25]. The maximum adsorption capacity obtained from the Langmuir isotherm is 34.12 mg/g .

TABLE 1: Equilibrium model parameters for the adsorption of dye Methylene Blue onto activated carbon. Experimental conditions: 0.10 g of activated carbon, 120 meshes of particle size, contact time of 200 min, 293 K, 100 rpm and pH 5.0

Langmuir model			Freundlich model		
q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2
34.12	0.34	0.9938	0.021	0.505	0.9754

Adsorption kinetics

The influence of contact time on the removal of dye Methylene Blue in solution by activated carbon is shown in Figure 3.

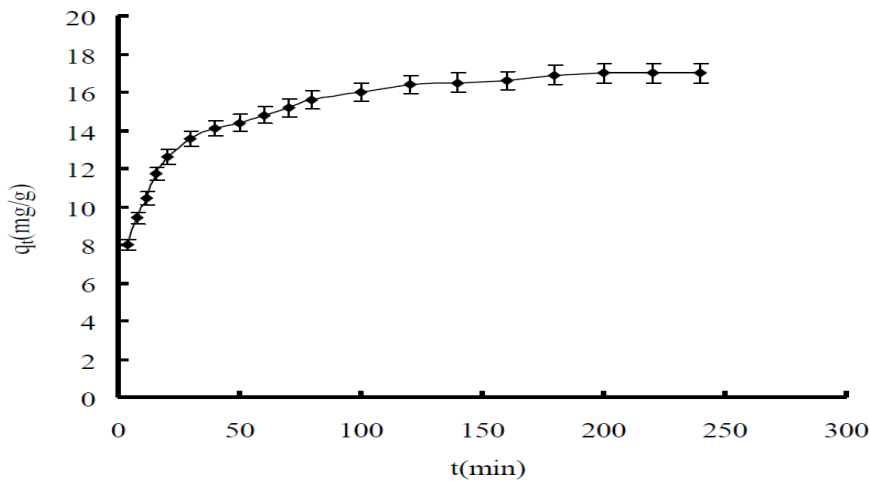


Figure 3: Effect of contact time on adsorption of dye Methylene Blue in solution onto activated carbon. Experimental conditions: 0.10 g of activated carbon, 20mg/L of initial dye Methylene Blue concentration, 120 meshes of particle size, 293 K, 100 rpm and pH 5.0

It can be concluded that adsorption rate of dye Methylene Blue increases sharply at short contact time and slowed gradually as equilibrium was approached. It may be due to the availability of initial large number of vacant surface active sites for adsorption and adsorption rate is very fast. As equilibrium was approached, the filling of vacant sites becomes difficult due to repulsive forces between dye Methylene Blue adsorbed on solid surface and dye Methylene Blue from solution.

In order to investigate the mechanism of dye Methylene Blue sorption, three models were used in this study.

The linear pseudo-first-order model of Lagergren is given as follows^[19]:

$$\ln(q_e - q_t) = \ln q_e - k_1 \times t \quad (4)$$

Where q_e and q_t are the amounts of dye Methylene Blue adsorbed onto the adsorbent (mg/g) at equilibrium and at t respectively. k_1 is the rate constant of first-order adsorption (min^{-1}).

The pseudo-second-order kinetic model developed by Ho and McKay^[20] is based on the experimental information of solid-phase sorption. The linear pseudo-second-order model can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where k_2 is the rate constant of second-order adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$).

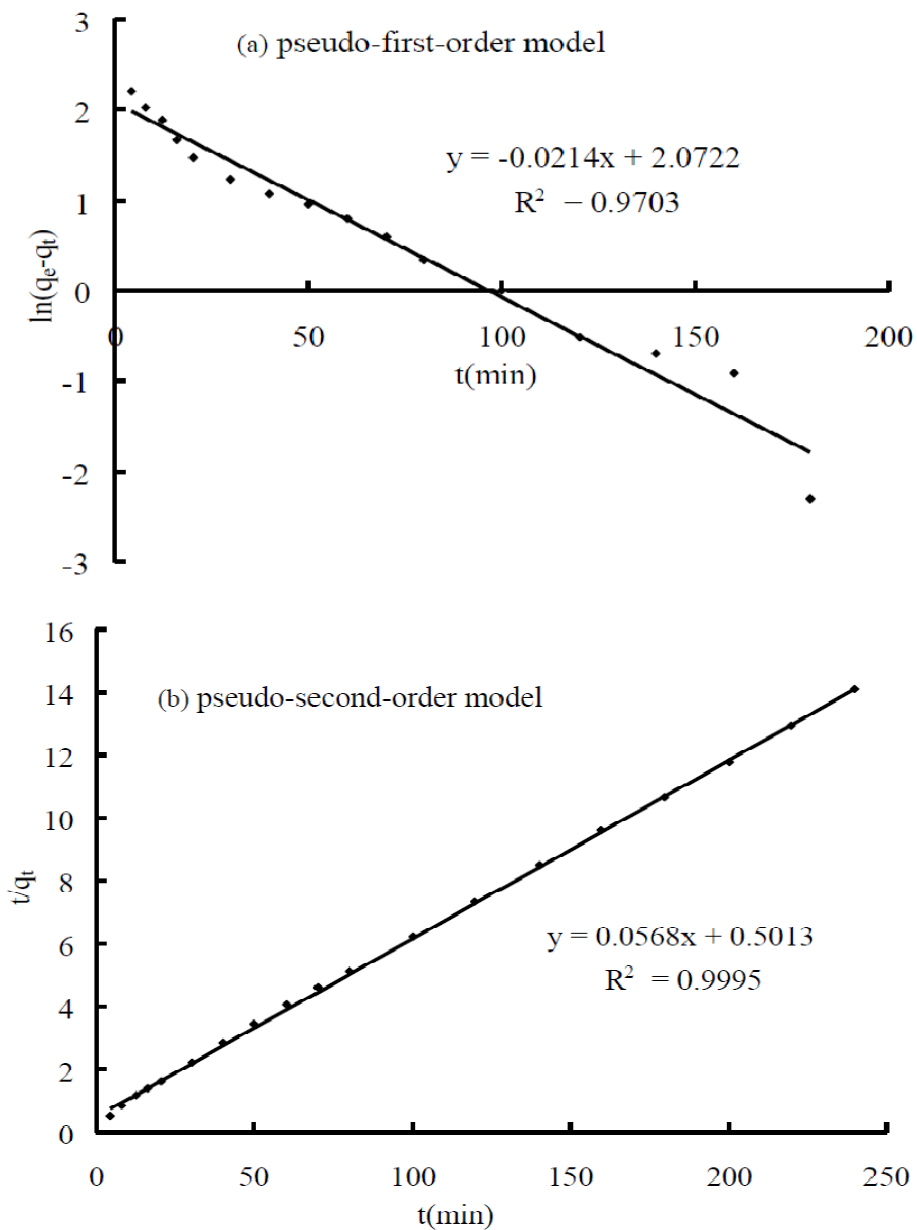
The intraparticle diffusion model can be expressed as follows:

$$q_t = k_i t^{\frac{1}{2}} \tag{6}$$

Where k_i is the constant of intraparticle diffusion rate. It is obtained from the slope of the straight line of q_t versus $t^{\frac{1}{2}}$.

The adsorption kinetic models were shown in Figure 4. The rate constant (k_1 , k_2 and k_i), correlation coefficient R^2 , and equilibrium adsorption density of q_e could be derived from this line.

The validity of the exploited models is verified by the correlation coefficient (R^2). R^2 values of the pseudo-first-order model, the pseudo-second-order model and the intraparticle diffusion model for adsorption of dye Methylene Blue onto activated carbon were 0.9703, 0.9995 and 0.8688 respectively. This result confirmed that the adsorption of dye Methylene Blue onto activated carbon better fits to pseudo-second order kinetic model. It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent^[21,22].



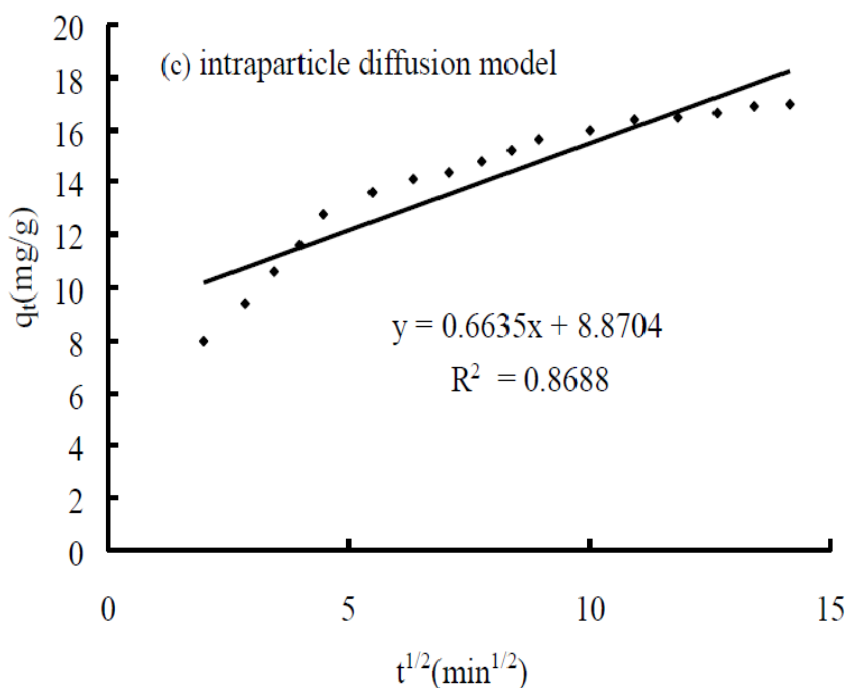


Figure 4: (a) pseudo-first-order model for adsorption of dye Methylene Blue onto activated carbon at 293 K, (b) pseudo-second-order model for adsorption of dye Methylene Blue onto activated carbon at 293 K, (c) intraparticle diffusion model for adsorption of dye Methylene Blue onto activated carbon at 293K. Experimental conditions: 0.10 g of activated carbon, 20mg/L of initial dye Methylene Blue concentration, 120 meshes of particle size, 293 K, 100 rpm and pH 5.0

Effect of temperature and thermodynamics parameters

The effect of temperature was shown in Figure 5. It was found that the adsorption rate of dye Methylene Blue increased with increasing solution temperature from 293K to 313K. It also indicated that the adsorption is an endothermic process. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of adsorbate molecules into the pores of the activated carbons at higher temperatures^[26].

The thermodynamic parameters of free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were used to describe thermodynamic behavior of the adsorption of dye Methylene Blue onto the activated carbon. These parameters were calculated from the following equations^[27].

$$\Delta G^0 = -RT \ln K_a \quad (7)$$

$$\ln K_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

$$K_a = \frac{q_e}{C_e} \quad (9)$$

where T is the solution temperature (K), K_a is the adsorption equilibrium constant, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), q_e is the amount of adsorbate adsorbed per unit mass of adsorbate at equilibrium (mg/g) and C_e is the equilibrium concentration of the adsorbate (mg/L).

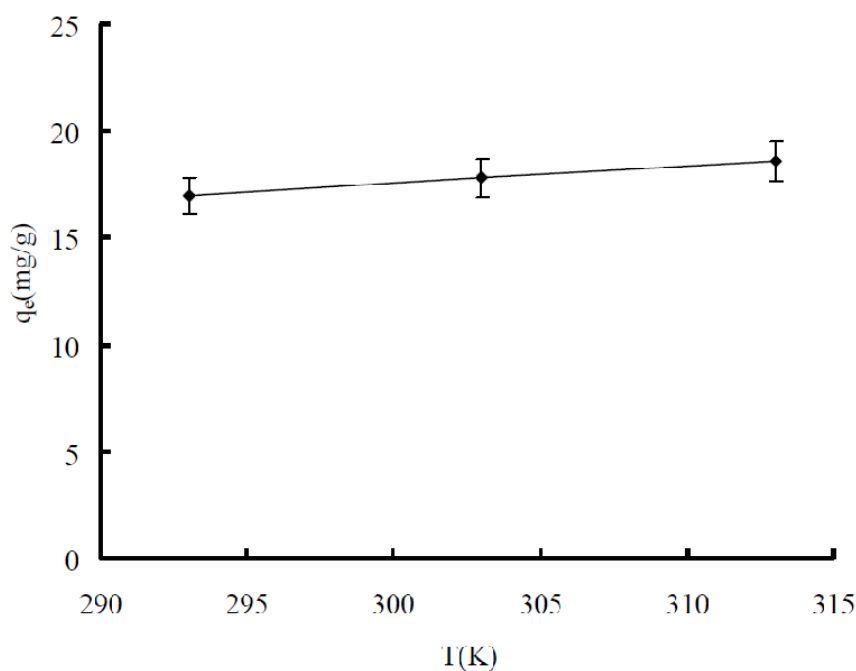


Figure 5: Effect of temperature on adsorption of dye Methylene Blue onto activated carbon. Experimental conditions: 0.10 g of activated carbon, 20mg/L of initial dye Methylene Blue concentration, 120 meshes of particle size, contact time of 200 min, 100 rpm and pH 5.0

Thermodynamic parameters (ΔH^0 , ΔS^0 and ΔG^0) for dye Methylene Blue adsorption were evaluated using Eqs. (7)-(9). The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of $\ln K_a$ versus $1/T$ (Figure 6).

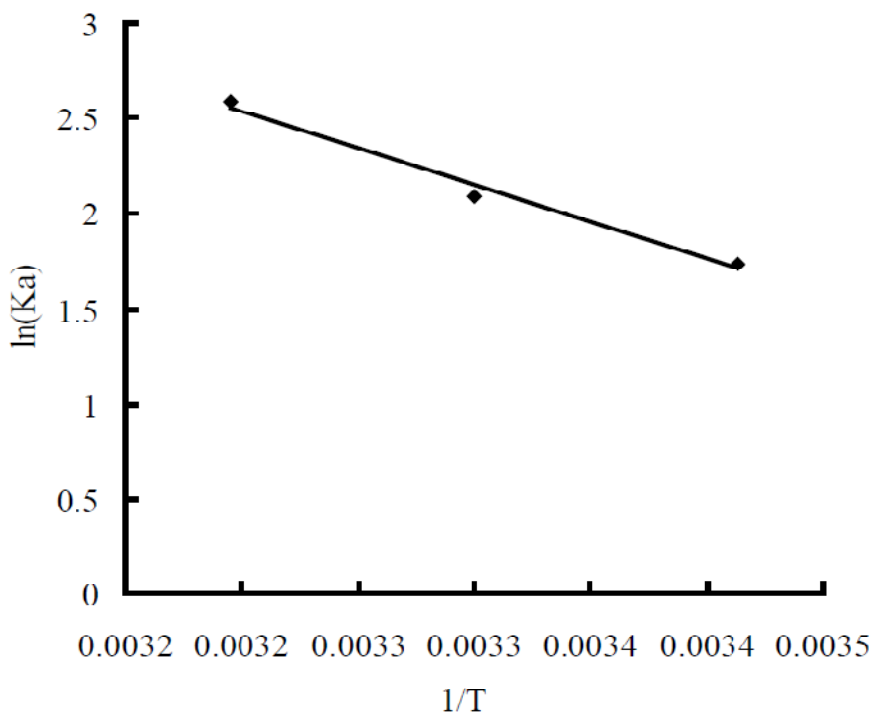


Figure 6: Determination thermodynamic parameters for adsorption of dye Methylene Blue onto activated carbon. Experimental conditions: 0.10 g of activated carbon, 20mg/L of initial dye Methylene Blue concentration, 120 meshes of particle size, contact time of 200 min, 100 rpm and pH 5.0

The values of ΔH^0 , ΔS^0 and ΔG^0 are listed in TABLE 2. As the temperature increases, and the value of ΔG^0 decreases. It indicated that less driving force and hence resulting in lesser adsorption capacity at higher temperatures. Above 303K, the negative values of ΔG^0 indicates the adsorption of dye Methylene Blue onto activated carbon is spontaneous and thermodynamically favorable. The positive value of ΔH^0 indicated that the sorption process was endothermic in nature. The positive value of ΔS^0 showed the increasing randomness at solid/solution interfaced with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent.

TABLE 2: Thermodynamic parameters for the adsorption of dye Methylene Blue onto activated carbon

Temperature (K)	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (KJ/mol)
293	-4.23	32.41	0.13
303	-5.27	32.41	0.13
313	-6.73	32.41	0.13

CONCLUSIONS

Activated carbon was obtained from capsicum straw by chemical activation process. The adsorption studies for the removal of dye Methylene Blue from aqueous solutions were carried out. The activated carbon contains porous structures and presents an adequate morphology for dye Methylene Blue adsorption. It was shown that the adsorption isotherm studies showed that Langmuir isotherm fits better than the Freundlich isotherm. The pseudo-second order kinetic model better described the sorption data. The maximum adsorption capacity obtained from the Langmuir isotherm is 34.12 mg/g. The thermodynamic parameters showed a spontaneous, thermodynamically favorable and endothermic adsorption.

ACKNOWLEDGEMENTS

This study was financially supported by the natural science foundation of Zhejiang Province (LY12D01002) and the project of science and technology plan in Shaoxing City (2013B70050).

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