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Kinetics and Thermodynamics of Adsorption Methylene Blue onto Tea Waste/$CuFe_2O_4$ Composite

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ABSTRACT

Tea waste/$CuFe_2O_4$ (TW/C) composite was prepared by co-precipitation method. The TW and TW/C samples are characterized by FTIR, XRD, SEM and N_2 physical adsorption. The results showed that specific surface area of 350 and 570 $m^2 \cdot g^{-1}$ for TW and TW/C, respectively. The average pore size of TW/C is ca. 100 nm. Adsorption of methylen blue onto TW/C composite has been studied. Measurements are performed at various contact time, pH and adsorbent dosage. The adsorption kinetics of methylen blue (MB) could be described by the pseudo-second order kinetic model. The adsorption isotherms are described by means of Langmuir and Freundlich isotherms. It was found that the Freundlich model fit better than the Langmuir model. The thermodynamic constants of the adsorption were calculated to predict the nature of adsorption. The values of thermodynamic parameters indicate that a spontaneous and endothermic process was occurred.

Keywords: Adsorption; $CuFe_2O_4$ Composite; Kinetic; Methylen Blue (MB); Tea Waste; Thermodynamic

1. Introduction

One of the major problems concerning textile waste waters is colored effluent. This waste water contains a variety of organic compound and toxic substances, which are harmful to fish and aquatic organisms [1]. This dictates the necessity of dye containing water to undergo treatment before disposal to the environment. Several techniques are available for treatment of industrial waste waters [2-6], among these methods, adsorption technique for waste water treatment has more popular in recent years owing to their efficiency in the removal of pollutants which are too stable for biological methods. Adsorption can produce high quality water while also being a process that is economically feasible [7]. Methylen blue (MB) is one of the basic dyes with the structure of heterocyclic aromatic chemical compound. The cationic dyes were commonly used initially for dyeing of silk, leather, plastics, paper, and in manufacturing of paints and printing inks [8].

Though MB is not strongly hazardous, but it can cause some harmful effects. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis in humans [9,10]. The adsorption characteristics of MB on various adsorbents have previously been extensively investigated. Senthil Kumar *et al*. studied the adsorption mechanisms of MB onto fly ash and demonstrated that fly ash can be used as an adsorbent for the removal of MB from its waste water [11]. Ghosh *et al*. investigated the adsorption of MB using kaolinite as adsorption and showed that kaolinite clay could be effective in removing MB in relatively low concentration from the aqueous medium [12]. The adsorption of MB was investigated by rice husk [13], jute fiber carbon [14], glass fiber [15], clay [16], stainless steel surface [17], perlite [18], tea waste [19], wood sawdust [20], rejected tea [21], peanut shell [22] and wheat shells [23].

Tea waste is a cost effective adsorbent. The objective of this work was to evaluate the adsorption potential of TW, $CuFe_2O_4$ and TW/C composite for MB from aqueous solution. The effects of contact time, pH, initial MB concentration and tea waste mass on the amount of MB removal were investigated. The kinetic and thermodynamic involved in the sorption process were evaluated.

2. Materials and Method

2.1. Materials and Chemicals

Tea waste was used as sorbent. The tea waste was

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washed with tap water and distilled water for several times to remove all the dirt particles. It was then boiled with distilled water to remove caffeine, tannin and other dyes and washed with distilled water till the washing water contains no color. The tea waste preheated in an oven at 100˚C for about 48 h to reduce the moisture content. They were then crushed with a high speed mill and sieved on a sieve mechanical shaker, and size fraction of lower than 180 µm that has been passed through US standard sieve number 80. MB was purchased from Merck and used without further purification. The stock solution of MB was prepared with distilled water (100 $mg \cdot L^{-1}$). The test solutions were prepared by diluting stock solution to the desired concentrations.

2.2. Preparation of $CuFe_2O_4$ and Tea Waste/$CuFe_2O_4$

Analytical grade copper (Π) chloride dehydrates and ferric chloride were obtained from Merck. $CuFe_2O_4$ and TW/C composite were prepared using a co-precipitation method. The TW was added into a 400 ml solution containing copper (Π) chloride (0.02 mol) and ferric chloride (0.04 mol) at room temperature. The amount of TW was adjust to obtain TW/C mass ratio of 10:1 under vigorous magnetic- stirring, slowly raised the pH by adding NaOH (5 $mol \cdot L^{-1}$) solution to around 10 and stirring was continued for 30 min, and the stopped stirring. The suspension was heated to 95˚C - 100˚C for 2 h. After cooling, the prepared composite was repeatedly washed with distilled water. By a simple magnetic procedure, the obtained materials was separated from water and dried in an oven at 105˚C [24,25].

2.3. Characterization of Sorbent and Sorbat

Fourier transform infrared spectroscopy of the adsorbents was done by using an FTIR spectrophotometry (Bruker Tesor-27), where the spectra were recorded from 4000 - 400 cm^{-1}. Scanning electron microscopy (SEM) analysis was carried out for tea waste, TW/C and TW/C after dye adsorption to study their surface textures. MB was analyzed by Shimadzu 160A UV-Vis spectrophotometer.

2.4. Sorption Experiments

The sorption experiments were carried out in 100 ml stopper conical flask containing varying amount of MB solution and adsorbent dosage. The temperature was controlled at 25˚C ± 1˚C by air bath. pH adjusted by addition of 0.1 M HCl or NaOH solution. The suspensions containing 0.1 g composite varying amount of MB were shaken on an orbital shaker at 130 rpm. Samples were taken at different time intervals and then centrifuged and concentration of MB analyzed using UV-Vis spectrophotometer. The chemical structure of MB is shown in **Figure 1**.

3. Results and Discussion

3.1. Characterization Experiments

The composite was prepared by the chemical co-precipitation of $CuFe_2O_4$ and tea waste. The FTIR spectroscopic characteristics of TW and TW/C are listed in **Table 1**. The FT-IR spectra display a number of absorption peaks, indicating the complex nature of tea waste. The FTIR spectroscopic analysis indicated broad bands 3421 cm^{-1} representing bonded-OH groups. The band at 1634 cm^{-1} represents the C=O stretching mode conjugated with NH_2. The peaks observed at 607 correspond to the aromatic nitro compound and C-C group. These three significant bands in the spectrum indicate the possible involvement of the functional group on the surface of tea waste [25]. **Figure 2** shows FTIR of TW (a), TW/C (b). Presence of $CuFe_2O_4$ does not significant change on the surface of TW.

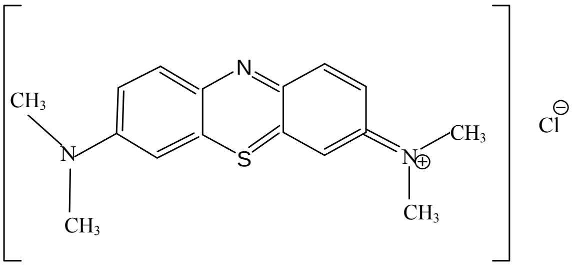

Figure 1. Chemical structure of MB.

Table 1. FTIR spectral characteristic of TW and TW/C before and after sorption of MB.

Assignment	TW before adsorption	TW after adsorption	TW/C before adsorption	TW/C after adsorption of (MB)
Bonded-OH groups	3421	3414	3417	3569 - 3421
Aliphatic C-H groups	-	2924	-	2924
C=O stretching	1634	1638	1623	1634
Secondary amine group	-	1556	-	1556
-C-C- group	1045	1041	607	620
Fe-O or Cu-O	-	-	-	470

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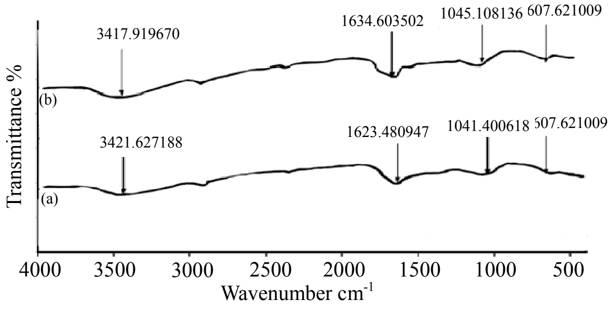

Figure 2. FTIR of TW (a), TW/C (b).

The FTIR TW and TW/C before and after adsorption of MB also was recorded (**Figure 3**). For TW after adsorption of MB bands 3421 and 1634 cm^{-1} shift to 3414 and 1638 cm^{-1}, but for TW/C 3421 has broad band shift to 3417 - 3569 and bands at 1634 was constant.

Figure 4(a) shows the bar sharp of TW particles. **Figure 4(c)** shows the bar sharp of TW/C with particle size of about 100 nm. **Figure 4(b)** shows the surface of TW is covered with dye molecules [24]. **Figure 4(d)** shows TW/C loaded with MB. It was found the BET surface area of TW and TW/C were 350 and 570 m^2·g^{-1}, respectively. The average pore diameter of TW and TW/C was 45 and 59 Å, respectively.

3.2. Effect of Contact Time on MB Adsorption

Figure 5 shows the effect of the contact time on the adsorption of MB onto TW and TW/C. It was observed that MB adsorption was rapid for the first 30 min and there after it proceeded at a slower rate and finally reached saturation. For TW the uptake of MB after 60 min of contact time was 72% but for TW/C after 60 min of contact time is raised to 95%. The higher percentage of dye removal for TW/C is due to catalytic effect of $CuFe_2O_4$ on the TW.

3.3. Effect of pH

MB is a cationic dye, which exists in aqueous solution in from of positively charge ion as a charged species. The degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH [19]. The surface charge Q of the adsorbent was calculated from the experimental titration data according to the following equation:

$$Q = 1/W\left(C_A - C_B - \left[H^+\right] - \left[OH^-\right]\right)$$

where W is the dry weight of adsorbent in aqueous system (g·L^{-1}), C_A is the concentration of added acid in aqueous system (mol·L^{-1}), C_B is the concentration of added base in aqueous system (mol·L^{-1}), [H$^+$] is the concentration of H$^+$(mol·L^{-1}) and [OH$^-$] is the concentration

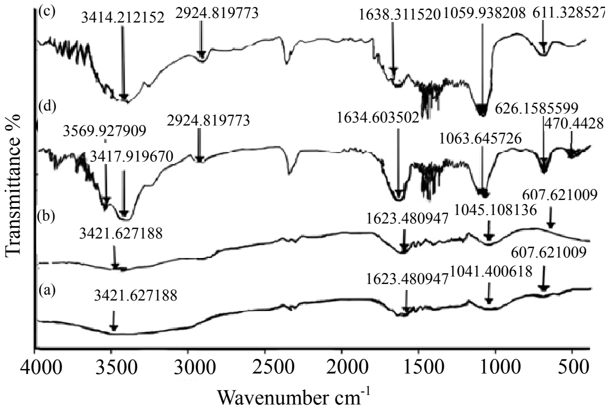

Figure 3. FTIR (a) TW, (b) TW/C before and (c) TW, (d) TW/C after adsorption of MB.

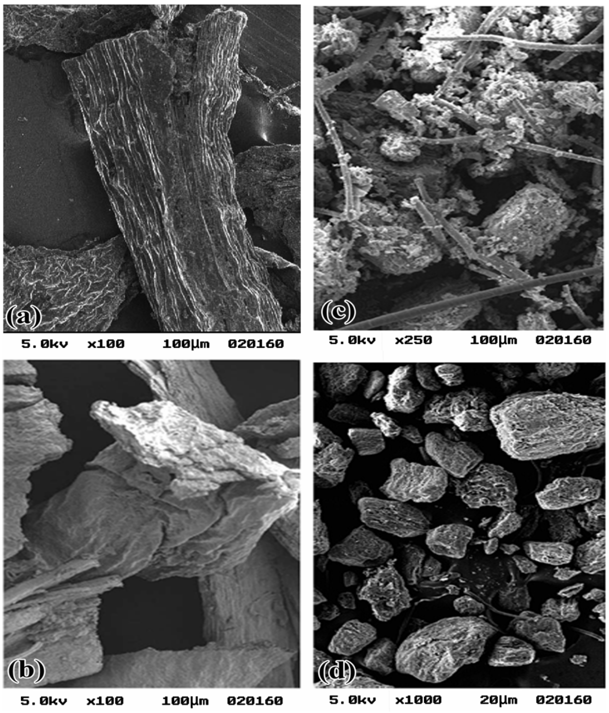

Figure 4. SEM micrographs of (a) TW, (c) TW/C before and (b)TW, (d) TW/C after MB adsorption.

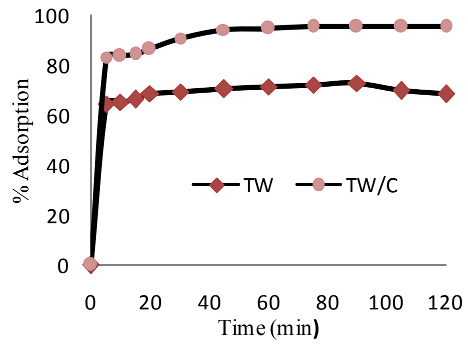

Figure 5. Effect of the contact time on the adsorption of MB onto TW, TW/C.

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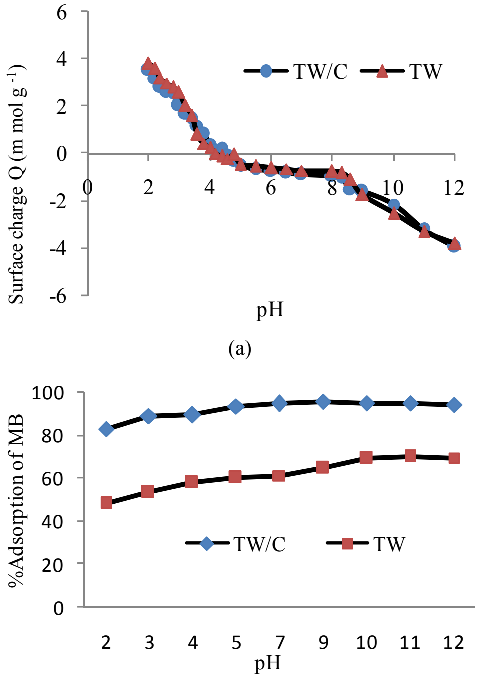
of OH^- ($mol \cdot L^{-1}$). Then, the pH value at the point of zero charges was determined by plotting Q versus pH. **Figure 6(a)** shows the surface charge of the adsorbent as a function of pH. From **Figure 6(a)**, it is obvious that the surface charge of the TW, TW/C adsorbent at pH 4.2 and 4.6 ± 0.2 is zero, respectively. Therefore, the pH_{pzc} of the TW and TW/C composite is 4.2 and 4.6 ± 0.2, respectively.

Figure 6(b) shows the effect of pH on the adsorption of MB. The experiments were conducted at 10 $mg \cdot L^{-1}$ initial MB concentration, 0.10 g sorbent and 25˚C ± 1˚C. It was observed that pH gives a significant influence on the adsorption process. The percentage MB adsorption increased from 25% to 55% for TW and 83% to 95% for TW/C when the pH value increased from 2 - 10. The percentage adsorption was minimum at pH 2, this increased up to 10. Lower adsorption of MB at acidic pH is due to the presence of excess H^+ ions competing with the cation group on the dye for adsorption sites. At pH < pH_{pzc}, sorbent surface may get positively charged due to the adsorption of H^+. This could be explained by the fact that at low pH, more protons will be available to protonate hydroxyl groups, reducing the number of binding sites for the adsorption of MB. At higher solution pH, the TW possibly negatively charged and enhance the positively charge dye cation through electrostatic process of attraction. A similar result was reported [19,24,25].



(a)

(b)

Figure 6. (a) Surface charge of adsorbent as a function of pH; (b) Effect of pH on the adsorption of MB onto TW, TW/C composite for 100 $mg \cdot L^{-1}$ initial MB concentration, 0.10 g sorbent.

3.4. Effect of Adsorbent Dosage

The effect of TW/C adsorbent dosage on the removal of MB in illustrated in **Figure 7**. The percentage removal of MB increased with the increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption active sites resulting from the increase dosage of the adsorbent.

3.5. Adsorption Isotherms

Review absorption isotherms of both experimental and theory is important. In order to represent the equilibrium adsorption process, two different isotherm equations were used for experimental data analysis. The Langmuir theory presumes a specific homogeneous type of the adsorption with the adsorbent [26], *i.e.*, once a molecule of MB takes a site, no other one can take same site. The linear form of the Langmuir model was used the following equation:

$$1/q_e = 1/q_m + 1/(q_m K_L C_e)$$

The Freundlich isotherm assumes that adsorption process occur heterogeneous surfaces and the capacity of adsorption is related to the concentration of MB at the equilibrium [27]. A linear form of Freundlich is expressed as follows:

$$\text{Log } q_e = \text{Log } K_F + 1/n \text{ Log } C_e$$

where q_e is the adsorbed amount at the equilibrium ($mg \cdot g^{-1}$), q_m is the maximum adsorbed amount ($mg \cdot g^{-1}$), C_e is the equilibrium concentration of MB dye in the solution ($mg \cdot L^{-1}$), K_L, K_F are the equilibrium constants, and n are constant. The isotherm parameters of Langmuir and Freundlich for TW/C composite are shown in **Figures 8** and **9**. All calculated isotherm constants by both models are listed in **Table 2**. By comparing the values obtained R^2 charts, which was intended adsorption process by adsorbing pollutants MB by adsorbent TW/C absorb isotherms model Freundlich follows.

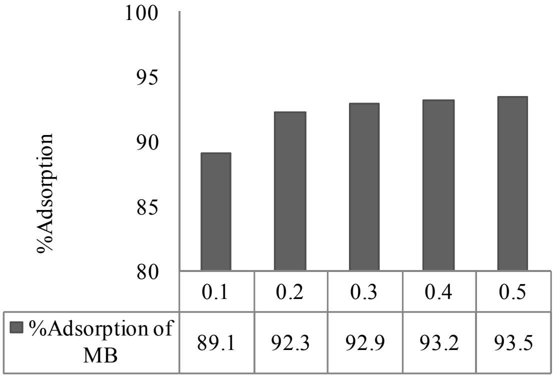


Figure 7. Effect of adsorbent dosage on the adsorption of MB onto TW/C.

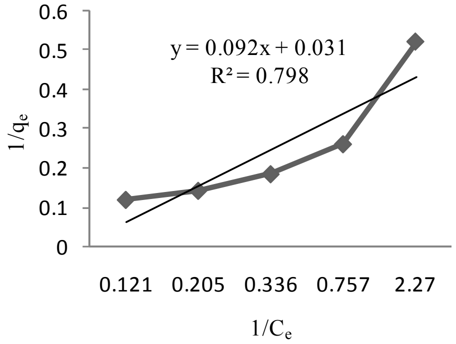


Figure 8. Adsorption isotherm Langmuir models of MB adsorption onto TW/C at 25˚C.

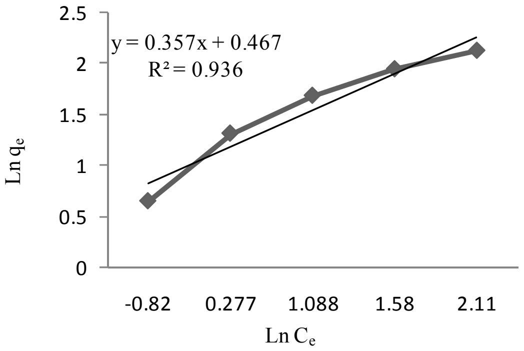


Figure 9. Adsorption isotherm Freundlich models of MB adsorption onto TW/C at 25˚C.

Table 2. Isotherm parameters for the removal of MB by TW/C composite.

		Langmuir			Freundlich		
Temperature	Pollutant	$(mg \cdot g^{-1}) \cdot q_m$	$(L \cdot mg^{-1}) \cdot K_L$	R^2	K_f	$1/n$	R^2
25˚C	MB	32.25	0.337	0.798	1.59	0.8	0.936

3.6. Adsorption Kinetics

The pseudo-first-order kinetic model was appropriate for lower concentration, with the equation expressed as follows [28]:

$$\mathrm{Ln}\left(q_e - q_t\right) = \mathrm{Ln}\ q_e - k_1 t$$

The rate of pseudo-second-order reaction depends on the amount of adsorbed solution, the surface of adsorbent and the amount of adsorption at the equilibrium. The model was represented in the following linear form [29]:

$$t/q_t = 1/kq_e^2 + t/q_e$$

where q_t is the amount of dye adsorbed at time t ($mg \cdot g^{-1}$), q_e is the adsorption capacity at equilibrium ($mg \cdot g^{-1}$), and k_1 and k_2 are the apparent rate constants.

During this study, the two adsorption kinetic modes were used. The pseudo-first order and pseudo-second older were shown in **Figures 10** and **11**, respectively. The related parameters are listed in **Table 3**. As shown, the R^2 value of the pseudo-second-order model is higher than R^2 values pseudo-first-order model. Therefore, the adsorption kinetics could well be satisfactorily more favorably described by pseudo-second-order kinetic model for MB adsorption onto TW/C composite [21].

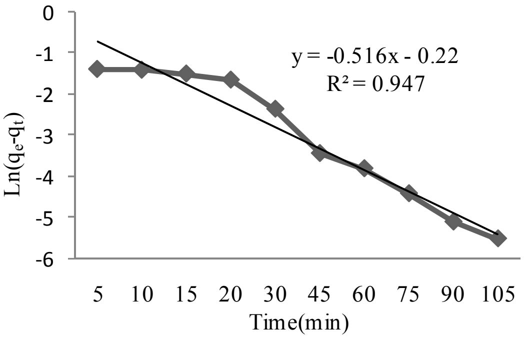


Figure 10. Pseudo-first-order kinetic of MB adsorption onto TW/C composite for 30 ml of an initial concentration 100 mg·L^{-1}, pH 10, 0.1 g adsorbent for pseudo-first order model.

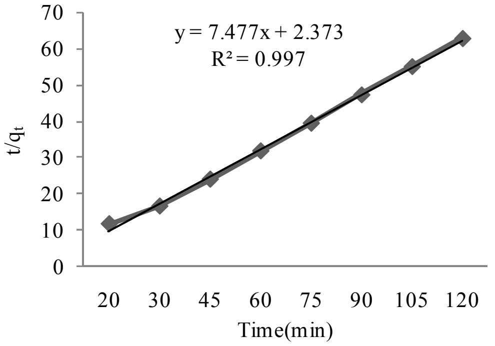


Figure 11. Pseudo-second-order kinetic of MB adsorption onto TW/C composite for 30 ml of an initial concentration 100 mg·L^{-1}, pH 10, 0.1 g adsorbent for pseudo-second order model.

Table 3. Kinetics parameters for the removal of MB by TW/C composite.

First order		Second order	
R^2	K_1	R^2	K_2
0.947	0.516	0.997	0.40

3.7. Adsorption Thermodynamics

Thermodynamic parameters including Gibbs free energy ΔG˚, standard enthalpy ΔH˚ and standard entropy ΔS˚ are the parameters to better understand the temperature effect on absorption was studied. For this purpose solution 10 mg·L^{-1} MB was prepared and at different temperatures absorbs it notes using the standard curve concentrations were obtained at different temperatures.

Gibbs free energy ΔG˚ by using equilibrium constant

K_C is calculated:

$$\Delta G^{o} = -RTLnK_C$$

K_C value is calculated from the following formula:

$$K_C = C_{AE}/C_{SE}$$

C_{AE} amount absorbed by the absorbent paint and color balance of C_{SE} concentration is the solution.

Standard enthalpy ΔH˚ and standard entropy ΔS˚:

$$LnK_C = -\Delta H^{o}/RT + \Delta S^{o}/R$$

In this equation R is the gas constant equal to the public (8.314 $J \cdot mol^{-1} \cdot k^{-1}$). The amount of dye adsorbed at equilibrium at different temperatures 20˚C - 60˚C, have been examined to obtain thermodynamic parameters for the adsorption system. ΔH˚ and ΔS˚ were calculated the slope and intercept of vant Hoff plots of ln K_C versus 1/T (**Figure 12**). The results of thermodynamic parameters are given in **Table 4**. As observed in **Table 4** negative value ΔG˚ at different temperatures shows that the adsorption process to be spontaneous. The ΔH˚ positive value indicates that the uptake is endothermic [30,31].

4. Conclusion

The results of this study indicate that TW/C can be successfully used as a cost effective adsorbent for removal of MB from water and waste water. MB is found to adsorb strongly on the surface of TW/C. Adsorption behavior is described by Freundlich isotherm model. Kinetic data follows pseudo second-order kinetic model. The negative values of ΔG˚ indicated that the MB dye adsorption processes spontaneous and an endothermic. The positive value for ΔH˚ indicated that the adsorption is an endothermic process. The positive value of ΔS˚ reflects the affinity of the adsorbent for MB.

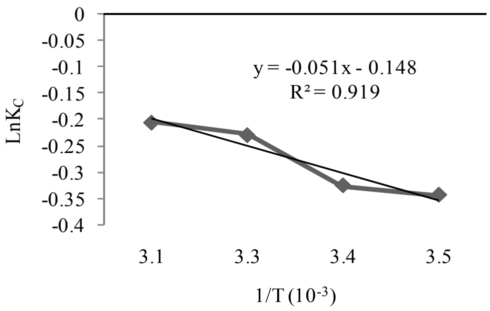


Figure 12. Plot of LnKc verses 1/T (30 mL MB solution, initial concentration 100 mg·L⁻¹ and 0.1 g sorbent).

Table 4. Thermodynamic parameters for the adsorbent TW/C at different temperatures for a solution MB.

T (K)	ΔG˚ ($KJ \cdot mol^{-1}$)	ΔS˚	ΔH˚ ($KJ \cdot mol^{-1}$)
293	−7.429	28.79	0.68
303	−7.809		
313	−8.483		
323	−8.969		
333	−9.246		

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