



Removal of methylene blue from aqueous solution using cotton stalk, cotton waste and cotton dust

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ABSTRACT

In this study, cotton stalk (CS), cotton waste (CW) and cotton dust (CD) was used as sorbents to remove methylene blue (MB) from aqueous solution by batch sorption technique. Effects of initial dye concentration, solution pH, solution temperature and sorbent dose on sorption were studied. It was seen that the removal of methylene blue increased with increasing initial dye concentration (from 25 to 100 mg/l), solution pH (from 5 to 10), solution temperature (from 20 to 50 °C) and sorbent dose (from 0.25 to 1.50 g/50 ml). The maximum dye removal was reached at 90 min. Sorption isotherms were analyzed by Langmuir and Freundlich models at different temperatures of 20, 30, 40 and 50 °C, and the results were discussed in detail. Moreover, the thermodynamics of sorption were also studied. It was found that the values of standard free energy (ΔG°) were positive for cotton stalk and negative for cotton waste and cotton dust. The values of standard enthalpy (ΔH°) and entropy (ΔS°) were found to be positive, and the obtained results were interpreted in detail. The results of this study showed that cotton stalk, cotton waste and cotton dust could be employed as effective and low-cost materials for the removal of dyes from aqueous solution.

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1. Introduction

Wastewaters from textile, cosmetics, printing, dyeing, food coloring, paper-making industries are polluted by dyes. These colored effluents are known to be carcinogenic and highly toxic to living beings [1]. For example, these can cause allergic dermatitis, skin irritation, cancer, and mutations [1,2]. Therefore, the undesirable dye pollutions are required to remove from wastewaters before being discharged to the environment. For this purpose, many methods such as activated carbon sorption, chemical coagulation, ion exchange, electrolysis, biological treatments, etc have been developed [3,4]. Of these methods, activated sorption is highly effective for the removal of dyes and pigments as well as other organic and inorganic pollution [2,5–9]. However, commercially available activated carbons are very expensive, and thus the use of activated carbon is not suitable for developing countries because of its high cost. Therefore, the use of low-cost and effective sorbents instead of activated carbon should be preferred in removing the undesirable pollution from environment. In recently, some researchers have

focused on the use of low-cost sorbents. Some low-cost materials used as sorbent for dye sorption from wastewaters were as follows: bagasse pith [10], wood [11,12], peanut shell [13] and peat [14], bark [15], fly ash [1], perlite [2,16], fungi [17], sawdust [18], orange peel [19,20], banana peel [20], rice husk [21].

On the other hand, cotton stalks (CS), cotton waste (CW) and cotton dust (CD) may be thought as other inexpensive materials which will be used as sorbents. Cotton stalks are an agricultural waste. Cotton waste is named as the rest wastes after mechanic cleaning process (i.e. willow process) to product pure white cotton from raw cotton, which is generally dirty by 40–45% and their colour is brown. Cotton dust is flying-dust in the air, which are arisen during the production of yarn in the textile factory. These three wastes do not have any economical values. In this work, a more rational use of these low-cost wastes was aimed for the removal of dyes. Therefore, the use of cotton waste and cotton dust as sorbents for the removal of methylene blue (MB) from aqueous solution have not found in the literature, so far. The use of cotton stalks as a sorbent for the removal of methylene blue is very restricted. Therefore, herein, these wastes were utilized as alternative sorbents for the removal of methylene blue from aqueous solution by sorption technique. Moreover, effects of initial dye concentration, pH, temperature and sorbent dosage on sorption were investigated. On the other had, the sorption isotherm and thermodynamics were studied in detail.

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Table 1
Chemical analysis of cotton stalk, cotton waste and cotton dust.

Component	Percent values		
	Cotton stalk	Cotton waste	Cotton dust
Cellulose	47.80	62.20	100
Hollocellulose	77.50	81.70	
Lignin	21.20	14.60	
Alcohol–benzene extraction	4.70	5.60	
Ash	1.30	0.90	

2. Materials and methods

2.1. Materials

2.1.1. Sorbents

Cotton stalk (CS): Cotton stalks, *Gossypium hirsutum* L., were collected from an agriculture area in Kahramanmaraş, a province located in the southern of Turkey. CS was ground using a Willey mill and dried in an oven at 105 °C for 24 h. Chemical composition of CS was determined using the methods in Ref. [22], and the results are given in Table 1. The CS particles were passed through 20-, 100- and 200-mesh sieves for sorption experiments, respectively.

Cotton waste (CW): Cotton waste is named as the rest wastes from washing of the residue cotton wastes after mechanic cleaning process (i.e. willow process) during the production of yarns with cotton. Cotton waste samples were obtained from a private textile factory (TEKSAN textile factory) in Kahramanmaraş. Chemical composition of CW was determined using the methods in Ref. [22], and the results are given in Table 1.

Cotton dust (CD): Cotton dust is the dust of pure white cotton which is captured by air in environment during the production of yarns with cotton. The cotton dust consists of 100% cellulose. Cotton dust samples were supplied from a private spinning mill (KARSAN textile and dye factory) in Kahramanmaraş. The particle sizes of CW and CD for experiments was used as 20 mesh (in 0.85 mm) due to their fiber properties. All sorbents were used without any pretreatment in the sorption experiments, respectively.

2.1.2. Adsorbate

Methylene Blue, a cationic dye, (CI 52015) was purchased from Merck, and it was used as received without further purification. The structure of the dye containing a secondary amine group is presented in Fig. 1. Its stock solutions of 1000 mg/l for desired concentrations were prepared with pure distilled water. Initial solution pHs of the dye were adjusted by dropping of 0.1 N HCl and NaOH solutions.

2.2. Methods

Batch sorption experiments were done by shaking 0.25 g of sorbents with 50 ml aqueous solution of methylene blue of known concentration in 250 ml-erlenmayer flasks placed in a temperature controlled shaking water bath at different concentrations (between 25 and 100 mg/l), pHs (between 5 and 10), temperatures (between 20 and 50 °C) and sorbent doses (between 0.25 and 1.50 g) at a con-

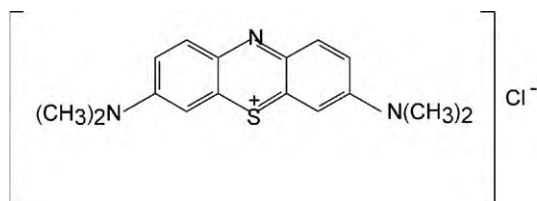


Fig. 1. Chemical structure of methylene blue.

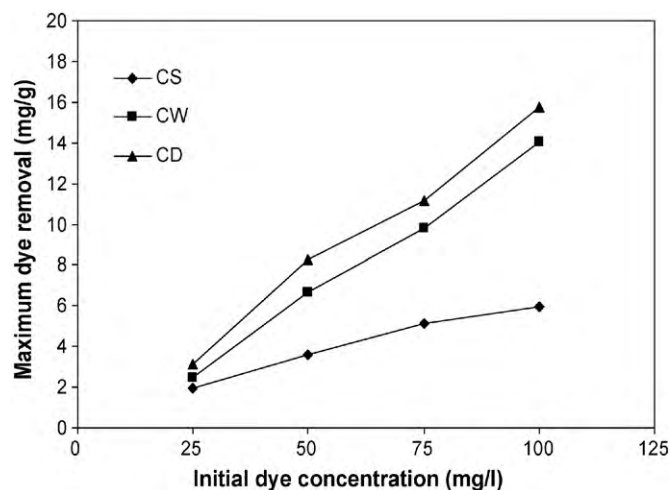


Fig. 2. Effect of initial dye concentration on the removal of MB by CS, CW and CD (conditions: $T=20\text{ }^{\circ}\text{C}$; $\text{pH } 6.33$; $W/V=0.25\text{ g}/50\text{ ml}$, $t=90\text{ min}$).

stant shaking rate of 125 rpm. After the desired contact time, the samples were withdrawn from mixture by using a micropipette and centrifuged for 5 min at 5000 rpm. After centrifuged, supernatants were analyzed for the determination of the final concentration of methylene blue by using an UV–vis spectrophotometer (Janway 6100) set at a wave-length of 663 nm, maximum absorbance.

The amounts of dye removed by sorbents, $q_{e(\text{exp})}$, can be calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q_e is the amount of dye adsorbed (mg/g). C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye (mg/g), respectively. V is the volume of the solution (l), and W is the weight of the sorbent used (g).

3. Results and discussion

3.1. Effect of contact time and initial dye concentration on dye removal

Firstly, sorption experiments were performed for different contact time with fixed concentration, temperature and pH using sorbents CS, CW and CD. The maximum dye removals by CS, CW and CD were determined to occur nearly at 90 min under all conditions. After this time, the amount of dye removed did not any change. Therefore, this time was assumed as an equilibrium time which indicates a saturation time. The maximum amounts of dye removed at equilibrium time are named as an equilibrium sorption capacity.

Secondly, the effects of initial concentration on the removal of MB by CS, CW and CD were studied at 20 °C and pH 6.33 (natural dye pH) at equilibrium times, and the results were graphed in Fig. 2. The figure shows maximum dye removal on all sorbents at equilibrium time. If it notices to Fig. 2, it is seen that the equilibrium sorption capacities of the sorbents increase with an increase in initial dye concentration. For example, when the initial MB concentration increases from 25 to 100 mg/l, the equilibrium sorption capacities of CS, CW and CD increase from 1.96 (39.20%) to 5.95 mg/g (29.75%), from 2.50 (50.0%) to 14.04 mg/g (70.20%) and from 3.10 (62.0%) to 15.78 mg/g (78.90%), respectively. Similar trends have also been observed for methylene blue sorption onto bamboo-based activated carbon [23], and fly ash [24]. When initial MB concentration increases from 25 to 100 mg/l, the percent removals of MB by CW and CD increase from 50.0% to 70.20% and from 62.0% to 78.90%,

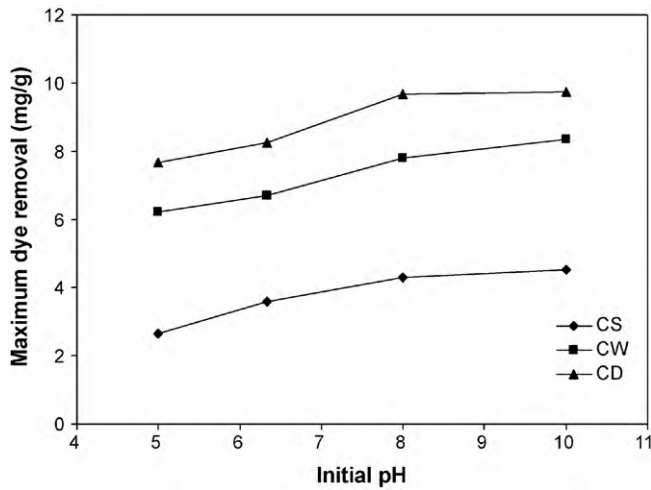


Fig. 3. Effect of initial solution pH on the removal of MB by CS, CW and CD (conditions: $C_0 = 50$ mg/l, $T = 20$ °C; $W/V = 0.25$ g/50 ml, $t = 90$ min).

respectively. This increase in the proportion of removed dye may be probably due to equilibrium shift during sorption process. A similar result has also been recorded for adsorption of Congo red from aqueous solution onto calcium-rich fly ash [1]. Herein, it is found that CD is more effective than SC and CW to remove the MB from aqueous solution.

3.2. Effect of pH on dye removal

The sorption of dye onto sorbent varies essentially with pH because pH causes to change the charge of sorbent surface. For example, the surface charge of a sorbent has become generally positively charged at lower pH and negatively charged at higher pH. Namely, the positive charge in acidic medium and the negative charge basic medium develop on the surface of sorbent. Therefore, while the removal of a cationic dye by sorption increases at higher pH, it decreases at lower pH. Herein, the effect of initial pH on the dye removal by CS, CW and CD was studied in the pH range between 5 and 10 for initial MB concentration of 50 mg/l at 20 °C, and the obtained results are shown in Fig. 3. It is obvious from the figure that the removal of the MB increases with increasing initial pH from 5 to 10. For example, while the maximum dye removals by CS, CW and CD are 2.66 mg/g (26.60%), 6.22 mg/g (62.10%) and 7.66 mg/g (76.60%) at pH 5, they are found as 4.52 mg/g (45.20%), 8.33 mg/g (83.30%) and 9.75 mg/g (97.50%) at pH 10, respectively. The fact that the maximum dye removal is more at higher pH indicates that the surface of sorbent has become more negatively, and therefore the interaction between negatively charged sorbent and positively charged MB molecules is greater. This interaction may be probably via electrostatic interactions between negatively charged sorbents and positively charged MB molecules. Also, lower dye removal at acidic pH is probably due to the presence of excess H^+ ions competing with positively charged MB molecules for the sorption sites of sorbents. Similar results have also been reported for MB sorption onto jackfruit peel [25] and wheat shells [26]. Herein, it is also found that CD is more effective than SC and CW to remove the MB from aqueous solution.

3.3. Effect of temperature on dye removal

The effect of temperature on dye removal by CS, CW and CD was studied in the range of temperature between 20 and 50 °C for initial MB concentration of 50 mg/l at pH 6.33, and the obtained results are shown in Fig. 4. As can be seen from the figure, with

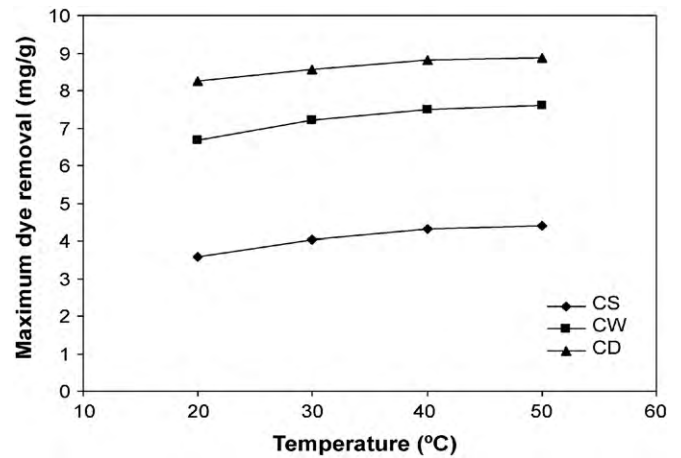


Fig. 4. Effect of temperature on the removal of MB by CS, CW and CD (conditions: $C_0 = 50$ mg/l, pH 6.33; $W/V = 0.25$ g/50 ml, $t = 90$ min).

an increase in temperature from 20 to 50 °C, the removals of MB by CS, CW and CD are slightly endothermic. For example, with increasing temperature from 20 to 50 °C, the maximum amounts of MB removed by CS, CW and CD are found to be increased from 3.58 (35.80%) to 4.52 mg/g (45.20%), 6.68 (66.80%) to 8.33 mg/g (83.30%), from 8.26 (82.60%) to 9.75 mg/g (97.50%), respectively. This increase may indicate the increased tendency of MB due to an increase in its kinetic energy with increasing temperature, and this situation leads to more sorption on the surfaces of CS, CW and CD. A similar result has also been reported for the removal of methylene blue by adsorption on biosolid [27].

3.4. Effect of sorbent dosage on dye removal

The removal of MB by CS, CW and CD were studied by changing the quantities of sorbents (0.25, 0.50, 0.75, 1.0 and 1.50 g/50 ml) for the initial dye concentration of 50 mg/l at 20 °C and pH 6.33. Fig. 5 shows that an increase in sorbent dose is in favor of dye removal. When the sorbent dose increases from 0.25 to 1.50 g, the percent dye removals by CS, CW and CD increase from 35.08% to 48.36%, from 68.03% to 85.41% and from 83.93% to 91.47% at an equilibrium time of 90 min, respectively. This can be simply attributed to the increased sorbent surface area and availability of more sorption sites [18]. On the other hand, unit sorption indicating the amount of solute sorbed per unit sorbent decreases with an increase in sorbent dose. For example, when the sorbent dosages increases from 0.25

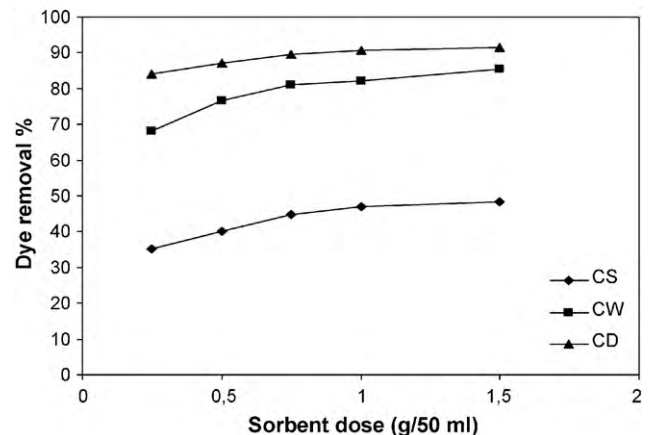


Fig. 5. Effect of sorbent dosage on the removal of MB by CS, CW and CD (conditions: $C_0 = 50$ mg/l, $T = 20$ °C; pH 6.33, $t = 90$ min).

Table 2

The comparison of experimental sorption capacities of cotton stalk, cotton waste and cotton dust to some sorbents for methylene blue sorption.

Capacity, mg/g (percentage)	Experimental conditions	Biosorbent/adsorbent	References
4.52 (45.20%)	$C_0 = 50 \text{ mg/l}$, $T = 20^\circ\text{C}$, pH 10, $V = 50 \text{ ml}$, $W = 0.25 \text{ g}$	Cotton stalk	This study
5.95 (29.75%)	$C_0 = 100 \text{ mg/l}$, $T = 20^\circ\text{C}$, pH 6.33, $V = 50 \text{ ml}$, $W = 0.25 \text{ g}$	Cotton stalk	This study
8.33 (83.30%)	$C_0 = 50 \text{ mg/l}$, $T = 20^\circ\text{C}$, pH 10, $V = 50 \text{ ml}$, $W = 0.25 \text{ g}$	Cotton waste	This study
14.04 (70.20%)	$C_0 = 100 \text{ mg/l}$, $T = 20^\circ\text{C}$, pH 6.33, $V = 50 \text{ ml}$, $W = 0.25 \text{ g}$	Cotton waste	This study
9.75 (97.50%)	$C_0 = 50 \text{ mg/l}$, $T = 20^\circ\text{C}$, pH 10, $V = 50 \text{ ml}$, $W = 0.25 \text{ g}$	Cotton dust	This study
15.78 (78.90%)	$C_0 = 100 \text{ mg/l}$, $T = 20^\circ\text{C}$, pH 6.33, $V = 50 \text{ ml}$, $W = 0.25 \text{ g}$	Cotton dust	This study
0.73 (97.33%)	$C_0 = 10.0 \text{ mg/l}$, $T = 50^\circ\text{C}$, pH 11, $V = 75 \text{ ml}$, $W = 1.0 \text{ g}$	Perlite	[2]
15.90 (15.90%)	$C_0 = 100 \text{ mg/l}$, $T = 30^\circ\text{C}$, pH 6, $V = 100 \text{ ml}$, $W = 0.10 \text{ g}$	Banana peel	[20]
13.90 (13.90%)	$C_0 = 100 \text{ mg/l}$, $T = 30^\circ\text{C}$, pH 7.2, $V = 100 \text{ ml}$, $W = 0.10 \text{ g}$	Orange peel	[20]
10.60 (93.33%)	$C_0 = 35. \text{mg/l}$, $T = 30^\circ\text{C}$, pH 6.5, $V = 200 \text{ ml}$, $W = 0.60 \text{ g}$	Jackfruit peel	[25]
114.69 (86.0%)	$C_0 = 400. \text{mg/l}$, $T = 30^\circ\text{C}$, pH 6.5, $V = 200 \text{ ml}$, $W = 0.60 \text{ g}$	Jackfruit peel	[25]
24.40 (97.60%)	$C_0 = 250 \text{ mg/l}$, $T = 25^\circ\text{C}$, pH 7.0, $V = 1000 \text{ ml}$, $W = 10 \text{ g}$	Biosolid	[27]
80.63 (74.77%)	$C_0 = 380. \text{mg/l}$, $T = 30^\circ\text{C}$, pH 6.5, $V = 200 \text{ ml}$, $W = 0.70 \text{ g}$	Grass waste	[28]
102.14(92.20%)	$C_0 = 390 \text{ mg/l}$, $T = 30^\circ\text{C}$, pH 6.5 $V = 200 \text{ ml}$, $W = 0.70 \text{ g}$	Spent tea leaves	[29]
15.33 (91.98%)	$C_0 = 25 \text{ mg/l}$, $T = 30^\circ\text{C}$, pH 11, $V = 200 \text{ ml}$, $W = 0.30 \text{ g}$	Pumpkin sheel hull	[34]
3.30 (82.54%)	$C_0 = 8.0 \text{ mg/l}$, $T = 40^\circ\text{C}$, pH 6.33, $V = 50 \text{ ml}$, $W = 0.10 \text{ g}$	Aspegillus wentii	[35]
3.40 (85.04%)	$C_0 = 8.0 \text{ mg/l}$, $T = 40^\circ\text{C}$, pH 10, $V = 50 \text{ ml}$, $W = 0.10 \text{ g}$	Aspegillus wentii	[35]
263.33(79%)	$C_0 = 100 \text{ mg/l}$, $T = 20^\circ\text{C}$, pH 11, $V = 50 \text{ ml}$, $W = 0.015 \text{ g}$	Phellinus igniarius	[36]
249.92 (75%)	$C_0 = 100 \text{ mg/l}$, $T = 20^\circ\text{C}$, pH 11, $V = 50 \text{ ml}$, $W = 0.015 \text{ g}$	Fomes fomentarius	[36]

C_0 = initial dye concentration (mg/l), T = temperature, V = solution volume, W = sorbent/biosorbent amount.

to 1.50 g, the values of unit sorption onto CS, CW and CD decrease from 3.51 to 0.81 mg/g, from 6.80 to 1.42 mg/g and from 8.39 to 1.52 mg/g, respectively. This may be attributed that dye molecules with the same concentration is more shared per unit sorbent due to an increase in total sorbent surface. Therefore, this situation causes to less unit sorption.

If notice to the obtained results, it can be seen that the adsorption of the dye increases in the order of $CD > CW > CS$ under all conditions studied such as concentration, temperature, pH and sorbent dose. The fact that the adsorption of MB onto CD is more than CW and CS indicates that the chemical structure of CD consists of only cellulose, and therefore the cationic methylene blue molecules may be probably adsorbed to negatively charged surface of cellulose on CD.

3.5. The comparison of experimental sorption capacities of cotton stalk, cotton waste and cotton dust to some sorbents

In this study, the removal of methylene blue by cotton stalk, cotton waste and cotton dust were studied at various initial dye concentrations (between 25 and 100 mg/l), solution pHs (between 5 and 10) and solution temperatures (between 20 and 50 °C) for a contact time of 90 min, respectively. Under all condition studied, the most sorption is occurred at 20 °C and pH 10 for each sorbent. For example, the maximum amounts of MB sorbed per unit CD, CW and CS is 4.58 mg/g (45.20%), 8.33 mg/g (83.30%) and 9.75 mg/g (97.50%) mg/g at 20 °C and pH 10 for initial dye concentration of 50 mg/l, respectively. Also, for initial dye concentration of 100 mg/l, the maximum amounts of MB sorbed per unit CS, CW

and CD are found to be 5.95 mg/g (29.75%), 14.04 mg/g (70.20%) and 15.78 mg/g (78.90%) mg/g at 20 °C and pH 6.33, respectively. These values obtained for the sorption of MB onto CS, CW and CD has been compared to the sorption of MB by another sorbents under different conditions, and they are presented in Table 2.

The maximum amounts of dye adsorbed by various adsorbents in equilibrium time vary as a function of experimental conditions. Especially the amount of adsorbent dose has a very important effect on the estimation of the maximum amounts of dye adsorbed per unit adsorbent. As shown in Table 2, for example, when the mass of banana peel and orange peel used for the biosorption of methylene blue is 0.10 g (ratio adsorbent dose/solution = 1.0 g/l), the maximum amount of methylene blue sorbed on banana peel and orange peel has been found as 15.90 and 13.90 mg/g, and their percentages are 15.90% and 13.90%, respectively [20]. On the other hand, when the mass of biosolid used for the biosorption of methylene blue is 1.0 g (ratio adsorbent dose/solution = 10 g/l), the maximum amount of methylene blue sorbed on biosolid has been found as 24.40 mg/g, and its percentage is 96.80% [27]. Also, in two different papers of Hameed, when the mass of grass waste and spent tea leaves used for the biosorption of methylene blue is 0.70 g (ratio adsorbent dose/solution = 3.5 g/l), the maximum amounts of methylene blue sorbed on grass waste and spent tea leaves has been found as 80.63 and 102.14 mg/g, and their percentages are 74.77% and 92.20%, respectively [28,29].

Herein, the mass of the sorbents used for the sorption of methylene blue is 0.25 g (ratio sorbent dose/solution = 5 g/l), and the maximum percentage of MB sorbed onto CS, CW and CD is found to be 45.20 and 83.30 and 97.50 at 20 °C and pH 10, respectively. These

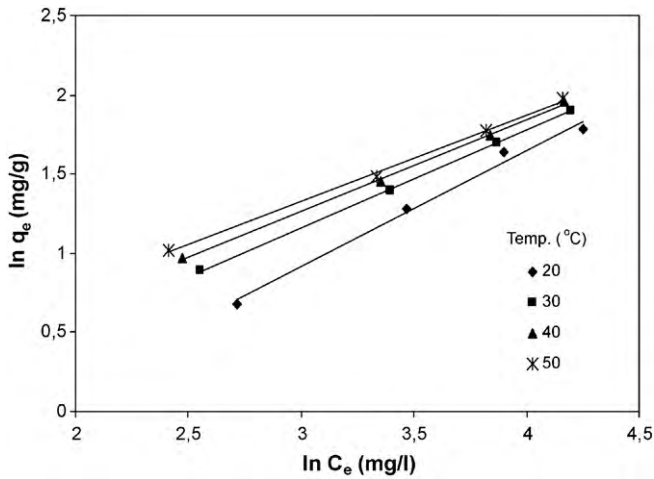


Fig. 6. Freundlich isotherms of the MB sorption onto CS at different temperatures (conditions: pH 6.33, W=0.25 g, V=50 ml).

indicate that CS, CW and CD will be used preferably as sorbents for the sorption of MB.

3.6. Isotherm study

The isotherm analysis of sorption process was performed using the Freundlich and Langmuir equations at different temperatures. The Freundlich isotherm can be expressed as

$$q_e = kC_e^{1/n} \tag{2}$$

The linear equation of the Freundlich isotherm is as follows:

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \tag{3}$$

where q_e is the amount of dye sorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of the dye in solution (mg/l). k and n are isotherm constants which indicate the capacity and intensity of the sorption, respectively.

Figs. 6–8 show the plots of $\ln q_e$ against $\ln C_e$ for the sorption of MB onto CS, CW and CD at 20, 30, 40 and 50 °C and pH 6.33, respectively. As seen in the Figs. 6 and 7, the plots obtained for SC and CW are in harmony with the Freundlich model with correlation coefficients between 0.990–0.999 and 0.85–0.917, respectively. The correlation coefficients of plot obtained for CD in Fig. 8 are low values between 0.514 and 0.60. Therefore, the adsorption of MB onto

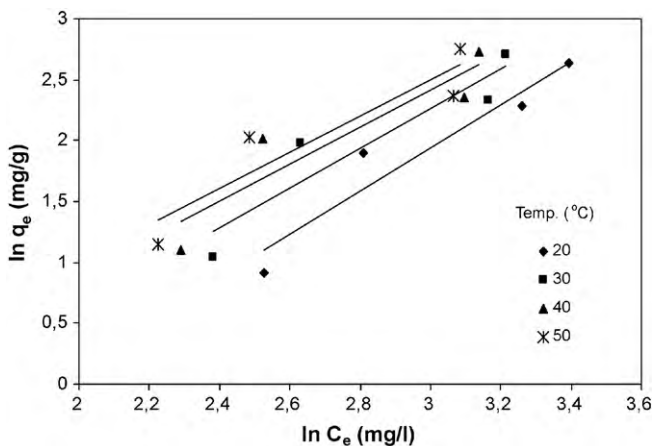


Fig. 7. Freundlich isotherms of the MB sorption onto CW at different temperatures (conditions: pH 6.33, W=0.25 g, V=50 ml).

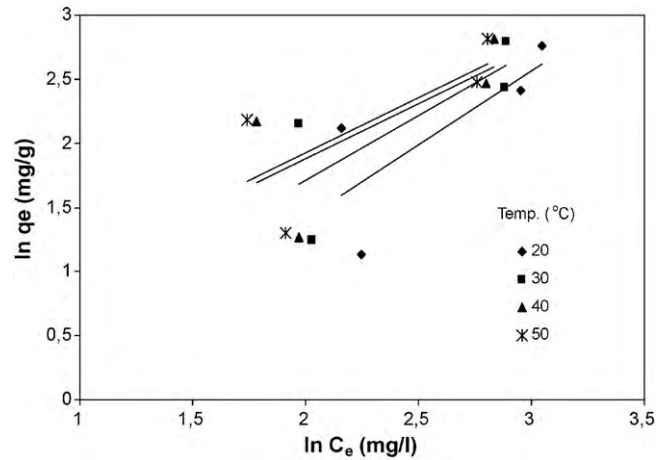


Fig. 8. Freundlich isotherms of the MB sorption onto CD at different temperatures (conditions: pH 6.33, W=0.25 g, V=50 ml).

Table 3

Isotherm parameters for MB sorption onto CS at different temperature at a fixed pH of 6.33 and a sorbent dose of 0.25 g.

This study	Freundlich constants			Langmuir constants		
	Temperature (°C)	1/n (l/g)	k (mg/g)	r ²	Q ₀ (mg/g)	b (l/g)
20	0.735	0.274	0.990	13.71	0.0113	0.973
30	0.612	0.509	0.999	11.60	0.0192	0.973
40	0.580	0.619	0.999	11.50	0.0227	0.966
50	1.545	0.734	0.997	11.07	0.0265	0.963

CD does not fit well with Freundlich isotherm. The values of k and n are calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$, respectively. These constants obtained from Freundlich isotherm are given in Tables 3 and 4, respectively.

On the other hand, the Langmuir isotherm is as follows:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{4}$$

the rearranged Langmuir isotherm is expressed as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{5}$$

where Q_0 and b are Langmuir constants, which indicate the sorption capacity (mg/g) and energy of sorption, respectively.

Fig. 9 demonstrates the plots of C_e/q_e against C_e for the sorption of MB onto CS at 20, 30, 40 and 50 °C and pH 6.33. As seen in the figure, the obtained plot for only SC obey Langmuir isotherm with high correlation coefficients between 0.963 and 0.973 at all temperatures. There is no any compliance to Langmuir isotherm for CD and CW. Therefore, the plots of CW and CD are not shown. The values of Q_0 and b are determined from the slope and intercept of the plot of C_e/q_e versus C_e , respectively. The Langmuir constants obtained at different temperatures, Q_0 and b , for CS are given in Table 3.

Table 4

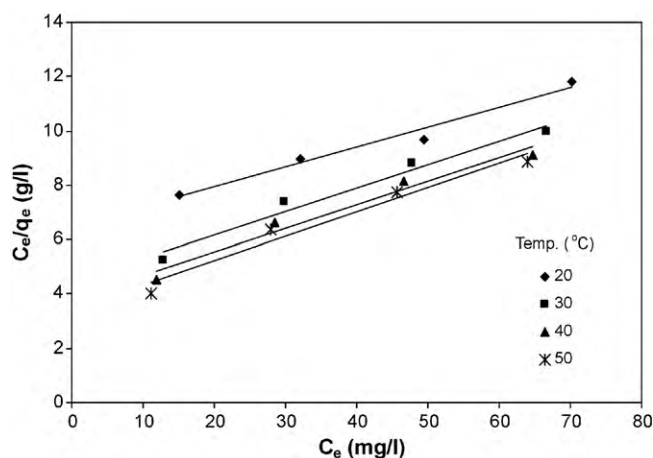
Freundlich Isotherm parameters for MB sorption onto CW and CD at different temperatures at a fixed pH of 6.33 and a sorbent dose of 0.25 g.

Temperature (°C)	For CW			For CD		
	1/n (l/g)	k (mg/g)	r ²	1/n (l/g)	k (mg/g)	r ²
20	1.77	0.033	0.917	1.154	0.866	0.581
30	1.63	0.070	0.872	1.008	0.994	0.600
40	1.52	0.114	0.850	1.865	0.858	0.514
50	1.48	0.142	0.861	1.860	0.163	0.537

Table 5

The thermodynamic parameters for the sorption of MB onto CS, CW and CD at different temperatures at a fixed pH of 6.33 and a sorbent dose of 0.25 g.

Temperature (°C)	K_c	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹)	R^2	Sorbent
20	0.559	1.416	8.94	25.86	0.934	CS
30	0.676	0.986				
40	0.754	0.735				
50	0.785	0.650				
20	2.010	-1.701	12.01	47.14	0.931	CW
30	2.601	-2.408				
40	3.010	-2.867				
50	3.172	-3.099				
20	4.762	-3.802	13.33	58.75	0.952	CD
30	5.954	-4.494				
40	7.403	-5.209				
50	7.768	-5.505				

**Fig. 9.** Langmuir isotherms of the MB sorption onto CS at different temperatures (conditions: pH 6.33, $W=0.25$ g, $V=50$ ml).

The fact that the sorption well obeys the Freundlich isotherm suggests that the surface of the sorbent has some heterogeneity, and sorption is local. This situation is attributed to the fact that that various active sites on sorbents have different affinities to methylene blue molecules. The fact that the sorption obeys the Langmuir isotherm indicates that the surface of sorbent is monolayer covered with dye molecules.

3.7. Thermodynamic study

The various thermodynamic parameters, i.e. standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°), associated the sorption of MB onto CS, CW and CD were determined by using the following equations [30–33]:

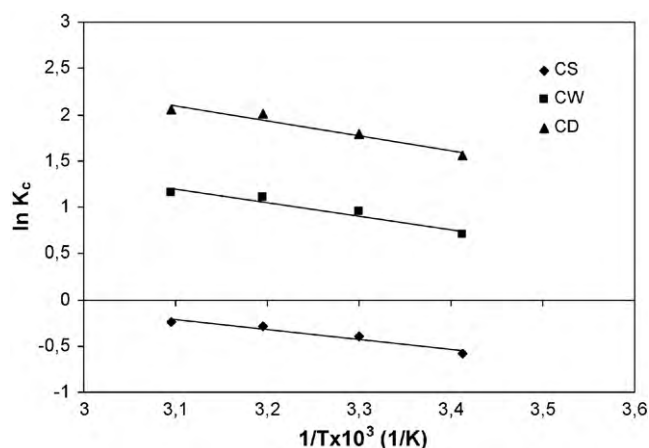
$$\Delta G^\circ = -RT \ln K_c \quad (6)$$

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (7)$$

$$K_c = \frac{C_{Ae}}{C_{Se}} \quad (8)$$

where R is the gas constant, K_c is the equilibrium constant, T is absolute temperature (in Kelvin). C_{Ae} and C_{Se} are the equilibrium constants of dye on sorbent and in solution (mg/l), respectively.

Eq. (7) is known as van't Hoff equation, and it express relationship between equilibrium constant and temperature. Plots of $\ln K_c$ versus $1/T$ are linear, and their plots are shown in Fig. 10. The values of ΔH° and ΔS° were calculated from the slope and intercept of van't Hoff plots, respectively. The thermodynamic parameters are given in Table 5. It is clear from the table that the values of

**Fig. 10.** van't Hoff plots for the MB sorption onto CS, CW and CD (conditions: pH 6.33, $W=0.25$ g, $V=50$ ml).

ΔG° are positive for CS and negative for CW and CD. The negative and positive values of ΔG° at various temperatures indicate the spontaneous and non-spontaneous nature of the sorption process, respectively. The fact that the values of the ΔG° decrease with increasing temperature indicates the increase of spontaneous effect. For all the sorbents, the values of ΔH° of sorption were found to be positive, indicating endothermic process. Moreover, the positive values of ΔS° point out the increased randomness at the solid/liquid interface during the sorption of dye on CS, CW and CD. Similar thermodynamic results have been recorded on adsorption of Congo red onto activated coir pith carbon [31].

4. Conclusions

It was seen that cotton stalk (CS), cotton dust (CD) and cotton waste (CW) could be used successfully as sorbents for the removal of methylene blue (MB) from aqueous solution by sorption technique. Sorption increased with an increase in initial dye concentration, temperature, sorbent dose and solution pH. Required time for maximum dye removal was 90 min. The maximum dye removals for CS, CW and CD were between 26.0% and 48.36%, between 50.0% and 85.41%, between 62.0% and 97.50% under all the experimental conditions studied, respectively. Moreover, it was determined that CD was more effective than SC and CW to remove the MB from aqueous solution for each experimental condition. While sorption on cotton stalk was following the Freundlich and the Langmuir isotherms at all the temperatures, sorption on cotton waste and cotton dust followed only the Freundlich isotherm. Furthermore, from the thermodynamic parameters, it was found that the values of standard free energy (ΔG°) were positive for cot-

ton stalk and negative for cotton waste and cotton dust. The values of standard enthalpy (ΔH°) and entropy (ΔS°) were found to be positive for all sorbents. As a result of this study, it could be suggested that the cotton stalk, cotton dust and cotton waste would be employed as low-cost alternative sorbents to commercial activated carbon for the removal of another dyes from environment and aquatic mediums.

References

- [1] B. Acemioğlu, Adsorption of congo red from aqueous solution onto calcium-rich fly ash, *J. Colloid Interf. Sci.* 269 (2004) 303–309.
- [2] B. Acemioğlu, Batch kinetic study of sorption of methylene blue by perlite, *Chem. Eng. J.* 106 (2005) 73–81.
- [3] P. Nigam, G. Armour, I.M. Banat, D. Singh, R. Marchant, Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agriculture residues, *Bioresour. Technol.* 72 (2000) 219–226.
- [4] D.S. Kim, B.Y. Park, effect of the removal of lead (II) from aqueous solution by crab shell, *J. Chem. Technol. Biotechnol.* 76 (2001) 1179–1184.
- [5] G. McKay, Use of sorbents for the removal of pollutants from wastewaters, CRC Press, Boca Raton, 1996.
- [6] S.H. Gharaibeh, S.V. Moore, A. Buck, Effluent treatment of industrial wastewater using processed solid residue of olive mill products and commercial activated carbon, *J. Chem. Technol. Biotechnol.* 71 (4) (1998) 291–298.
- [7] A. Pala, E. Tokat, Color removal from cotton textile industry wastewater in an activated sludge system with various additives, *Water Res.* 36 (11) (2002) 2920–2925.
- [8] S.V. Mohan, J. Karthikeyan, Removal of lignin and tannin colour from aqueous solution by adsorption onto activated charcoal, *Environ. Pollut.* 97 (1–2) (1997) 183–187.
- [9] M. Sankar, G. Sekaran, S. Sadulla, T. Ramasami, Removal of diazo and triphenyl-methane dyes from aqueous solutions through an adsorption process, *J. Chem. Technol. Biotechnol.* 74 (4) (1999) 337–344.
- [10] M.M. Nassar, M.S. El-Geundi, Comparative cost of colour removal from textile effluents using natural adsorbents, *J. Chem. Technol. Biotechnol.* 50 (1991) 257–264.
- [11] H.M. Asfour, O.A. Fadali, M.M. Nassar, El-Guendi MS, Equilibrium studies on adsorption of basic dyes on hardwood, *J. Chem. Technol. Biotechnol.* 35A (1985) 21–27.
- [12] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, *Trans. IChemE* 76 (B) (1998) 183–191.
- [13] N. Şakalar, M. Hilal Bilir, B. Acemioğlu, M.H. Alma, Adsorption of basic red 2 onto peanut shell: batch and column studies, *Asian J. Chem.* 22 (7) (2010) 5649–5662.
- [14] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (2) (1998) 115–124.
- [15] G. McKay, J.F. Porter, G.R. Prasad, The removal of dye colours from aqueous solutions by adsorption on low-cost materials, *Water, Air, Soil Pollut.* 114 (1999) 423–438.
- [16] M. Dogan, M. Alkan, Removal of methyl violet from aqueous solutions by perlite, *J. Colloid Interf. Sci.* 267 (2003) 32–41.
- [17] B. Acemioğlu, M. Kertmen, M. Digrak, M.H. Alma, F. Temiz, Biosorption of crystal violet onto *Aspergillus wentii* from aqueous solution, *Asian J. Chem.* 22 (2) (2010) 1394–1402.
- [18] V.K. Garg, M. Amita, R. Kumar, R. Gupta, Basic dye (methylene blue) removal from simulated wastewater by sorption using Indian rosewood sawdust: a timber industry waste, *Dyes Pigments* 63 (2004) 243–250.
- [19] C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, K. Ranganathan, Removal of dyes from aqueous solution by cellulose waste orange peel, *Bioresour. Technol.* 57 (1996) 37–43.
- [20] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *J. Hazard. Mater.* B92 (2002) 263–274.
- [21] V. Vadivelan, K.V. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, *J. Colloid Interf. Sci.* 286 (2005) 90–100.
- [22] M. Ertaş, Metilen mavisi ve kongo kırmızısının lignoselülozik materyaller kullanılarak sulu çözeltiden adsorpsiyon tekniği ile uzaklaştırılması, M.Sc. Thesis, Karadeniz Teknik University, Trabzon, 2005 (in Turkish).
- [23] B.H. Hameed, A.T.M. Din, A.L. Ahmad, Sorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies, *J. Hazard. Mater.* 141 (2007) 819–825.
- [24] V.V. Basava Rao, S. Ram Mohan Rao, Adsorption studies on treatment of textile dyeing industrial effluent by fly ash, *Chem. Eng. J.* 116 (2006) 77–84.
- [25] B.H. Hameed, Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost sorbent, *J. Hazard. Mater.* 162 (2009) 344–350.
- [26] Y. Bulut, H. Aydin, A kinetics and thermodynamics study of methylene blue sorption on wheat shells, *Desalination* 194 (2006) 259–267.
- [27] M. Sarioglu, U.A. Atay, Removal of methylene blue by using biosolid, *Global NEST J.* 8 (2) (2006) 113–120.
- [28] B.H. Hameed, Grass waste: a novel sorbent for the removal of basic dye from aqueous solution, *J. Hazard. Mater.* 166 (2009) 233–238.
- [29] B.H. Hameed, Spent tea leaves: a new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions, *J. Hazard. Mater.* 161 (2009) 753–759.
- [30] B. Acemioğlu, Removal of Fe(II) ions from aqueous solution by Calabrian pine bark wastes, *Bioresour. Technol.* 93 (2004) 99–102.
- [31] B. Acemioğlu, M.H. Alma, Removal of Cu (II) from aqueous solution by Calabrian pine bark wastes, *Freesias Environ. Bull.* 13 (7) (2004) 585–590.
- [32] K.P. Yadava, B.S. Tyagi, V.N. Singh, Effect of temperature on the removal of lead (II) by adsorption on china clay and wollastonite, *J. Chem. Technol. Biotechnol.* 51 (1991) 47–60.
- [33] C. Namasivayam, D. Kavitha, Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, *Dyes Pigments* 54 (2002) 47–58.
- [34] B.H. Hameed, M.I. El-Khaiary, Removal of basic dye from aqueous medium using a novel agricultural waste material: pumpkin seed hull, *J. Hazard. Mater.* 155 (2008) 601–609.
- [35] B. Acemioğlu, M. Kertmen, M. Digrak, M.H. Alma, Use of *Aspergillus wentii* for biosorption of methylene blue from aqueous solution, *African J. Biotechnol.* 9 (6) (2010) 874–881.
- [36] N.S. Maurya, A.K. Mital, P. Cornel, E. Rother, Biosorption of dyes using dead macro-fungi: effect of dye structure, ionic strength and pH, *Bioresour. Technol.* 97 (2006) 512–521.