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Removal of methylene blue, methyl violet, rhodamine B, alizarin red, and bromocresol green dyes from aqueous solutions on activated cotton stalks

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ABSTRACT

The adsorption behavior of methylene blue (MB), methyl violet (MV), rhodamine B (RB), alizarin red (AR), and bromocresol green (BG) dyes from aqueous solution on cotton stalks-activated carbon (CSAC) was investigated. The experimental procedure used activated carbon produced by chemical activation and physical activation using 50% $ZnCl_2$ at 850˚C. For this purpose, batch tests were carried out as a function of solution pH value, contact time, dye concentration, agitation rate, temperature, and particle diameter. The experimental findings showed that the maximum adsorption capacities of adsorbent for BG and AR dyes were at pH 5. As comparison, the maximum adsorption capacity of adsorbent for MB dye was at an initial pH 12. In addition, the maximum adsorption capacities of adsorbent for RB and MV dyes were at pH 2 and 7, respectively. The maximum adsorption capacities of adsorbent for RB, MV, MB, AR, and BG were found to be 133.33, 135.14, 153.85, 196.08, and 222.22 mg/g, respectively. Kinetic studies of five dyes followed the pseudo-second-order model. Freundlich isotherm described the equilibrium data of BG, AR, and RB dyes on CSAC better than Langmuir isotherm, but Langmuir isotherm showed a better fit to the equilibrium data of MB and MV dyes. The R_L results show that the adsorption of five dyes onto CSAC is favorable.

Keywords: Adsorption; Dyes; Activated cotton stalks; Adsorption isotherm; Kinetics

1. Introduction

Waste effluent from industry such as dyestuff, textiles, rubber, plastics, leather, cosmetics, and pharmaceutical can be particularly problematic due to the presence of color in the final effluent. The dyestuffs have a complex chemical structure and are stable to light, heat, and oxidation agents [1]. Some of the reports show that today, there are more than 10,000 dyes available commercially with a production greater than 7×10^5 metric tones per year [2]. The discharge of colored wastewater with the synthetic origin and complex aromatic molecular structures into natural streams has caused many significant problems such as increasing the toxicity and chemical oxygen demand

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of the effluent. Kadirvelu et al. reported that dyes could cause severe damage such as dysfunction of kidney, reproductive systems, liver, brain, and central nervous system [3]. The adsorption technology onto activated carbon is one of the most effective technologies for the decolorization of wastewater. However, the commercially activated carbons are considered very expensive. Therefore, as technology has advanced, scientists are attempting to overcome the cost of treatment process by using inexpensive, efficient, and easily available activated carbons for the decolorization of dyes [4–8]. There have been many studies to obtain low-cost activated carbons from agricultural wastes such as pistachio shell [9], granular activated carbon from fruit stones and nutshells [10], pistachio nut shell [11], bamboo-based activated carbon [12], bagasse and rice husk [13], coffee husks [14], modified waste sugarcane bagasse [15], olive stones [16], walnut shells [16], sugar cane bagasse, sunflower seed hull [17], and cotton stalk [18–21].

Cotton is a plant extensively cultured in Turkey. Turkey is one of the eight countries producing 85% of the world's cotton. In spite of its use for various applications, such as composting, paper production, and energy production, today much of the available cotton waste in the world is still disposed. These disposals can result in the environmental pollution. Cotton plant wastes are composed primarily of cellulose (30–50%), hemicellulose (20–30%), and lignin (20–30%) [22,23]. Therefore, we have used the activated carbon from cotton stalks. In a previous paper [18], the use of cotton stalks as a precursor for the preparation of the activated carbon material was proposed. In the present study, the feasibility of cotton stalks-activated carbon (CSAC) as sorbent was investigated for the removal of dyes: methyl violet (MV), methylene blue (MB), rhodamine B (RB), alizarin red (AR), and bromocresol green (BG) from aqueous solution. Equilibrium and kinetic data of the adsorption process of the dyes onto this adsorbent were investigated. These features will be helpful in some degree for the researchers to study the adsorption of dyes on activated carbon prepared from cotton stalks.

2. Materials and methods

2.1. Dyes

The dyes selected as sorbate were MB (FW = 373.9, λmax = 664 nm), AR (FW = 342, λ_{max} = 420 nm), BG (FW = 698, λ_{max} = 424 nm), RB (FW = 479.01, λ_{max} = 543 nm), and MV (FW = 393.94, λ_{max} = 543 nm). All chemicals used in this study were purchased from Merck and used without any further purification.

2.2. Preparation of activated carbon

Cotton stalks were obtained from Harran in Şanlıurfa province of Turkey. The CSAC was prepared as described previously [18]. The starting materials were manually chosen, cleaned with deionized water, dried at 120˚C for 48 h in a furnace, and ground using a roller mill, sieved to a size range of 3.35–4.75 mm, and stored in sealed containers for experimentation. Afterward, 4 g of washed cotton stalks was put into the baker including $ZnCl_2$ 50% for the duration time of 96 h. The impregnated waste samples were placed into the ash furnace and carbonized under nitrogen (N_2) flow. After carbonization at 850˚C, the sample was cooled down under N_2 flow and washed sequentially several times with hot water. Then, the sample was dried at 110˚C. In the physical activation, approximately 4 g of the pre-carbonized material was placed into an ash furnace and set to 900˚C along with the N_2. Upon reaching the desired temperature, the gasifying agent CO_2 was allowed into the furnace at a desired flow rate and activated for 30 min. BET surface area, DR micropore volume, and BJH mesopore volume of CSAC were 1,379 m^2/g, 0.335, and 1.13 cc/g [18], respectively.

2.3. Adsorption experiments

The effects of various operating parameters on adsorption, such as sorbent particle size, contact time, initial dye concentration, agitation rate, temperature, and pH were monitored, and the optimal experimental conditions were decided.

The studies of the kinetics of adsorption were carried out at 30˚C. One hundred and fifty milliliter of the solution containing the desired quantity of the dye was treated with 0.05 g of CSAC in Stoppard conical flasks for different times using a temperature-controlled shaker. The solution—CSAC mixtures were stirred at 150 rpm and at the end of the predetermined time interval, the reaction mixtures were filtered out and analyzed for its dyes using a Perkin Elmer Analys 700 UV–vis spectrophotometer. Experimental measurements were carried out twice.

The pH effect of the initial solution on the equilibrium adsorption of dyes was analyzed over a range of pH 2–12. The pH effect of the solution was adjusted by either 0.05 M NaOH or 0.05 M HCI solutions. The batch adsorption studies were conducted as a function of contact time (5, 10, 20, 30, 45, 60, 90, 120, 150, and 180 min) and dye concentration (10, 25, 50, and 100 mg/L) for maximum adsorption. Under the experimental conditions, the adsorption capacity for each concentration of dye at equilibrium was determined using Eq. (1).

$$q_e = \left[\frac{(C_i - C_e)}{M}\right] \times V \tag{1}$$

where q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium. C_i and C_e were the initial and final concentrations of dyes in the solution, respectively. V is the volume of solution (L) and M is the mass of adsorbent in (g) used.

3. Results and discussion

3.1. Effect of pH

The pH value of dye solutions plays an important role in the adsorption process and particularly in the adsorption capacities because of negative and positive ions. Dyes are complex aromatic organic compounds with unsaturated bond and different functional groups. Therefore, they have different degrees of ionization at different pH values, and this alters the net change on dye molecules. The adsorption of dyes by CSAC was studied over a pH range of 2–12 at 30˚C, and the studies were carried out for 3 h. Initial dye concentration was 100 mg/L and the adsorbent dose was kept at 0.05 g/150 mL for dyes. Fig. 1 presents the relation between the initial solution pH and adsorption capacity. It was clear that the maximum dye adsorption capacities of adsorbent for BG and AR dyes were at a pH 5, and decreased with further increase in pH. As comparison, the maximum adsorption capacity of adsorbent for MB dye was at an initial pH 12. In addition, the maximum adsorption capacities of adsorbent for RB and MV were at pH 2 and 7, respectively.

An increase in the pH of the adsorption system can be attributing to the increase in the negatively charged hydroxide ions, which will compete with anionic ions of the dyes on the activated carbon, and thus decreasing the adsorbate uptaken. Moreover, this increase in pH of the adsorption system can be attributing to the decrease in positively charged sites. At pH values ranging from 2.0 to 12.0, the negatively charged groups are available to adsorb the positively charged dyes. In contrast, the positively charged groups are available to adsorb the negatively charged dyes. Higher uptakes on the activated carbon at lower pH values are because of the electrostatic attractions between negatively charged functional groups. However, lower uptakes on the activated carbon at lower pH values are because of the electrostatic repulsion between the negatively charged functional groups. Further experiments were carried out at respective optimum pH for dyes. Similar results were reported for the removal of MV, RB, and MB dyes by several non-conventional adsorbents [24–29].

3.2. Effect of contact time

The effect of contact time on the amount of dye adsorbed was investigated for a period of 3 h for initial dye concentrations of 100 mg/L at 30˚C. CSAC dosage was 0.05 g/150 mL of dye solution for all of the dyes, at respective optimum pH. The removal of dyes by CSAC was found to increase, reach maximum value with an increase in the contact time (Fig. 2). It almost becomes constant with an increase in the contact time after 120 min based on the results, 120 min was taken as the equilibrium time in adsorption.

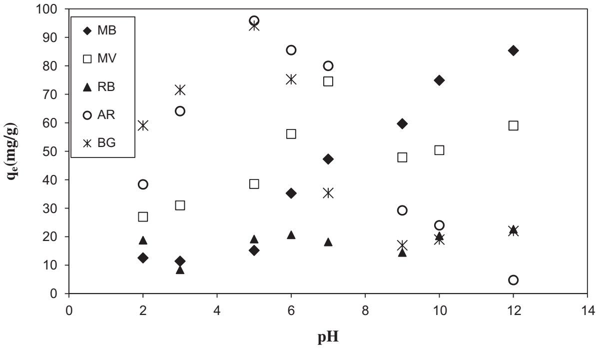

Fig. 1. Effect of pH on the adsorption of dyes (initial concentration = 100 mg/L, agitation rate = 150 rpm, temperature = 30˚C, particle diameter = 300 μm, contact time = 180 min, and adsorbent dosage = 5.0 g/L).

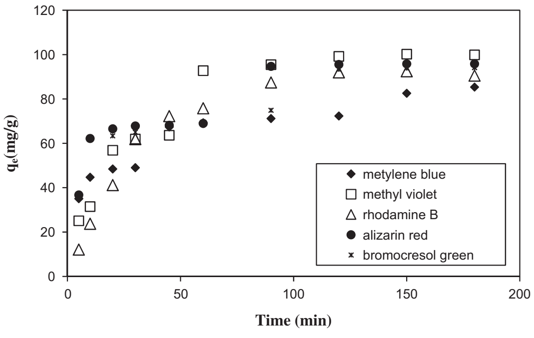

Fig. 2. Effect of contact time on the adsorption of dyes (initial concentration = 100 mg/L, agitation rate = 150 rpm, temperature = 30˚C, particle diameter = 300 μm, and adsorbent dosage = 0.05 g/150 mL).

3.3. Effect of initial dye concentration

In batch adsorption processes, the initial dye ion concentration of dyes in the solution plays an important role. Therefore, the amount of dye adsorbed is expected to be higher with a higher initial concentration of dye ions. The effects of initial concentration of MV, MB, RB, AR, and BG dyes at respective optimum pH, while keeping the dosage of the activated carbon (0.05 g/150 mL) constant and temperature at 30˚C on the adsorption process, are shown in Fig. 3. When the initial dye concentration increased from 10 to 50 mg/L, the adsorption was increased as shown in Fig. 3. When further increasing the initial dye concentration in the range 50–100 mg/L, the adsorption of dyes was slightly increased.

The amount of all dyes adsorbed at equilibrium appeared to follow the same increasing trend with the initial dye ion concentration. Because of the above observations, the adsorption process of different dyes on CSAC was found to be dependent on the concentration of adsorbate.

3.4. Effect of agitation rate

Fig. 4 shows the experimental results obtained from a series of experiments performed, using different agitation rates in the range of 50–200 rpm at 100 mg/L initial dye concentration, 30˚C and at respective optimum pH. As seen in Fig. 4, it can be stated that the agitation rate had a significant effect on the adsorption rate around the CSAC particles being a result of increasing the degree of mixing. With an increase in the agitation rate, the film resistance to mass transfer surrounding the sorbent particles decreases, thus increases the sorption of dye molecules [30].

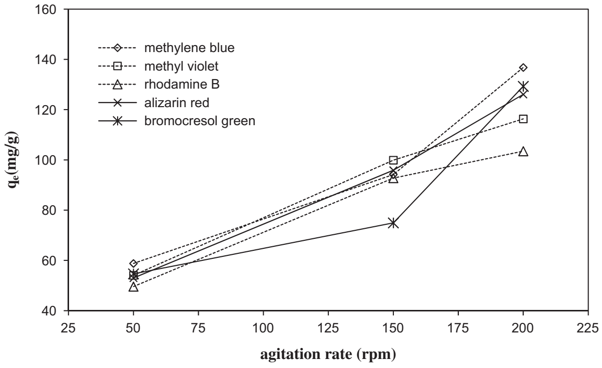

Fig. 4. Effect of agitation rate on the adsorption of dyes (initial concentration = 100 mg/L, contact time = 180 min, temperature = 30˚C, particle diameter = 300 μm, and adsorbent dosage = 0.05 g/150 mL).

3.5. Effect of particle size on dyes' adsorption

The batch adsorption experiments were carried out using three different particle sizes at desired pH, time, amount of adsorbent, and temperature. The adsorption capacities of adsorbent for all dyes were decreased with an increase in the particle size of adsorbent. This is because adsorption is a surface phenomenon, so the smaller adsorbent particle size offers a comparatively larger and more accessible surface area. The adsorption capacities (mg/g) of adsorbent for all dyes at the particle size range of 300–400 μm were 90.10, 107.53, 102.88, 99.51, and 115.07 mg/g, respectively (Fig. 5). This result therefore stated that

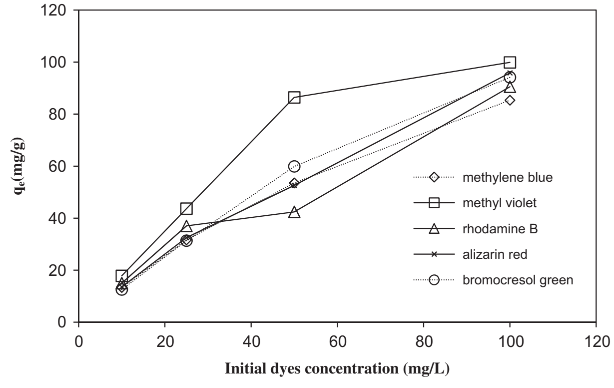

Fig. 3. Effect of initial dye concentration on the adsorption (contact time = 180 min, agitation rate = 150 rpm, temperature = 30˚C, particle diameter = 300 μm, and adsorbent dosage = 0.05 g/150 mL).

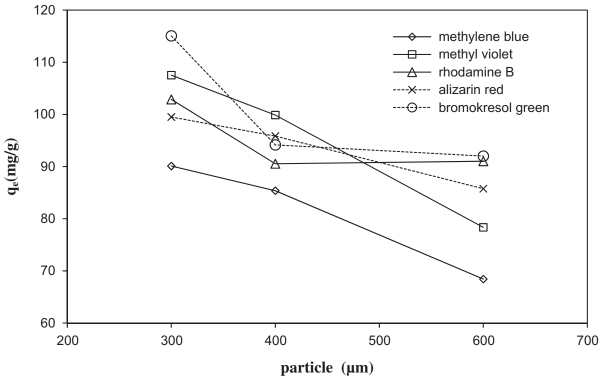

Fig. 5. Effect of particle diameter on the adsorption of dyes (initial concentration = 100 mg/L, contact time = 180 min, agitation rate = 150 rpm, temperature = 30˚C, and adsorbent dosage = 0.05 g/150 mL).

the size of the adsorbent plays an important role in the adsorption process of AR, BG, MB, RB, and MV dyes.

3.6. Adsorption kinetic studies

The kinetics of adsorption describes the rate of adsorption capacities of adsorbent for all dyes and it controls the equilibrium time. The pseudo-first-order and pseudo-second-order kinetic models are investigated for better understanding of the dynamics of adsorption of dyes onto CSAC.

3.6.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model is known as the Lagergren equation [31]:

$$\ln(q_{\mathrm{e}} - q_t) = \ln q_{\mathrm{e}} - k_1 t \tag{2}$$

where q_{e} and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (min), respectively, and k_1 (1/min) is the adsorption rate constant. The values of k_1 and correlation coefficient, R^2 obtained from the plots for adsorption of dyes onto CSAC are listed in Table 1.

3.6.2. Pseudo-second-order kinetic model

The pseudo-second-order equation based on equilibrium adsorption is expressed as [32]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{t}{q_{\mathrm{e}}} \tag{3}$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. The linear plot of t/q_t vs. t gave $1/q_{\mathrm{e}}$ as the slope and $1/k_2 q_{\mathrm{e}}^2$ as the intercept. This procedure is more likely to predict the behavior over the whole range of adsorption. q_{e} and k_2 can be determined from the slope and intercepts of plot t/q_t vs. t. The experimental adsorption data fitted the pseudo-second-order model. Table 1 presents the values of correlation coefficients (R^2). The values of R^2 for the adsorption of dyes on CSAC from all the systems are found to be 0.99 and 0.98 for pseudo-second-order

Table 1
Comparison of adsorption rate constants, experimental, and calculated q_{e} values for the pseudo-first- and pseudo-second-order reaction kinetics for the removal of dyes onto CSAC

	Initial metal concentration (mg/L)	$q_{\mathrm{e,exp}}$ (mg/g)	Pseudo-first-order			Δq (%)	Pseudo-second-order			Δq (%)
			k_1 (g/mg min)	$q_{\mathrm{e,calc}}$ (mg/g)	R^2		k_2 (g/mg min)	$q_{\mathrm{e,calc}}$ (mg/g)	R^2	
Methylene blue	10	13.351	0.036	12.268	0.963	35.64	0.004699	14.701	0.999	12.41
	25	33.651	0.059	33.115	0.968		0.002036	35.714	0.995	
	50	53.54	0.039	69.546	0.934		0.000648	62.5	0.996	
	100	85.368	0.013	39.80	0.548		0.000877	90.909	0.997	
Methyl violet	10	17.844	0.025	14.775	0.853	25.38	0.002973	19.607	0.992	12.52
	25	37.203	0.021	45.422	0.943		0.000233	62.5	0.980	
	50	86.423	0.046	57.168	0.923		0.001042	100	0.998	
	100	99.887	0.039	97.905	0.976		0.000669	111.111	0.989	
Rhodamine B	10	15.031	0.056	21.671	0.961	28.21	0.002973	19.607	0.992	28.26
	25	37.203	0.034	31.689	0.982		0.000233	62.5	0.980	
	50	42.442	0.025	46.525	0.957		0.000372	55.555	0.99	
	100	90.548	0.037	100.685	0.990		0.000324	111.111	0.990	
Alizarin red	10	13.575	0.042	19.414	0.960	33.55	0.002259	16.129	0.982	30.29
	25	32.553	0.037	35.516	0.977		0.001026	38.461	0.995	
	50	52.941	0.045	72.240	0.956		0.000302	76.923	0.963	
	100	95.852	0.045	106.165	0.860		0.001538	100	0.991	
Bromocresol green	10	12.583	0.016	6.128	0.976	36.76	0.006237	13.513	0.996	15.25
	25	31.360	0.039	35.531	0.925		0.001395	35,714	0.996	
	50	59.912	0.037	38.783	0.968		0.001584	66.666	0.998	
	100	94.156	0.034	93.037	0.837		0.000555	111.11	0.988	

kinetic model. Based on the values of R^2, it is evident that the pseudo-second-order kinetic model can best describe the adsorption of dyes on CSAC and it further suggested that the overall rate of dye adsorption process follows the chemisorption process. The linear plots of t/q vs. t show a good agreement of experimental data with the second-order kinetic model (Fig. 6).

To compare the validity of each model, a normalized standard deviation, Δq (%) was calculated using the following equation:

$$\Delta q\,(\%) = 100 \times \sqrt{\sum \frac{[(q_t^{\text{exp}} - q)/q_t^{\text{exp}}]^2}{N-1}} \tag{4}$$

where q_t^{exp} and q^{cal} are experimental and calculated amounts of the dyes adsorbed on CSAC at time "t" and N is the number of measurements made. Table 1 presents the values of Δq (%) and correlation coefficients (R^2). The values of Δq (%) for pseudo-first-order kinetic models are low compared to those of pseudo-second-order kinetic models. Based on Δq (%) values, it is evident that the adsorption of dyes can be best described by the pseudo-second-order kinetic model.

3.7. Adsorption isotherms

The Langmuir model assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes. The data of the equilibrium studies for the adsorption of dyes onto CSAC may follow the following form of Langmuir model [33]:

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

where q_m shows the monolayer adsorption capacity (mg/g), b is the Langmuir constant (L/mg), C_e is the equilibrium concentration of dyes in the solution (mg/L), and q_e is the solid-phase concentration of adsorbate at equilibrium (mg/g). The plot of C_e/q_e vs. C_e is employed to generate the intercept value of $1/bq_m$ and slope of $1/q_m$ (Fig. 7). Comparisons of the maximum monolayer adsorption of used dyes onto low-cost adsorbents from various sources are presented in Table 2 [19,21,34–43].

Another characteristic parameter of the Langmuir isotherm is the dimensionless factor R_L, called separation factor [44]:

$$R_L = 1/(1 + bC_0) \tag{6}$$

where b is the Langmuir constant and C_0(mg/L) is the highest dye concentration. The value of R_L is related to the type of the isotherm, and can indicate either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) adsorption. The results in Table 3 show that the adsorption of five dyes onto CSAC is favorable.

The Freundlich model [45] is an empirical equation based on sorption of heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with an increase in the degree of site occupation. The well-known logarithmic form of Freundlich isotherm is given by the following equation:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{7}$$

where K_F and n represent adsorption capacity and intensity, respectively. K_F is an important constant

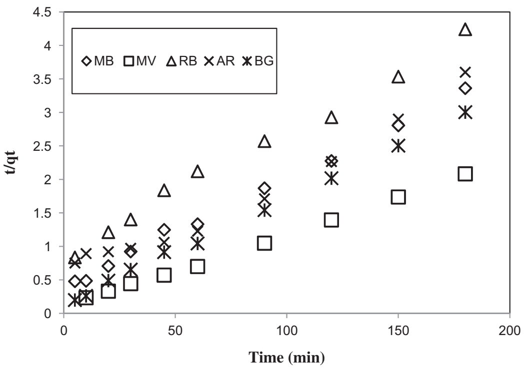

Fig. 6. Second-order kinetic equation for the adsorption of dyes on CSAC at 100 mg/L initial dye concentration.

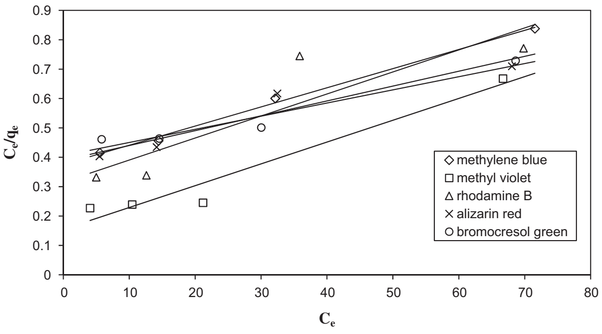

Fig. 7. Langmuir adsorption isotherm plots for the adsorption of dyes at 30°C.

Table 2
Comparison of the maximum monolayer adsorption of dyes onto adsorbents from various sources

Dye	Adsorbents	Maximum monolayer adsorption capacity (mg/g)	Solution volume used (mL)	Adsorbent amount (g)	Refs.
Methylene blue	AC-Apricot shell	4.11	100	0.1	[10]
	AC-Hazelnut shell	8.82	100	0.1	[10]
	AC-Walnut shell	3.53	100	0.1	[10]
	Modified waste sugarcane bagasse	571	20	0.01	[15]
	Groundnut shell carbon	164.9	50	10 g/L	[11]
	Bamboo dust carbon	143.2	50	10 g/L	[12]
	Microwave heating treated onion skins	142.67	200	0.15	[36]
	Pre-boiling treated onion skins	55.55	200	0.15	[36]
	Cold plasma treated onion skins	250	200	0.15	[38]
	Formaldehyde treated onion skins	166.67	200	0.15	[38]
	Cotton stalk,	4.52	50	0.25	[43]
	Cotton waste	8.53	50	0.25	43]
	Cotton dust	9.75	50	0.25	[43]
	CSAC	153.85	150	0.05	This study
Methyl violet	Sunflower (*Helianthus annuus* L.) seed hull	92.56	25	0.04	[37]
	Bagasse fly ash	26.24	50	0.2	[25]
	Granular activated carbon	95	25	0.04	[39]
	Activated charcoal	0.202	25	0.01	[26]
	CSAC	135.14	150	0.05	This study
Alizarin red	Activated charcoal	0.064	25	0.01	[26]
	CSAC	196.08	150	0.05	This study
Rhodamine B	Surfactant-modified coconut coir pith	14.9	50	0.05	[41]
	Activated carbon from industrial solid waste	16.12	50	0.1	[42]
	Activated carbon rice husk	6.110	25	0.4	[27]
	CSAC	133.33	150	0.05	This study
Bromocresol green	CSAC	222.22	150	0.05	This study

used as a relative measure for the adsorption efficiency. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [46]. The value of $1/n$ below 1 indicates a normal Langmuir isotherm, while $1/n$ above 1 is indicative of cooperative adsorption. The plots of $\ln q_e$ vs. $\ln C_e$ for the adsorption of dyes onto CSAC are presented in Fig. 8. The results in the Table 3 show that the value of n is greater than unity ($n =$ at the range 1.21–1.60) indicating that the dyes are favorably physically adsorbed on CSAC.

Equilibrium isotherms were analyzed by Freundlich and Langmuir isotherm equations using correlation coefficients. Langmuir and Freundlich isotherm models are found to best fit the experimental data over the whole concentration range as indicated from the high values of the correlation coefficients ($R^2 > 0.99$). The Freundlich equation, which indicates a heterogeneous surface binding, is found to best represent the equilibrium data for BG, AR, and RB dyes on CSAC system, while Langmuir equation better fits the data for MB and MV dyes on CSAC system, which indicates a monolayer adsorption.

Table 3
Isotherm parameters for the removal of dyes onto CSAC at 30˚C

	Methylene blue	Methyl violet	Rhodamine B	Alizarin red	Bromocresol green
Langmuir					
q_m (mg/g)	153.85	135.14	133.33	196.08	222.22
b (L/mg)	0.01729	0.04786	0.02376	0.0131	0.01109
R_L	0.3664	0.1727	0.2962	0.4329	0.4741
R^2	0.996	0.952	0.799	0.915	0.945
Freundlich					
K_F (mg/g)	4.176	9.122	6.096	3.938	3.218
n	1.38	1.59	1.60	1.31	1.21
R^2	0.988	0.881	0.939	0.992	0.983

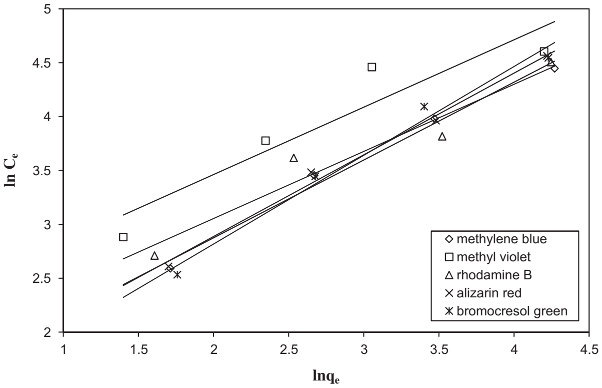

Fig. 8. Freundlich adsorption isotherm plots for the adsorption of dyes at 30˚C.

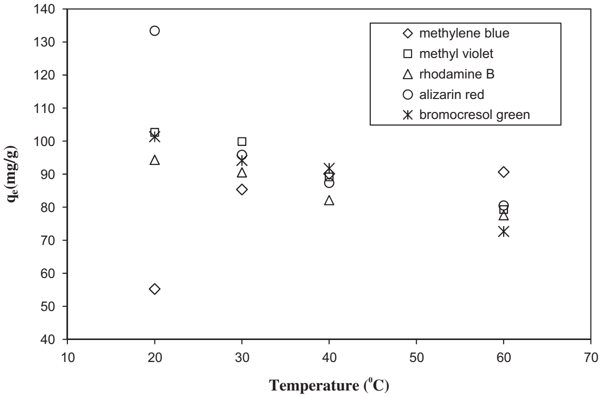

Fig. 9. Effect of temperature on the adsorption of dyes (initial concentration = 100 mg/L, contact time = 180 min, agitation rate = 150 rpm, particle diameter = 300 μm, and adsorbent dosage = 0.05 g/150 mL).

3.8. Effect of temperature

Temperature is a highly significant parameter in the adsorption processes. For the adsorption of MV, MB, RB, AR, and BR dyes onto CSAC, adsorption experiments were run to study the effect of temperature variation at 20, 30, 40, and 60˚C at respective optimum pH and adsorbent dose level of 0.05 g/150 mL. It was observed that the adsorption of MV, AR, RB, and BG dyes onto CSAC decreased with an increase in the temperature, indicating that the process is exothermic, while the adsorption of MB increased with an increase in the temperature, indicating that the process is endothermic (Fig. 9).

The parameters such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) can be estimated by the change of equilibrium constants with temperature. The dependence on the temperature of adsorption of dyes on the CSAC was evaluated using the following equations:

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{8}$$

$$\Delta G^\circ = -RT \ln K_c \tag{9}$$

$$K_c = \frac{q_e}{C_e} \tag{10}$$

where ΔG° is the free energy change (kJ/ mol), R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K), and K_c states the equilibrium constant (q_e/C_e). The values of ΔH° and ΔS° can be calculated from the Van't Hoff equation. When $\ln K_c$ is plotted against $1/T$, a straight line with the slope ($-\Delta H^\circ/R$) and intercept ($\Delta S^\circ/R$) are found.

The thermodynamic parameters are listed in Table 4. The ΔG° for MV, AR, RB, and BG is negative, which suggests that the adsorption process is

Table 4
The thermodynamic parameters for the removal of dyes onto CSAC

	ΔH (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)
Methylene blue	−24.684	0.082	−48.606
Methyl violet	7.934	−0.023	14.962
Rhodamine B	5.647	−0.017	10.830
Alizarin red	6.653	−0.019	13.068
Bromocresol green l	9.587	−0.029	17.534

spontaneous in nature. The positive value of ΔG° for MB showed that the adsorption was not a spontaneous one and that the system gained energy from an external source [43,47,48].

The positive value of ΔH° indicates the endothermic nature of adsorption. The negative values of ΔH° indicated that the adsorption process is exothermic, and occurs mainly by physical process. The positive value of ΔS° implies the increasing randomness at the solid/solution interface during the adsorption. The negative ΔS° values signify that there is a decrease in the randomness at the solid–solution interface of dyes onto CSAC surface.

4. Conclusions

CSAC was investigated for the removal of MV, MB, RB, AR, and BG dyes from aqueous solutions. The experimental results showed that CSAC was a suitable adsorbent for the removal of five dyes from both synthetic and textile effluents. The following conclusions can be derived from the present study.

(1) Adsorption of five dyes on the CSAC was found to be dependent on the initial pH of solution. The experimental findings showed that the maximum adsorption capacities of adsorbent for BG and AR dyes were at pH 5. As comparison, the maximum adsorption capacity of adsorbent for MB dye was at an initial pH 12. In addition, the maximum adsorption capacities of adsorbent for RB and MV were at pH 2 and 7, respectively. Adsorption equilibriums were reached within 120 min for all dyes. An increase in the initial dye concentration enhanced the adsorption capacity.
(2) Adsorption processes for the five dyes were found to follow the pseudo-second-order kinetics rate expression.
(3) The Freundlich isotherm described the equilibrium data of BG, AR, and RB dyes on CSAC better than Langmuir isotherm, but the Langmuir isotherm showed a better fit to the equilibrium data of MB and MV dyes. The adsorption capacities of adsorbent for RB, MV, MB, AR, and BG were found to be 133.33, 135.14, 153.85, 196.08, and 222.22 mg/g, respectively.
(4) The R_L results show that the adsorption of five dyes onto CSAC is favorable.
(5) Adsorption of MV, AR, RB, and BG dyes onto CSAC decreased with an increase in the temperature, indicating that the process is exothermic, while the adsorption of MB increased with an increase in the temperature, indicating that the process is endothermic.

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