ORIGINAL ARTICLE

The wastage of the cotton stalks (*Gossypium hirsutum* L.) as low-cost adsorbent for removal of the Basic Green 5 dye from aqueous solutions

Elchin O. Akperov[1] · Oktay H. Akperov[1]

Abstract

Cotton stalks (*Gossypium hirsutum* L.) waste was investigated as a low-cost and effective adsorbent for the adsorption of Basic Green 5 dye from aqueous solution. The effects of pH solution, initial dye concentration, contact time, sorbent dosage and temperature on the adsorption parameters were investigated. The Langmuir, Freundlich and Dubinin–Radushkevich adsorption models were evaluated using the experimental data. The maximum adsorption capacity was found to be 42.37 mg g^{-1} from the Langmuir isotherm model at 20 °C. The dimensionless separation factor (R_{L}) values lie between 0.129 and 0.423, indicated favorable adsorption. The adsorption rate data were analyzed according to the Lagergren pseudo-first- and pseudo-second-order kinetic models. It was found that kinetic followed a pseudo-second-order model. The negative values of the $\Delta G°$ at 293–323 K and the positive value of the $\Delta H°$ (13.585 kJ mol^{-1}) indicate that the sorption process is spontaneous and endothermic in nature. The positive value of $\Delta S°$ (0.0467 kJ mol^{-1} K^{-1}) shows the increasing randomness during adsorption process. The mean adsorption energy from Dubinin–Radushkevich equation was found to be 11.63 kC mol^{-1}, indicating that the adsorption of the Basic Green 5 by cotton stalks occurred through chemical interaction mechanism. The offered mechanism of adsorptive process of the Basic Green 5 dye on a surface of the sorbent, obtained on the basis of cotton stalks, considers forming a complex between dye and sorbent.

Keywords Basic Green 5 dye · Cotton stalks · Adsorption · Isotherms · Sorption mechanism

Introduction

Wastewater containing dyes is very difficult to be treated, since the dyes are recalcitrant organic molecules, resistant to aerobic degradation, and stable to light, heat and oxidizing agents (Kyzas et al. 2012). A considerable amount of dyes is released into the aquatic ecosystems through the wastewater streams of industries such as textile, carpet, leather, paper, printing, food, cosmetics, paint, pigments, petroleum, solvent, rubber, plastic and pesticide. (Chowdhury and Saha 2012). Several treatment methods have been developed for dye removal including coagulation, chemical oxidation, membrane separation, electrochemical process and adsorption technique (Gupta 2009; Mohammed et al. 2014; Oladipo et al. 2013). Among these processes, adsorption is an effective method for color removal. Agrowaste materials are available in large quantities and may have potential as a sorbent due to their physicochemical properties and low cost. They contain various organic compounds such as lignin, cellulose and hemicellulose with polyphenolic groups that might be useful for binding dyes through different mechanisms. A number of agricultural waste materials are being studied for the removal of different dyes from aqueous solutions at different operating conditions. The adsorption of methylene blue on teak tree bark powder was carried out as a function of process of parameters including initial methylene blue concentration, dose of adsorbent, pH, agitation time, agitation speed, temperature and particle size (Patil et al. 2011). Freundlich, Langmuir and Temkin isotherm models were used to test the equilibrium data. The best-fitting isotherm models were found to be Langmuir and Freundlich. The monolayer (maximum) adsorption capacity was found to be 333.333 mg g^{-1}. Lagergren pseudo-second-order model

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best fits the kinetics of adsorption. Thermodynamic analysis showed negative values of ΔG indicating adsorption was favorable and spontaneous, positive values of $\Delta H°$ indicating endothermic physical adsorption and positive values of $\Delta S°$ indicating increased disorder and randomness at the solid-solution interface of methylene blue with the adsorbent. Adsorption of Direct Red 81 dye was investigated using bamboo sawdust (BSD) and treated with citric acid bamboo sawdust (TBSD) in a batch system with respect to initial dye concentration, adsorbent dose, pH, temperature and contact time (Tabrez et al. 2012). Maximum adsorption capacity obtained from the Langmuir isotherm plots was 6.43 mg g^{-1} (89%) (BSD) and 13.83 mg g^{-1} (92%) (TBSD) at 303 K. The adsorption dynamics conformed well to pseudo-second-order kinetic equation. Thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) suggested the adsorption process to be spontaneous, endothermic with increase in randomness at solid-solution interface. Modified Sugar cane bagasse, an agricultural by-product, acts as an effective sorbent for the removal of both basic and reactive dyes from aqueous solution (Wong et al. 2009). Batch adsorption studies were investigated for the removal of Basic Blue 3 and Reactive Orange 16. The adsorption isotherms fitted well into both the Langmuir and Freundlich equations. Results indicated that according to the Langmuir isotherm, the maximum sorption capacities are 37.59 and 34.48 mg g^{-1} for Basic Blue 3 and Reactive Orange, respectively. The kinetics of dye sorption processes fit a pseudo-second-order kinetic model. Coffee waste collected from coffee shops has been examined for the removal of two basic dyes, toluidine blue and crystal violet, from aqueous solutions (Lafi et al. 2014). Batch adsorption experiments were conducted under different conditions including contact time, the initial concentration of dye, pH, sorbent dosage and temperature. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms were tested to examine the adsorption behavior. The equilibrium data were well fitted by Langmuir isotherm model. The kinetic study indicates that adsorption follows the pseudo-second-order model. The maximum adsorption capacity was found to be as high as 142.5 mg g^{-1} for toluidine blue and 125 mg g^{-1} for crystal violet. In literature, there are few works on the research of adsorption of Basic Green 5 dye from aqueous solutions. In these works, modified natural and synthetic adsorbents were used for removal of Basic Green 5 from aqueous solutions. Spherical biochar derived from saccharides (glucose, sucrose and xylose) was used for removal of Basic Green 5 from water solutions (Tran et al. 2017a). Approximately 54–81% of the total concentration of dye in the solutions were removed within 1–4 min. The glucose biochar sample exhibited the highest adsorption toward Basic Green 5, and the maximum Langmuir adsorption capacity has been 144.7 mg g^{-1} at 30 °C. Thermodynamic calculations demonstrated that the adsorption process of Basic Green 5 onto glucose biochar occurred spontaneously ($-\Delta G°$) was endothermic nature

($\Delta H° = +80.34$ kJ mol^{-1}) and resulted in increased system randomness ($\Delta S° = +0.386$ kJ mol^{-1}). Obtained from *Eucalyptus lenceolata* wood, activated carbon was used for adsorption of Basic Green 5 from water solution (Alam et al. 2017). Batch studies were performed to address various experimental parameters like, contact time, temperature and adsorbent dosage for the removal of dye. Elovich and Bhangam models were used for adsorption kinetics studies. From adsorption kinetic data, thermodynamic parameters like ΔH, ΔS and ΔG were determined. The results show that the adsorption process is spontaneous and endothermic nature. The negative entropy shows that acid molecules on the surface of adsorbent take an oriented position.

The research results on the removal of the Basic Green 5 from water solutions by cotton stalk, which is an agrowaste material, were given in the presented work. The effects of the sorbent dosage, initial dye concentration, contact time and temperature were studied, and equilibrium isotherm data were analyzed by the Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. The sorption properties of the cotton stalks waste toward Basic Green 5 are executed for the first time, and it defines the novelty of this work.

Materials and methods

Preparation of the sorbent

The adsorbent used in the present study is cotton stalks (CS) that were collected from cotton plantations of the central regions of Azerbaijan Republic. CS of 1–2 mm in size were washed thoroughly with heated distilled water to remove dust and other impurities. Then, CS were washed repeatedly with acetone and were grounded in a mixer grinder. After grinding, the powders were again washed with acetone and dried at 40 °C in the vacuum oven.

Dye solutions

Basic Green 5 (BG5) or methylene green, used as an adsorbate in the present study, is a monovalent cationic dye. In dye classification, it is classified as C.I. Basic Green 5, and the chemical structure of the dye is in the following form (Wikipedia).
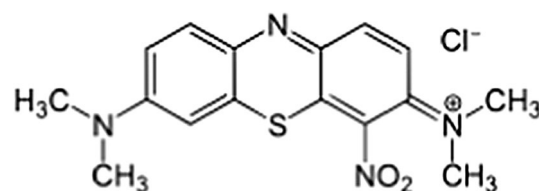
It has a molecular weight of 364.9 and absorption maximum 660.607 (Conn), 657.618 nm (Aldrich). A stock

solution of 250 mg L^{-1} was prepared in double-distilled water, and the experimental solutions of the desired concentration were obtained by successive dilutions.

Adsorption experiments

Adsorption of BG 5 on CS was carried out using a batch experiment method. A quantity of 40 mL of BG 5 dye solution of a certain concentration was placed in a 100-mL Erlenmeyer flask containing the sample of sorbent and was agitated in a thermocontrolled water bath to carry out the sorption experiment. At the end of the experiment, the mixture of adsorbent and adsorbate was immediately separated using glass fiber filter, and residual BG in solution was defined by a photometric method (UV–Vis spectrophotometry SPECORD 210 PLUS). For this purpose, 1 mL of the filtered dye solution placed in the 25-mL graduated flask, diluted with the buffer solution CH$_3$COOH/NH$_4$OH with pH 6, and the optical density has been defined. According to the obtained value of the optical density, the residual amount of BG has been determined using a calibration curve. The sorption degree (%) and sorption capacity (mg g^{-1}) of the sorbent have been calculated by Eqs. (1) and (2):

$$\text{Sorption degree} = \frac{(C_0 - C_e)}{C_0} \times 100\% \qquad (1)$$

$$\text{Sorption capacity} = \frac{(C_0 - C_e) \times V_{sol}}{m_{sorb}} \qquad (2)$$

where C_0 and C_e (mg L^{-1}) are initial and equilibrium concentrations of BG 5, respectively, V_{sol} (L) is the volume of the dye solution subjected to sorption, and m_{sorb} (g) is the weight of sorbent.

Result and discussion

Effect of pH

The pH factor is very important in the adsorption process especially for dye adsorption. The effect of pH on the adsorption of BG5 with CS was studied. It was observed that the pH has a significant influence to the adsorption process (Fig. 1). Figure 1 shows that the maximum uptake of BG dye was observed at pH 7 (70.1%). At pH between range 3–7, the removal was increased from 29.4 up to 70.1%. As the pH value increased from 7 to 9, the efficiency of the dye removal is slightly becoming lesser. The low adsorption of BG5 at acidic pH was suggested to be due to the presence of excess H+ ions in solution. Generally, at low pH solution, the percentage of dye removal will decrease for cationic dye adsorption, while for anionic dyes the percentage of dye

removal will increase (Salleh et al. 2011). For cationic dyes, lower adsorption of dye at acidic pH is probably due to the presence of excess H$^+$ ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in the pH solution, the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered, which may result in an increase in the extent of adsorption (Wang et al. 2008). With an increase in the pH of solution, the electrostatic repulsion between the positively charged cationic dyes and the surface of adsorbent is lowered and consequently the removal efficiency is increased (Ansari and Mosayebzadeh 2010).

Effect of sorbent dosage

The effect of the sorbent dosage was investigated by varying the amount of CS from 0.5 to 2.5 g L^{-1}. The effect of sorbent dosage on the removal degree of dye is shown in Table 1. Along with the increase in sorbent dosage from 0.5 to 2.5 g L^{-1}, the sorption degree of dye increased. This is due to the increase in active sites for adsorption of dye molecules with increasing sorbent dosage. The sorption equilibria of the dye were reached at 1.25 g L^{-1}, and the removal of dyes remained almost invariable above this dosage. Therefore, 1.25 g L^{-1} appears to be the optimum sorbent dosage for the studied conditions.

Effect of adsorption time

The effect of adsorption time on BG 5 sorption onto CS has been investigated at different contact time varying between 10 and 80 min at 20 °C, pH 6, dye initial concentration 50 mg L^{-1}, dye solution 0.04 L, sorbent dosage 1.25 g L^{-1}(Table 2). The sorption degree was rapidly increased with the increasing of adsorption time up to
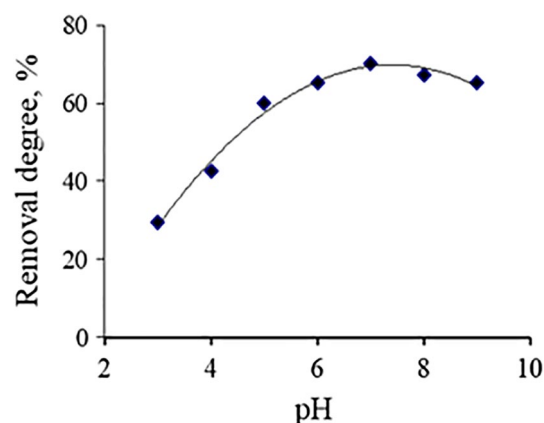

Fig. 1 Dependence sorption degree from pH solution ($C_0 = 50$ mg L^{-1}, time 30 min, $V = 0.04$ L, sorbent dosage 1.25 g L^{-1}, 20 °C)

Table 1 Dependence of sorption degree from sorbent dosage ($C_0 = 50$ mg L^{-1}, 30 min, 20 °C, pH 6, $V = 0.04$ L)

Sorbent dosage (g L^{-1})	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.25	2.5
R (%)	32.2	45.1	52.4	57.6	58.2	59.0	60.3	60.9	60.9

Table 2 Dependence of sorption degree from contact time ($C_0 = 50$ mg L^{-1}, sorbent dosage 1.25 g L^{-1}, 20 °C, pH 6, $V = 0.04$ L)

Time (min)	10	20	30	40	50	60	70	80
R (%)	31.5	46.8	57.6	65.3	70.2	73.2	74.8	75.6

50 min (70.2%), beyond which it attained almost a constant value (73.2–75.6%). Therefore, the adsorption time equal to 50 min was considered to be sufficient for sorption of BG 5 onto sorbent.

## Effect of initial concentration of dye and sorption isotherm of sorbent

The effect of the initial concentration of BG 5 dye on the adsorption efficiency of the CS was evaluated at different concentrations of the dye. It is visible that initial concentration of dye is one of the major factors influencing on removal degree of the dye from aqueous solution: With the increase in initial concentration from 20 to 100 mg L^{-1}, removal degree decreases from 75.5 to 45.1%. It can be explained with the fact that with the increase in dye concentration in solution, the quantity of active sites decreases on the adsorbent surfaces and therefore sorption degree decreases. The equilibrium sorption capacity of the sorbent was calculated from sorption isotherm (Fig. 2). The experimental results show that the sorption capacity of the sorbent increases rapidly with the increase in the equilibrium concentration of BG 5. When the equilibrium dye concentration reached a certain extent, the increasing of adsorption capacity became slower and comes nearer to a constant value. It can be concluded that the experimental equilibrium sorption capacity (q_{exp}) of the CS is equal to be 33.2 mg g^{-1}.

Langmuir, Freundlich and Dubinin–Radushkevich isotherms

In this study, the sorption isotherm of the BG 5 was analyzed using the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models, which are the most commonly used isotherms. The linear form of the Langmuir isotherm equation is represented by the following equation:

$$C_e/q_e = 1/(q_{max}K_L) + C_e/q_{max} \tag{3}$$

where C_e is the equilibrium concentration of BG 5 (mg L^{-1}), q_e is the amount of the BG adsorbed at equilibrium (mg g^{-1}), q_{max} is the monolayer maximum adsorption capacity of the
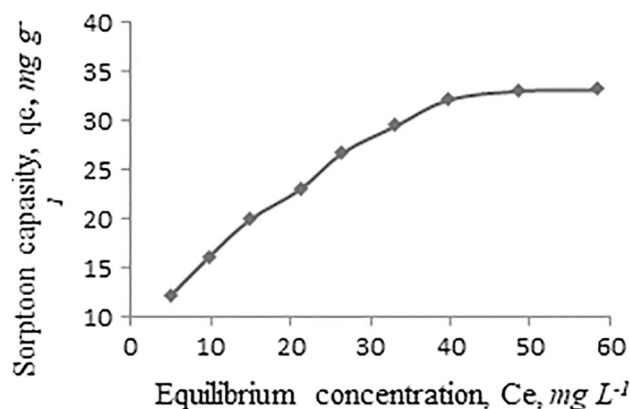
Fig. 2 Sorption isotherm

BG 5 (mg g^{-1}), and K_L is the Langmuir equilibrium constant (L mg^{-1}), related to the affinity between an adsorbent and adsorbate.

The Freundlich isotherm is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces, and it is represented by the equation below:

$$\log q_e = \log K_F + (1/n) \log C_e \tag{4}$$

where n is the Freundlich constant for intensity sorption, K_F is the Freundlich constant for sorption capacity, and $(1/n)$ is the heterogeneity factor. The obtained experimental equilibrium data were examined with Langmuir and Freundlich isotherm models.

The D–R isotherm equation, which is more generally used to distinguish between physical and chemical adsorption, is given by the following equation:

$$\ln q_e = -K\varepsilon^2 + \ln B_{DR} \tag{5}$$

where K_D is the D–R equation constant, B_{DR} is the theoretical isotherm saturation capacity (mol g^{-1}), q_e is the equilibrium concentration of metal ions (mol L^{-1}), and ε is Polanyi potential, which is defined by the equality

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{6}$$

where C_e is the equilibrium concentration of the BG 5 (mol L^{-1}) and R is the universal gas constant (8.314 J mol^{-1}). The D–R constant can give valuable information regarding the mean energy (E) of adsorption by the equality

$$E = 1/(2K_D)^{1/2}. \tag{7}$$

The linear curve of specific sorption versus equilibrium concentration of BG 5 in solution and the curve of the logarithmic equilibrium adsorption capacity versus logarithmic equilibrium concentration are given in Figs. 3 and 4, respectively. Parameters of the Langmuir and Freundlich equations are given in Table 3. The value of the maximum experimental sorption capacity calculated from the Langmuir equations is equal to 42.37 mg g^{-1}, which is close to value of equilibrium sorption capacity experimentally obtained from sorption isotherm (33.2 mg g^{-1}, Fig. 2), whereas the calculated value K_F (6.127 mg g^{-1}), corresponding to the sorption capacity of a sorbent, differs from the experimental value of sorption capacity. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor R_L. The separation factor R_L was calculated using Eq. (8)

$$R_L = 1/(1 + K_L C_0) \tag{8}$$

where C_0 is the initial BG concentration (mg L^{-1}). In the case of $1 > R_L > 0$, adsorption is favorable, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption, while the adsorption process is irreversible if $R_L = 0$ (Sumanjit and Mahajan 2012). The calculated values of R_L for the different initial concentrations of the BG5 (20–100 mg L^{-1}) were equal to be 0.423–0.129, indicating highly favorable adsorption for the BG dye onto adsorbent CS under experimental conditions used in this study.

Graphic of the D–R equation is given in Fig. 5. The calculated parameters of D–R equation are illustrated in Table 3.
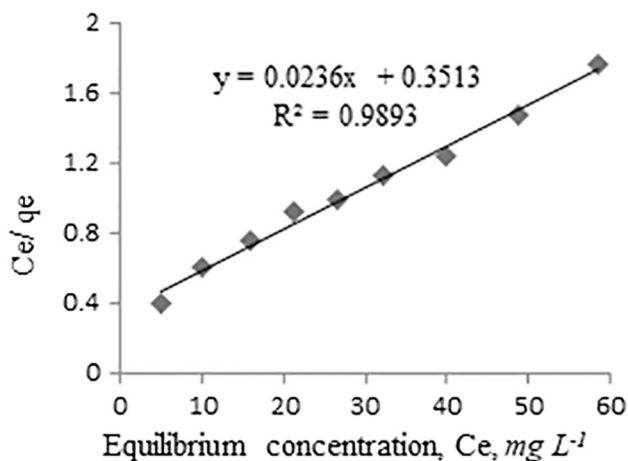

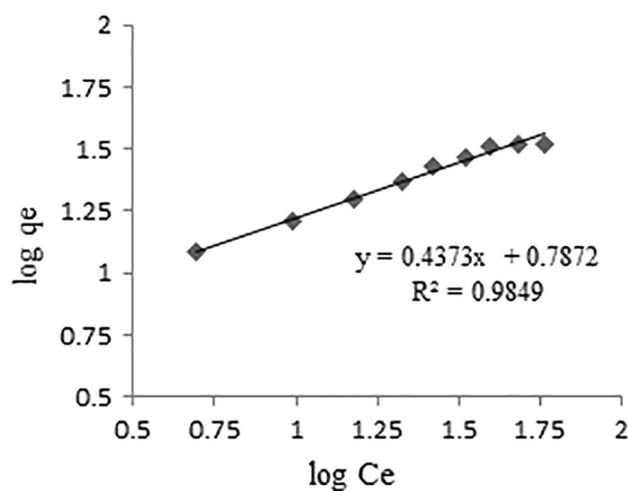**Fig. 3** Langmuir plots for sorption (pH 6, time 30 min, $C_0 = 20$–100 mg L^{-1}, $V = 0.04$ L, sorbent dosage 1.25 g L^{-1}, 20 °C)

Fig. 4 Freundlich plots for sorption (pH 6, time 30 min, $C_0 = 20$–100 mg L^{-1}, $V = 0.04$ L, sorbent dosage 1.25 g L^{-1}, 20 °C)

The E_D value is used to ascertain the type of adsorption process under consideration. If $8.0 > E_D > 16.0$ kJ mol^{-1}, the adsorption process can be assumed to involve chemical sorption; on the other hand, if $E_D < 8.0$ kJ mol^{-1}, the adsorption process is of a physical nature (Monika et al. 2009). In our case, the found value of the mean sorption energy E_D from D–R equation is equal to be 11.63 kC mol^{-1}, indicating that the adsorption of the BG 5 by CS occurred through chemical interaction mechanism. The theoretical isotherm saturation capacity of the sorbent (B_{DR}) from D–R equation is equal to be 0.000523 mol g^{-1} (190.85 mg g^{-1}).

## Kinetics and thermodynamic

Several sorption kinetic models have been established to describe the reaction order of sorption systems based on solution concentration. The pseudo-first-order and pseudo-second-order kinetic models are the most well-known model to study the sorption kinetics of dyes and have been widely used in the kinetic study of dye sorption using various kinds of sorbent materials. Kinetic studies of the sorption BG 5 by CS were carried out under the optimized conditions during from 10 to 80 min. The kinetic data obtained were fitted to linear form of Lagergren pseudo–first order and pseudo–second order kinetic models (Chowdhury and Saha 2010a; Akolo and Kovo 2015). The pseudo–first–order kinetic model known as Eq (9). The pseudo-second-order kinetic model is expressed by Eq. (10)

$$\log(q_e - q_\tau) = \log q_e - 0.434 K_1 \tau \tag{9}$$

where q_t and q_e are the amounts of dye adsorbed at time τ and at equilibrium (mg g^{-1}), respectively, and K_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}).

Table 3 Parameters of the Langmuir, Freundlich and D–R equations ($C_0 = 50$ mg L^{-1}, $V = 0.04$ L, sorbent dosage 1.25 g L^{-1}, 30 min, 20 °C)

Langmuir equation				Freundlich equation				D–R equation		
q_{max} (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	$1/n$	n	K_F	R^2	B_{DR} (mg g^{-1})	E (kC mol^{-1})	R^2
42.37	0.0672	0.423–0.129	0.9893	0.4373	2.31	6.127	0.9849	190.85	11.63	0.9884
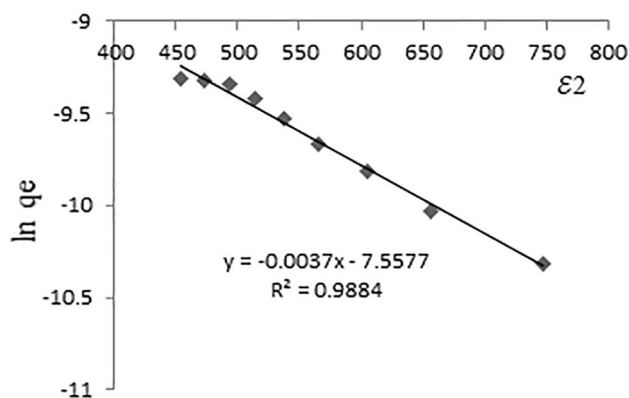
Fig. 5 D–R plots for sorption (pH 6, time 30 min, $C_0 = 20$–100 mg L^{-1}, $V = 0.04$ L, sorbent dosage 1.25 g L^{-1}, 20 °C)

The pseudo-second-order kinetic model is expressed by Eq. (7)

$$\tau/q_\tau = 1/(K_2 q_e^2) + \tau/q_e \qquad (10)$$

where q_t and q_e are the amounts of BG 5 sorbed at time τ and at equilibrium (mg g^{-1}), respectively, and K_2 is the pseudo-second-order equilibrium rate constant (L mg^{-1} min^{-1}). Schedules of the equations of the pseudo-first and pseudo-second model are illustrated in Figs. 6 and 7, respectively, and the obtained values of kinetic parameters are placed in Table 4.

Comparison of the obtained data shows that the sorption process of the BG 5 from aqueous solutions with CS is better described by the pseudo-second kinetic model with determination coefficient 0.9978. Calculated value of sorption capacity from the equation pseudo-second model is equal to be 38.46 mg g^{-1}, which is closer to the value of the experimental sorption capacity, obtained from the adsorption isotherm (33.2 mg g^{-1}).

For the purpose of assessment of the scientific and practical importance of our work we compared the obtained data on adsorption BG 5 by cotton stalks with some literature data on sorption BG 5 by other agricultural wastes (Table 5). We also provided in the Table 5 some literary data on adsorption a methylene blue (MB), which has almost identical structure with BG 5, by agricultural wastes. From Table 5, the adsorption parameters on removal of BG 5 dye from water solution by CS are comparable with data on adsorption of BG 5 and MB dyes from water solution, using other agricultural adsorbents.
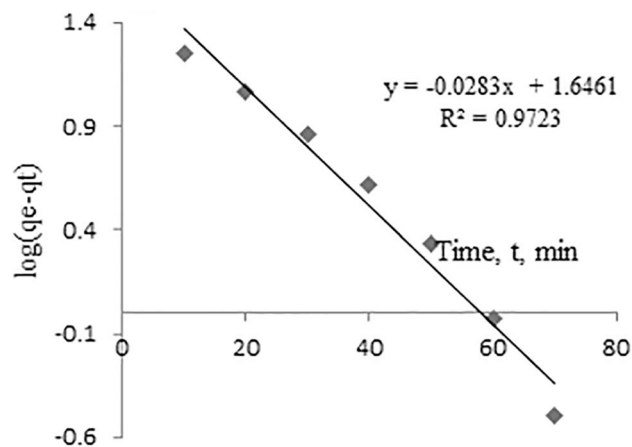
Fig. 6 Plots of pseudo-first order model
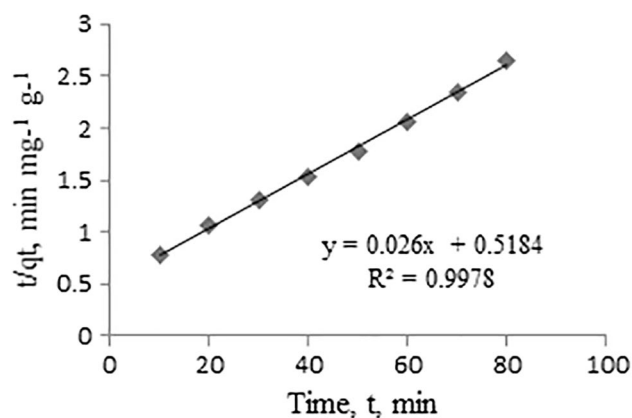
Fig. 7 Plots of pseudo-second order model

Thermodynamic consideration of an adsorption process is necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change ($\Delta G°$) is a critical factor for determining the spontaneity of a process and can be computed by the classical Van't Hoff equation (Chowdhury and Saha 2010b):

$$\Delta G° = -RT \ln K_d = -2303 \, RT \log K_d \qquad (11)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), and K_d is the distribution coefficient for sorption defined as:

$$K_d = q_e/C_e$$

Table 4 Regression parameters for the kinetic models $C_0 = 50$ mg L^{-1}, $V = 0.04$ L, sorbent dosage 1.25 g L^{-1}, 20 °C)

Kinetic model	q_e (mg g^{-1})	K_1 (min^{-1})	K_2 (L mg^{-1} min^{-1})	R^2
Pseudo-first order	44.27	0.0652	–	0.9723
Pseudo-second order	38.46	–	0.0013	0.9978
q_{eks}	33.2	–	–	–

Table 5 Comparison of BG 5 dye uptake data with other adsorbents on the basis of an agricultural wastage

| Sorbent	Dye	q_{max} (mg g^{-1})	pH	T (°C)	C_0 (mg L^{-1})	Adsorbent (g L^{-1})	Model	Source
Glucose biochar	BG5	144	6	30	250	2.5	Langmuir	Tran et al. (2017a)
Golden shower pod	BG5	45.5	7	30	300	4.0	Langmuir	Tran et al. (2017b)
Coconut shell	BG5	41.5	7	30	300	4.0	Langmuir	Tran et al. (2017b)
Orange peel	BG5	35.2	7	30	300	4.0	Langmuir	Tran et al. (2017b)
Cotton stalks	BG5	42.37	7	20	50	1.25	Langmuir, K2	In this study
Cotton stalks	MB	111.36	7	35	825	4.0	Langmuir, K2	Deng et al. (2011)
Wheat shells	MB	21.5	6.5	50	100	1.0	Langmuir	Bulut and Aydin (2006)
Brazil nut shells	MB	7.81	3–10	30	1100	–	Langmuir, K2	Oliveira Brito and Andrade (2010)
Corn husk	MB	30.33	6.2	25–28	30	0.5	Langmuir, K2	Malik et al. (2016)

in which q_e is the equilibrium adsorbate concentration (mg L^{-1}) on the sorbent and C_e is the equilibrium adsorbate concentration in solution (mg L^{-1}). It is also known that $\Delta G°$ is a function of change in enthalpy ($\Delta H°$, kJ mol^{-1}) as well as change in standard entropy ($\Delta S°$, kJ mol^{-1} K^{-1}) according to the following equation:

$$\Delta G° = \Delta H° - T\Delta S°. \tag{12}$$

The values of $\Delta G°$ were estimated to be -0.203, -0.46, -0.962 and -1.593 kJ mol^{-1} at 293, 303, 313 and 323 K, respectively. The negative value of $\Delta G°$ at different temperatures indicates spontaneous nature of the sorption process. Furthermore, decrease in the negative value of $\Delta G°$ with increasing temperature suggests that the sorption process was more favorable at higher temperatures. $\Delta H°$ and $\Delta G°$ were determined from the intercept and slope of the plot of $\Delta G°$ versus T (Fig. 8) and are placed in Table 6. The values of $\Delta H°$ and $\Delta S°$ were calculated as 13.585 kJ mol^{-1} and 0.0467 kJ mol^{-1} K^{-1}, respectively. The positive value of $\Delta H°$ indicates endothermic nature of adsorption. The positive value of $\Delta S°$ shows the increasing randomness during adsorption process.

Mechanism of the adsorption

There were many factors that may influence the sorption behavior BG 5 onto CS, such as dye structure, sorbent surface properties, steric effect and hydrogen bonding and van der Waals forces. The mechanism of adsorption and biosorption process of the cationic dyes on agricultural waste biomass includes chemisorption, a complex formation, an ionic
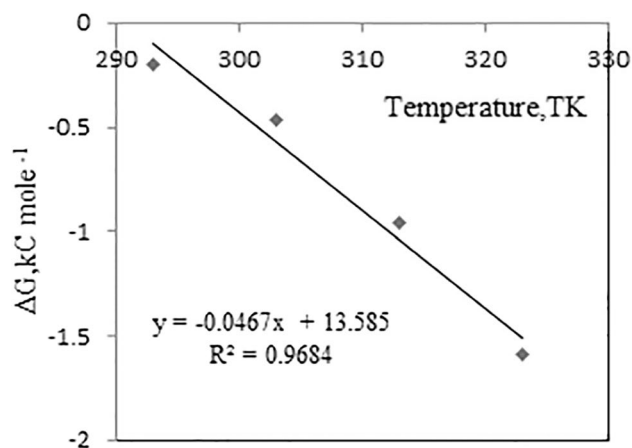
Fig. 8 Plot of $\Delta G°$ versus T

Table 6 Sorption thermodynamic parameters

Temp. (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})
293	-0.203	13.585	0.0467
303	-0.46		
313	-0.962		
323	-1.593		

exchange and physisorption on the surfaces and pores of the adsorbent. Macromolecular components of the CS include mainly of cellulose (41.6%), hemicelluloses (21.6%) and lignin (34.0%), which contain various functional groups,

such as hydroxyl, carboxyl, ether, ester groups (Karthyani et al. 2017). The complexation between BG 5 and CS can take place through weak and strong forces. The weak interactions occur due to the van der Waals forces, while the strong interactions occur due to (1) hydrogen-bonding interaction between CS surface and the nitrogen-containing amine groups of BG 5, (2) electrostatic interaction between the cationic dye [due to the presence of N^+ $(CH_3)_2$ group] and hydroxyl group in surface of the CS. Considering the above-named types of interaction between BG 5 and CS, it is possible to offer the adsorption mechanism BG 5 on a surface of the CS connected with forming of the complex illustrated in Fig. 9. The presence of the adsorbed BG 5 on a surface of an adsorbent has been confirmed with UV–Vis spectra. The UV–Vis spectra of the adsorbent before and after sorption are shown in Fig. 10. Figure 10 shows that, unlike the spectra of unused sorbent (a), in the UV–Vis spectra of the sorbent after sorption process (b), the absorbance is observed in about 650–660 nm, which can appear due to BG5 dye. Finally, it can be concluded that cotton stalks, as low-cost agrowaste material, can be used as a sorbent for the removal of BG 5 dye from aqueous solutions.

Conclusions

In this study, the efficiency of cotton stalks, collected from cotton plantations of the central regions of Azerbaijan as sorbent for removal of Basic Green 5 dye from aqueous solutions, was investigated. Batch mode sorption studies indicate that the sorption process was strongly dependent on initial dye concentration, sorbent dose, contact time and temperature. The equilibrium sorption data obtained at different initial concentrations of dye fitted well in the Langmuir and Freundlich isotherms model. The maximum monolayer sorption capacity was found to be 42.37 mg g^{-1}, which is close to value of equilibrium sorption capacity experimentally obtained from sorption isotherm (33.2 mg g^{-1}). Kinetic
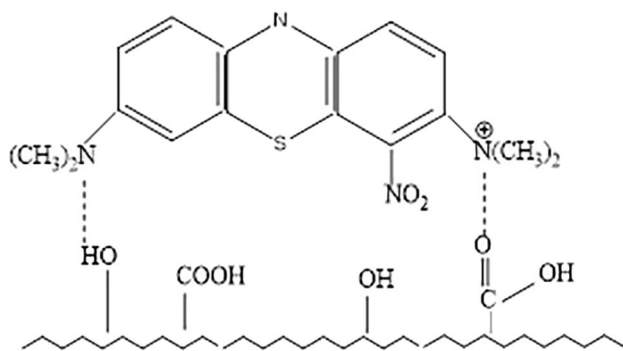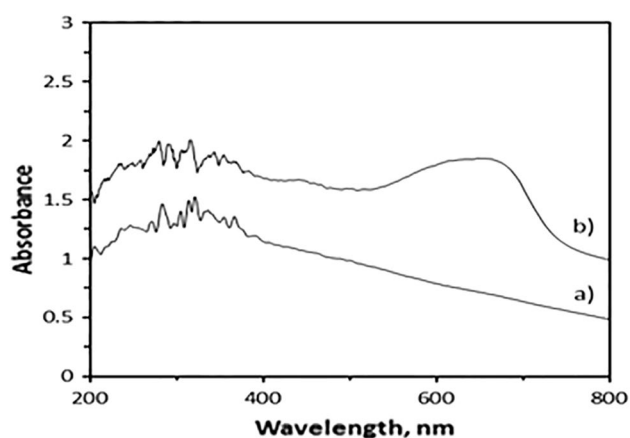

Fig. 10 UV–Vis spectra of the sorbent **a** before and **b** after adsorption

studies show that the dye removal followed pseudo-second-order rate equation, while thermodynamic studies suggest that the sorption process was spontaneous and endothermic in nature. The positive value of $\Delta S°$ shows the increasing randomness during adsorption process. The offered mechanism of adsorptive process of the Basic Green 5 dye on a surface of the sorbent, obtained on the basis of cotton stalks, considers forming a complex between dye and sorbent. Finally, it can be concluded that cotton stalks, common and easily available agrowaste material, can be used as a sorbent for the removal of BG from aqueous solutions.

Compliance with ethical standard

Conflict of interest The authors declare that they have no conflict of interest.

Fig. 9 The possible sorption mechanism of the BG5 on the CS surface

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