

## REMOVAL OF THE BASIC GREEN 5 DYE FROM AQUEOUS SOLUTIONS BY GRAPE (*Vitis Vinifera* L) BUSHES WASTES

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**Abstract.** Batch mode studies of adsorption of Basic Green 5 dye from aqueous solution on grape (*Vitis vinifera*) bushes wastes were carried out as a function of process of parameters includes initial dye concentration, contact time, sorbent dosage and temperature. The Langmuir and Freundlich adsorption models were evaluated using the experimental data and the experimental results showed that the Langmuir model fits better than the Freundlich model. The maximum adsorption capacity was found to be  $43.86 \text{ mg g}^{-1}$  from the Langmuir isotherm model at  $20^\circ\text{C}$ . The dimensionless separation factor ( $R_L$ ) values lie between 0.173 to 0.653 indicated favorable adsorption. Lagergren pseudo-first order, Lagergren pseudo second order were tested for the kinetic study. Lagergren pseudo second order model best fits the kinetics of adsorption ( $R^2 = 0.9951$ ). Calculated value sorption capacity from the equation's pseudo-second model is equal to be  $36.5 \text{ mg g}^{-1}$ , which closer to the value obtained from the adsorption isotherm ( $31.76 \text{ mg g}^{-1}$ ). The negative values of the  $\Delta G^0$  at 293-223 K ( $-1.463$ ) – ( $-0.119$ )  $\text{kJ mol}^{-1}$ ) and the positive value of the  $\Delta H^0$  ( $13.507 \text{ kJ mole}^{-1}$ ) indicate that the sorption process is spontaneous and endothermic in nature. The positive value of  $\Delta S^0$  ( $0.0462 \text{ kJ mole}^{-1} \text{ K}^{-1}$ ) shows the increasing randomness during adsorption process. The results of this research showed that the adsorption of the Basic Green 5 dye by grape bushes wastes occurred through chemical interaction mechanism.

**Keywords:** Basic Green 5 dye, grape bushes waste, kinetics, mechanism, thermodynamic.

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**Received:** 10 October 2019; **Accepted:** 14 November 2019; **Published:** 15 December 2019.

### 1. Introduction

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, pesticide etc. Several treatment methods have been developed for dye removal including coagulation, chemical oxidation, membrane separation, electrochemical process, photocatalytic degradation and adsorption technique (Gupta, 2009, Mohammed *et al.*, 2014, Oladipo *et al.*, 2013, Saravanan *et al.*, 2016, Saravanan *et al.*, 2015, Rajendran *et al.*, 2016). Among these processes, adsorption is an effective method for color removal. Agrowaste materials such as sawdust, wood, hen feather, sheep wool, corn cob, rice husk, coir pith, rice bran, wheat bran etc. are available in large quantities and may have potential as a sorbent due to their physico-chemical properties and low cost (Crini, 2005). They contain various organic compounds such as lignin, cellulose and hemicellulose with polyphenolic groups that might be useful for binding dyes through different mechanisms. The adsorption of methylene blue on teak tree bark powder were carried out as a function of process of parameters includes 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 monolayer maximum adsorption capacity was found to be  $333.333 \text{ mg g}^{-1}$ . Lagergen pseudo second order model best fits the kinetics of adsorption. 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 (Ali *et al.*, 2012). Maximum adsorption capacity obtained from the Langmuir isotherm plots were  $6.43 \text{ mg g}^{-1}$  (89%) (BSD) and  $13.83 \text{ mg g}^{-1}$  (92%) (TBSD) at 303K. The adsorption dynamics conformed well to pseudo-second order kinetic equation. Thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) 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 (BB3) and Reactive Orange 16 (RO16). 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  $34.48 \text{ mg g}^{-1}$  for BB3 and RO16, 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 (TB) and crystal violet (CV), from aqueous solutions (Lafi *et al.*, 2014). Batch adsorption experiments were conducted under different conditions including contact time, initial concentration of dye, pH, sorbent dosage and temperature. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherms were tested to examine the adsorption behavior. The equilibrium data were well fitted by Langmuir isotherm model. The maximum adsorption capacity was found to be as high as  $142.5 \text{ mg g}^{-1}$  for TB and  $125 \text{ mg g}^{-1}$  for CV. The kinetic study indicates that adsorption follows the pseudo second-order model.

In literature there are few works on a research of adsorption of Basic Green 5 dye (BG5) from aqueous solutions with agrowastes. Spherical biochar derived from saccharides (glucose, sucrose, and xylose) was used for removal BG5 from water solutions (Tran *et al.*, 2017a). Approximately 54–81% of total concentration of dye in the solutions were removed within 1-4 min. The glucose biochar sample exhibited the highest adsorption toward BG5 and the maximum Langmuir adsorption capacity has been  $144.7 \text{ mg g}^{-1}$  at  $30^\circ\text{C}$ . In work (Tran *et al.*, 2017b) investigated the mechanism and capacity of adsorption of BG5 dye onto various biochars derived from golden shower pod (GSB), coconut shell (CCB), and orange peel (OPB). Adsorption was greatly affected by the solution pH (2.0–10) and ionic strength (0–0.5 M). Equilibrium can be established rapidly in the kinetic study with low required activation energies ( $E_a = 3.05\text{--}23.3 \text{ kJ mol}^{-1}$ ). The maximum Langmuir adsorption capacities at  $30^\circ\text{C}$  indicated the order: GSB ( $45.5 \text{ mg g}^{-1}$ ) > CCB ( $41.5 \text{ mg g}^{-1}$ ) > OPB ( $35.2 \text{ mg g}^{-1}$ ). Thermodynamic studies suggested that the BG5 adsorption occurred spontaneously ( $-\Delta G^\circ$ ), in an endothermic nature ( $+\Delta H^\circ$ ), and with increased randomness ( $+\Delta S^\circ$ ). Desorption experiments confirmed the irreversible adsorption of BG5. In recently published by us work presented results on adsorption BG5 with cotton stalks waste (Akperov & Akperov, 2019). The adsorption of BG5 on cotton stalk were carried out as a function of process of parameters includes initial BG5 concentration, dose of adsorbent, pH, temperature and contact time. Freundlich, Langmuir and D-R isotherm models were

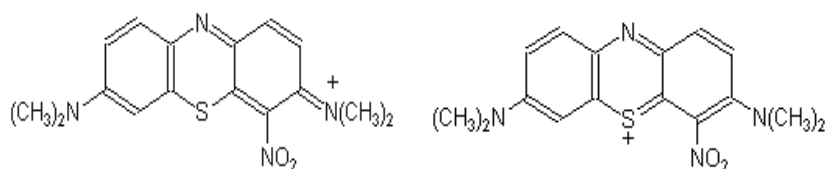
used to test the equilibrium data. The kinetics of dye sorption process fit a pseudo-second order kinetic model.

The research results on removal of the BG5 from water solutions by grape bushes waste, 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 and Freundlich isotherm models. Lagergren pseudo-first and pseudo-second order kinetic models were used to fit experimental data and the adsorption thermodynamic parameters were determined. The sorption properties of the cotton stalks waste toward BG5 are executed for the first time and it defines the novelty of this work.

## 2. Experimental

### 2.1. Materials and Methods

Adsorbent used in the present study is grape bushes waste (GBW) were collected from grape plantations of the Central regions of Azerbaijan Republic and washed thoroughly with heated distilled water to remove dust and other impurities. Then GBW was washed repeatedly with acetone and was dried at 40°C in the vacuum oven. Dried GBW was grounded in a mixer-grinder. After grinding, the powders were again washed with acetone and dried. Different sized GBW's were stored in plastic container for further use. BG5 was 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 form of two following isomers (Wikipedia):



It has a molecular weight of 364.9. A stock solution of 250 mg L<sup>-1</sup> was prepared in double distilled water and the experimental solutions of the desired concentration were obtained by successive dilutions.

### 2.2. Adsorption Experiments

Sorption of BG5 on GBW was carried out using a batch experiment method. A quantity of 40 ml of BG5 solution of a certain concentration was placed in a 100-ml Erlenmeyer flask containing 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 BG5 in solution were defined by a photometric method (UV-vis Specord 210, Germany). For this purpose, 1 ml of the filtered dye solution placed in the 25 ml graduated flask, diluted with the buffer solution CH<sub>3</sub>COOH/NH<sub>4</sub>OH with pH6 and the optical density has been defined. On value, optical density residual amount of BG5 has been determined using calibration curve. The sorption degree (%) and sorption capacity (mg g<sup>-1</sup>) of the sorbent have been calculated by the Eq (1) and (2):

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

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

where  $C_0$  and  $C_e$  ( $mg L^{-1}$ ) are initial and equilibrium concentrations of BG5, respectively,  $V_{sol}(L)$  is the volume of the dye solution submitted to sorption, and  $m_{sorb}(g)$  is the weight of sorbent.

### 3. Result and Discussion

#### 3.1. Effect of the sorbent dosage

The effect of the sorbent dosage was investigated by varying the amount of GBW 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 of sorbent dosage from 0.5 to 2.5  $g L^{-1}$ , the sorption degree of dye increased. This is due to the increase of 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.

**Table 1.** Dependence of sorption degree from sorbent dosage  
( $C_0=50 mg L^{-1}$ , 30 min, 20°C pH6, 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 %	30.3	42.6	51.8	56.8	58.2	59.4	60.3	60.6	60.7

#### 3.2. Effect of the contact time

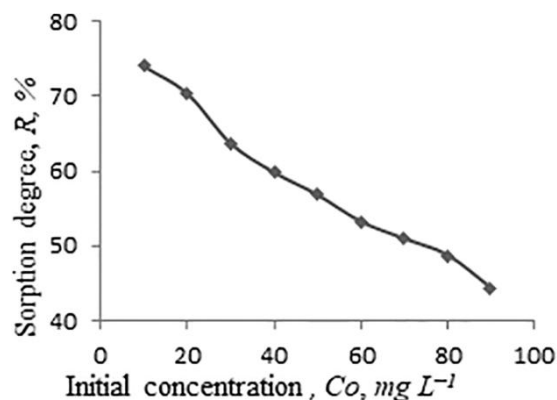
The effect of contact time on BG5 sorption onto GBW has been investigated at different contact time varying between 10 and 100 minutes at 20°C, pH 6, copper ions initial concentration 50  $mg L^{-1}$ , dye solution 0.04 L, sorbent dosage 1.25  $g L^{-1}$  (Table 2). The sorption degree rapid increased with the increasing of contact time up to 60 min (70.1%), beyond which it attained almost a constant value (73.9–74.1%). Therefore, the contact time equal to 60 minutes was considered to be sufficient for sorption of BG5 onto sorbent.

**Table 2.** Dependence of sorption degree from sorption time  
( $C_0=50 mg L^{-1}$ , sorbent dosage 1.25  $g L^{-1}$ , 20°C, pH6, V=0.04 L)

Time, min	10	20	30	40	50	60	70	80	90	100
R, %	28.7	42.1	56.8	62.3	66.7	70.1	72.3	73.6	73.9	74.1

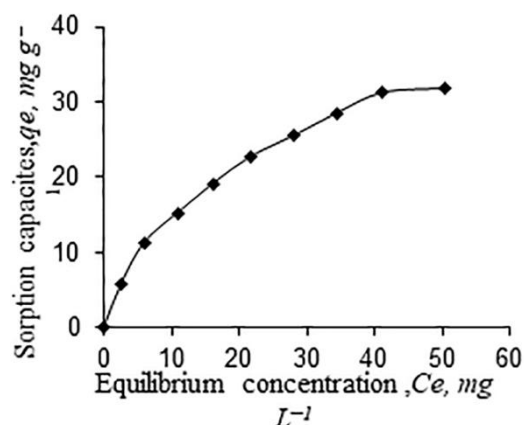
### 3.3. Effect of the initial concentration of BG5 dye

The effect of the initial concentration of BG5 on the adsorption efficiency of the GBW was evaluated at different concentrations of the dye from 10 to 90  $\text{mg L}^{-1}$  (Fig. 1).



**Figure 1.** Dependence sorption degree from initial concentration BG 5.

From Fig.1 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 increase in initial concentration from 10 to 90  $\text{mg L}^{-1}$ , removal degree decreases from 74.0 to 44.3%. It can be explained with the fact, that with increase of dye concentration in solution, the quantity active sites decrease on the adsorbent surfaces and, therefore sorption degree decreases. Equilibrium sorption capacity of sorbent was calculated from sorption isotherm (Fig.2).



**Figure 2.** Sorption isotherm

The experimental results show that the sorption capacity of the sorbent increases rapidly with the increasing of equilibrium concentration of BG5. The experimental results show that the sorption capacity of the sorbent increases rapidly with the increasing of equilibrium concentration of BG5. When the equilibrium dye concentration reached a certain extent, the increasing of adsorption capacity became slower and comes nearer to constant value. It can be concluded that the experimentally equilibrium sorption capacity ( $q_{\text{exp}}$ ) of the GBW is equal to be 31.76  $\text{mg g}^{-1}$ .

### 3.4. Langmuir and Freundlich isotherms

Several models have been published in the literature to describe the experimental data of adsorption isotherms. In this study the sorption isotherm BG5 was analyzed using the Langmuir and Freundlich models, which are the two most commonly used isotherms. The Langmuir equation is based on the assumption, that maximum sorption corresponds to a saturated monolayer of sorbate molecules on the sorbent surface. The energy of sorption is constant and there is no transmigration of the sorbate in the plane of the surface (Gong *et al.*, 2007). The linear form of Langmuir isotherm equation is represented by the following equation:

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

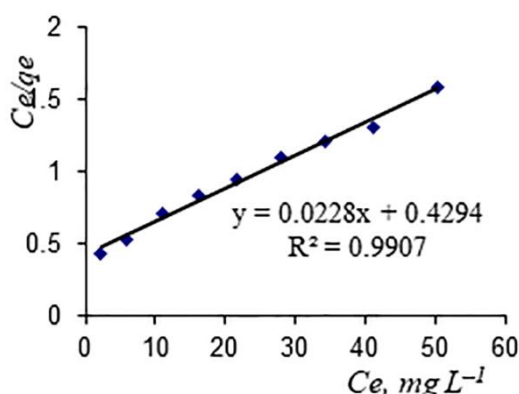
where  $C_e$  is the equilibrium concentration of BG5 ( $mg L^{-1}$ ),  $q_e$  -is the amount of the BG5 adsorbed at equilibrium ( $mg g^{-1}$ ),  $q_{max}$  - is the monolayer maximum adsorption capacity of the BG5 ( $mg g^{-1}$ ) and  $K_L$  -is the Langmuir equilibrium constant ( $L mg^{-1}$ ), related 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:

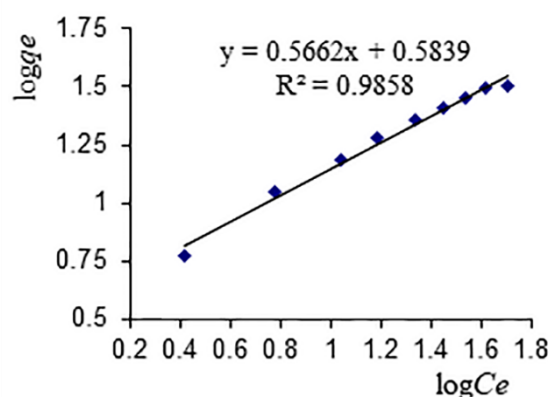
$$\log q_e = \log K_F + (1/n) \log C_e, \quad (4)$$

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 linear curve of specific sorption versus equilibrium concentration of BG5 in solution and the curve of the logarithmic equilibrium adsorption capacity versus logarithmic equilibrium concentration are given in Fig.3 and Fig.4, respectively.



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



**Figure 4.** Freundlich plots for sorption (pH 6, time 30 min,  $C_o = 20\text{--}100\text{ mg L}^{-1}$ ,  $V = 0.04\text{ L}$ , sorbent dosage  $1.25\text{ g L}^{-1}$ ,  $20^\circ\text{C}$ )

Fig. 3 shows that the sorption fitted the Langmuir isotherm well with higher coefficients compared to Freundlich isotherms. Parameters of the Langmuir and Freundlich equations were given in Table 3. The calculated value of the maximum experimental sorption capacity from the Langmuir equations is equal to be  $43.86\text{ mg g}^{-1}$ . Whereas, the calculated value  $K_F (3.837\text{ mg g}^{-1})$ , corresponding to sorption capacity of a sorbent, differs from the experimental value of sorption capacity. Obtained data shows the applicability of the Langmuir model, showing the formation of monolayer coverage of the dye molecules at the surface of the adsorbent.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor  $R_L$ , was adopted. The separation factor  $R_L$  was calculated using the Eq. (5)

$$R_L = 1 / (1 + K_L C_o), \quad (5)$$

where  $C_o$  is the initial BG5 concentration ( $\text{mg L}^{-1}$ ). If  $1 > R_L > 0$ , adsorption is favorable, while  $R_L > 1$  represent unfavorable adsorption, and  $R_L = 1$  represent linear adsorption, while the adsorption process is irreversible if  $R_L = 0$  (Sumanjit & Mahajan, 2012). The calculated values of  $R_L$  for different initial concentration of the BG5 ( $10\text{--}90\text{ mg L}^{-1}$ ) were equal to be  $0.653\text{--}0.173$ , indicates highly favorable adsorption for the BG5 onto adsorbent GBW under experimental conditions used in this study.

**Table 3.** Parameters of the Langmuir and Freundlich equations (BG 5 initial concentration  $50\text{ mg L}^{-1}$ ,  $V = 0.04\text{ L}$ , sorbent dosage  $1.25\text{ g L}^{-1}$ , 30 min,  $20^\circ\text{C}$ )

Langmuir equation				Freundlich equation			
$q_{max}\text{ mg g}^{-1}$	$K_L, \text{ L mg}^{-1}$	$R_L$	$R^2$	$1/n$	$n$	$K_F$	$R^2$
43.86	0.0531	0.653–0.173	0.9907	0.5662	1.766	3.837	0.9858

Obtained data shows the applicability of the Langmuir model, showing the formation of monolayer coverage of the dye molecules at the surface of the adsorbent. For the purpose of assessment scientific and practical significance of our work, we compared the obtained by us data on adsorption of BG5 dye with a GBW with some

literature data on sorption BG5 dye by other adsorbents on the basis of an agricultural wastage (Table 4). From Table 4, the adsorption parameters on removal of BG5 dye from water solution by GBW is comparable with data on adsorption of BG5 dye from water solution, using other agricultural adsorbents.

**Table 4.** Comparison of BG5 dye uptake data with other adsorbents on the basis of an agricultural wastage

Sorbent	Dye	$q_{max}$ ( $mg\ g^{-1}$ )	pH	T, ( $^{\circ}C$ )	$C_0$ ( $mg\ L^{-1}$ )	Model	Source
Glucose biocar	BG5	144	6	30	250	Langmuir,	Tran <i>et al.</i> , 2017 a
Golden shower pod	BG5	45.5	7	30	300	Langmuir,	Tran <i>et al.</i> , 2017b
Coconut shell	BG5	41.5	7	30	300	Langmuir,	Tran <i>et al.</i> , 2017b
Orange peel	BG5	35.2	7	30	300	Langmuir,	Tran <i>et al.</i> , 2017b
Cotton stalks	BG5	42.37	7	30	50	Langmuir, K2	Akperov & Akperov, 2019
<b>Grapebushes waste</b>	<b>BG5</b>	<b>43.86</b>	<b>7</b>	<b>20</b>	<b>50</b>	<b>Langmuir, K2</b>	<b>in this study</b>

### 3.5. 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-liked 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 (Chowdhury & Saha, 2010a; Akolo & Kovo 2015). Kinetic studies of the sorption BG5 by GBW were carried out under the optimized conditions from 10 to 100 *min*. The kinetic data obtained were fitted to linear form of Lagergren pseudo-first order and pseudo-second order kinetic models. The pseudo-first order kinetic model known as Eq. (6)

$$\log(q_e - q_t) = \log q_e - 0.434K_1\tau, \quad (6)$$

where  $q_t$  and  $q_e$  are the amounts of dye adsorbed at time  $\tau$  and at equilibrium ( $mg\ g^{-1}$ ), respectively, and  $K_1$  is the rate constant of pseudo-first order adsorption process ( $min^{-1}$ ). The pseudo-second order kinetic model is expressed by the Eq. (7)

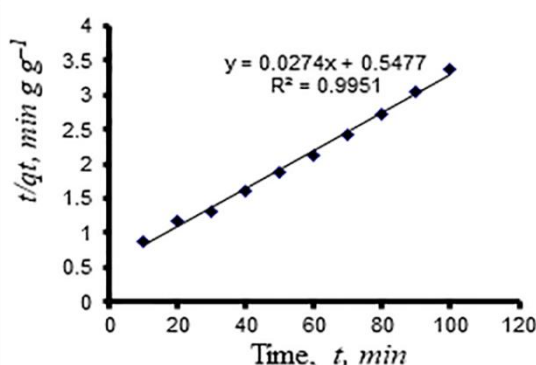
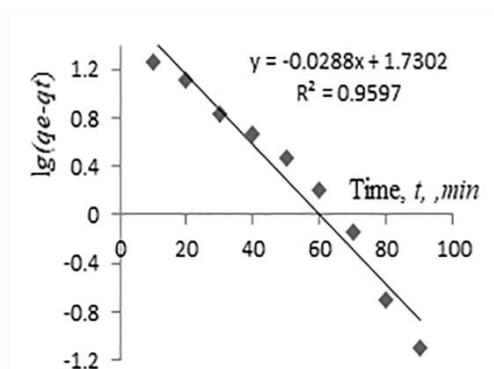
$$\tau/q_t = 1/(K_2q_e^2) + \tau/q_e, \quad (7)$$

where  $q_t$  and  $q_e$  are the amounts of BG5 sorbed at time  $\tau$  and at equilibrium ( $mg\ g^{-1}$ ), respectively,  $K_2$  is the pseudo-second order equilibrium rate constant ( $Lmg^{-1}\ min^{-1}$ ). Schedules of the equations of the pseudo-first and pseudo-second model are illustrated in Fig.5 and Fig.6, respectively and the obtained values of kinetic parameters are placed in Table 5.

**Table 5.** Regression parameters for the kinetics models (BG 5 initial concentration  $50\ mg\ L^{-1}$ ,  $V=0.04\ L$ , sorbent dosage  $1.25\ g\ L^{-1}$ ,  $20^{\circ}C$ )

Kinetic model	$q_e, mg\ g^{-1}$	$k_1, min^{-1}$	$k_2, L\ mg^{-1}min^{-1}$	$R^2$
Pseudo-first order	53.72	0.0664	-	0.9597
Pseudo-second order	36.5	-	0.0014	0.9951
$q_{ekp}$	31.76	-	-	-





**Figure 5.** Plots of pseudo–first order model      **Figure 6.** Plots of pseudo–second order model

Comparison of the obtained data shows that the sorption process of the BG5 from aqueous solutions with GBW is better described by the pseudo–second kinetic model with determination coefficient 0.9978. Calculated value sorption capacity from the equation's pseudo–second model is equal to be  $36.5 \text{ mg g}^{-1}$ , which closer to the value obtained from the adsorption isotherm ( $31.76 \text{ mg g}^{-1}$ ).

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

$$\Delta G^\circ = -RT \ln K_d = -2,303 RT \log K_d, \quad (8)$$

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

$$K_d = q_e / C_e,$$

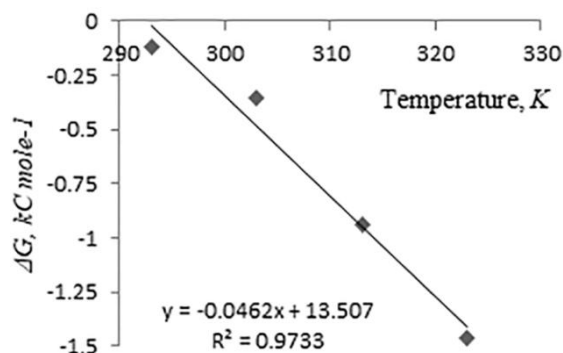
in which  $q_e$ - is the equilibrium adsorbate concentration on the sorbent ( $\text{mg L}^{-1}$ ) and  $C_e$  - is the equilibrium adsorbate concentration in solution ( $\text{mg L}^{-1}$ ). It is also known that  $\Delta G^\circ$  is a function of change in enthalpy ( $\Delta H^\circ$ ,  $\text{kJ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

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ. \quad (9)$$

The values of  $\Delta G^\circ$  were estimated to be  $-0.119$ ,  $-0.354$ ,  $-0.941$  and  $-1.463 \text{ kJ mole}^{-1}$  at 293, 303, 313 and 323K, respectively. The negative value of  $\Delta G^\circ$  at different temperatures indicates spontaneous nature of the sorption process. Furthermore, decrease in the negative value of  $\Delta G^\circ$  with increasing temperature suggests that the sorption process was more favorable at higher temperatures.  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the intercept and slope of the plot of  $\Delta G^\circ$  versus  $T$  (Fig.7) and are placed in Table 6.

**Table 6.** Sorption thermodynamic parameters

Temp., K	$\Delta G^\circ$ , $\text{kJ mole}^{-1}$	$\Delta H^\circ$ , $\text{kJ mole}^{-1}$	$\Delta S^\circ$ , $\text{kJ mole}^{-1} \text{ K}^{-1}$
293	-0.119	13.507	0.0462
303	-0.354		
313	-0.941		
323	-1.463		

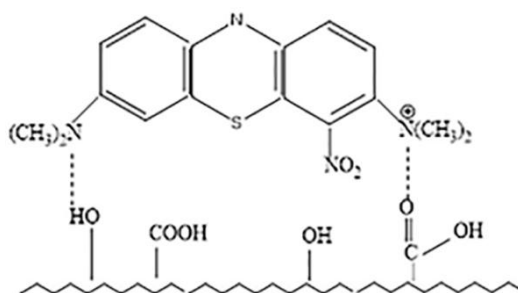


**Figure 7.** Plot of  $\Delta G^\circ$  versus  $T$

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated as  $13.507 \text{ kJ mole}^{-1}$  and  $0.0462 \text{ kJ mole}^{-1}\text{K}^{-1}$ , respectively. The positive value of  $\Delta H^\circ$  is indicative of the fact that the sorption process was endothermic in nature. The positive value of  $\Delta S^\circ$  shows the increasing randomness during adsorption process.

### 3.6. Mechanism of the adsorption

There were many factors that may influence the sorption behavior BG5 onto GBW, such as dye structure, sorbent surface properties, steric effect and hydrogen bonding, van der Waals forces, etc. The mechanism of adsorption and biosorption process of the cationic dyes on agricultural waste biomass includes chemisorption, a complex formation, an ionic exchange and physisorption on the surfaces and pores of the adsorbent. The chemical composition of macromolecular components of GBW have been evaluated and these are composed mainly of cellulose (30.3%), hemicelluloses (21.0%), lignin (17.4%), tannins (15.9%) and proteins (6.1%) (Prozil *et al.*, 2012). The mechanism of adsorption and biosorption process of the cationic dyes on agricultural waste biomass includes chemisorption, a complex formation, an ionic exchange and physisorption on the surfaces and pores of the adsorbent. The complexation between BG5 dye and various functional groups, such as hydroxyl, carboxyl, ether, ester groups of the GBW 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 surface GBW and the nitrogen-containing amine groups of BG5, (2) electrostatic interaction between the cationic dye (due to the presence of  $\text{N}^+$   $(\text{CH}_3)_2$  group) and hydroxyl group in surface of the GBW. Considering the above-named types of interaction between BG5 and GBW, it is possible to offer the adsorption mechanism BG5 on a surface of the GBW connected with forming of the complex illustrated in Fig. 8.



**Figure 8.** The possible sorption mechanism of the BG5 on the GBW surface

#### 4. Conclusions

In this study, the efficacy of grape bushes waste, collected from grape 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 concentration Basic Green 5 dye fitted well in the Langmuir isotherm model indicating monolayer sorption on a homogeneous surface. The maximum monolayer sorption capacity was found to be  $43.86 \text{ mg g}^{-1}$  at  $20^{\circ}\text{C}$ . Kinetic studies show that the Basic Green 5 dye removal followed pseudo-second-order rate equation. The negative value of  $\Delta G^{\circ}$  and positive value of  $\Delta H^{\circ}$  suggest that the sorption process was spontaneous and endothermic in nature. The positive value of  $\Delta S^{\circ}$  shows the increasing randomness during adsorption process. Finally, it can be concluded that grape bushes waste, a common and easily available agrowaste material can be used as a sorbent for the removal of Basic Green 5 dye from aqueous solutions.

#### Acknowledgements

The authors gratefully acknowledge Dr. Elvin Y. Malikov for the help for editing the English text. The authors declare that they have no conflict of interests.

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