Sys Rev Pharm 2020;11(4):725-730
A multifaceted review journal in the field of pharmacy

Removal of Brilliant Dyes from its Aqueous Solution by Adsorption on Siliceous Rocks

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ABSTRACT
In this study involves removing of Brilliant Dyes, were which (Brilliant Green {BG} and Brilliant Cresyl Blue {BCB}) by using Iraqi Siliceous Rocks Powder (SRP). Adsorption isotherms were studied and the factors which prefer it, like temperature and salt effect, Adsorption isotherms of dyes, Brilliant Cresyl Blue {BCB} was found to be comparable to Langmuir equation according to Giles classification, isotherms dye Brilliant Green {BG} was found to be comparable to Freundlich equation more than dye Brilliant Blue {BCB} according to Giles classification. The adsorption process on this surface (SRP) studied at different temperatures, the results showed that the adsorption of dyes (BCB, BG) on the surface increased with increased temperature (Endothermic process). According to valuable to the above results of the thermodynamic functions (ΔG, ΔS, ΔH) were calculated. The salt effect on the adsorption of dyes at (20C°) it was found that the adsorption increased by the presence of salt. The kinetics of the adsorption was studied, the results were treated according to (Lagergren equation) and treated according to the second-order equation model. The kinetics experimental data showed that the adsorption was pseudo order and changes according to the changing conditions.

Keywords: Siliceous Rock, Adsorption, Brilliant Green, Brilliant Cresyl Blue

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INTRODUCTION
Dyes are among the organic materials that pollute the water, and the reason for this is due to their great use in various industries, for example in the oil industries, in the textile industry, in dyeing, in the coloring of photography and various fields [1]. Dye {BG} it is used in the coloring of silk and wool, and in most countries of the Soviet Union an alcohol solution is sold Dilute as a local antiseptic [2]. Where it is effective against bacteria, it irritates the membranes Mucosa when accidental contact [3]. many kinds of research have been conducted on how to remove these dyes from water in several ways [4-11]. Adsorption on the surface was one-way other processes were used ،such as (silica [12], Zeolite [13]).

Materials
Siliceous Rocks
Siliceous rocks are obtained by the Geological Survey General Authority. The central laboratories were equipped from the western Iraqi desert from the Akashat region. Analyzing the chemical composition of Siliceous rocks using the X-RAY technique, the results showed a high level of silicon oxide (SiO_2) [14].

Fig.1: Siliceous Rocks powder (SRP)

Table (1) shows the proportions of the elements involved in the construction of Siliceous rocks.

Table 1. Rocks Analyses

Compound	*Wt%*
SiO2	*66.01*
Al2O3	*2.12*
Fe2O3	*0.62*
TiO2	*0.05*
P2O5	*0.93*
CaO	*8.44*
MgO	*6.47*
Na2O	*0.62*
K2O	*0.13*
Loss on Ignition	*14.11*
Total	***99.5***

Dyes
(BG) was supplied by (BDH), (BCB) and NaCl supplied by (Fluka), and deionized water had been used. Figuer.2 shows the structures of (BG and BCB).

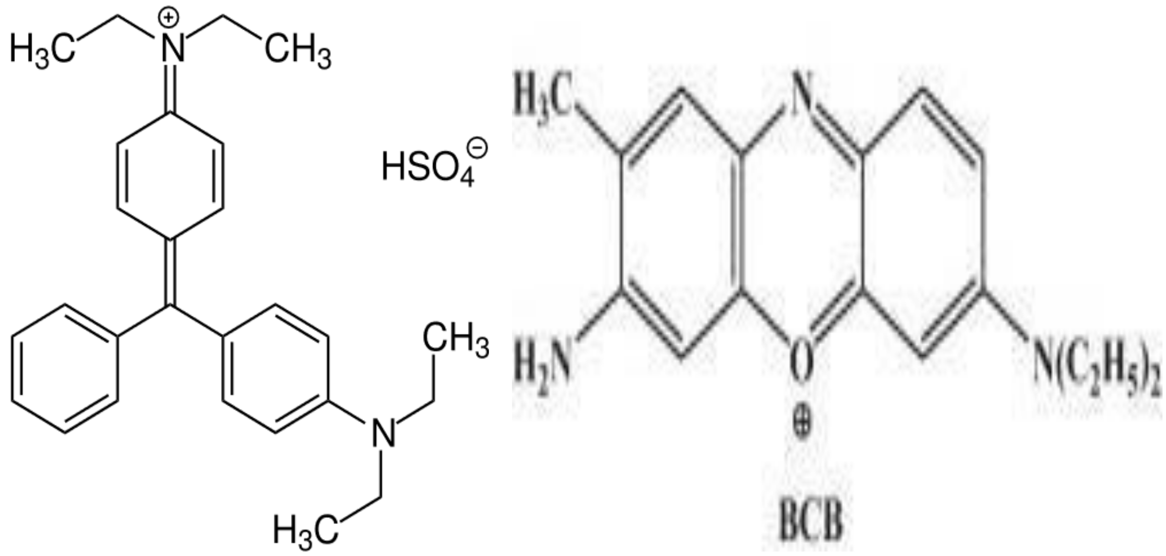

Fig 2. Structures of BG [15] and BCB [16]

Method

1- Technique: UV-Vis. spectroscopy determines the absorption as a function for concentration. the wavelengths of absorption were (625 nm) for Brilliant Green and (622 nm) for Brilliant Cresyl Blue.

2- Contact time: to determine the required time for equilibrium between adsorbent and adsorbate, some certain concentrations were mixed with (0.02gm) of Siliceous Rocks powder and they were put into water bath shaker under 20Co, samples were taken from the solution in different sequenced times to determine the change in the concentration with time passing.

3- Adsorption isotherms: to determine the adsorption isotherms for dyes solutions, (0.02gm) of the surface six round flask was weighed and then added to each (50ml) flask of dyes (BG, BCB) with a certain concentration. These flasks were placed in a water bath at (20 C°) for (BG=50 min, BCB=90min). After the separation of the mixture, adsorption was absorbed by (UV/Vis). The adsorption amount was calculated according to the following equation [17]:

$$Qe = \frac{Vsol(Co-Ce)}{m}$$

Qe= the quantity of adsorbate (mg/g). V= volume of solution (L).

C0= initial concentration (mg/L).

Ce= equilibrium concentration (mg/L). m= mass of the surfaces (g).

Results & Discussion

Effect of Contact Time

For increasing the adsorption as function of time, the results show the contact time for (BG) dye at (50 min) and (BCB) dye at (90 min).

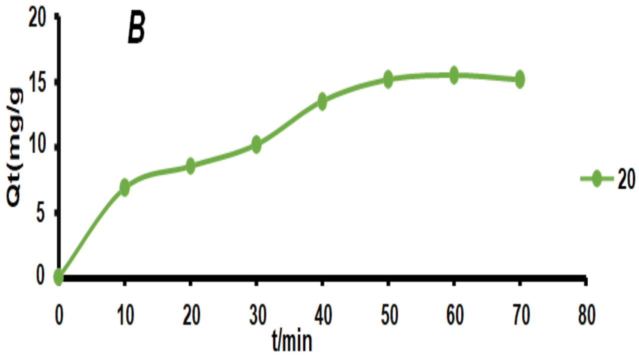

Fig.3: Effect of contact time on BG adsorption on SRP (temperature=20C°, concentration=16 ppm, rotations per minute=90 rpm, equilibrium time=50 min

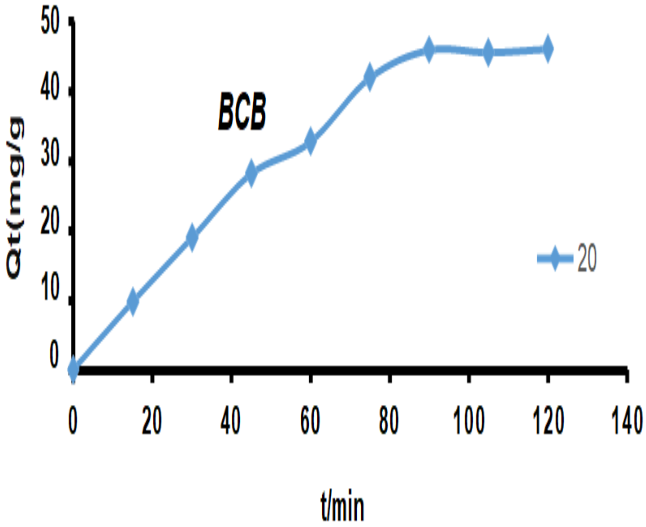

Fig.4. Effect of contact time on BCB adsorption on SRP (temperature=20C°, concentration=35 ppm, rotations per minute=90 rpm, equilibrium time=90 min

Adsorption Isotherms

The adsorbed quantities (Qe) were calculated for each equilibrium concentration. The adsorption isotherm is shown in Figure (5):

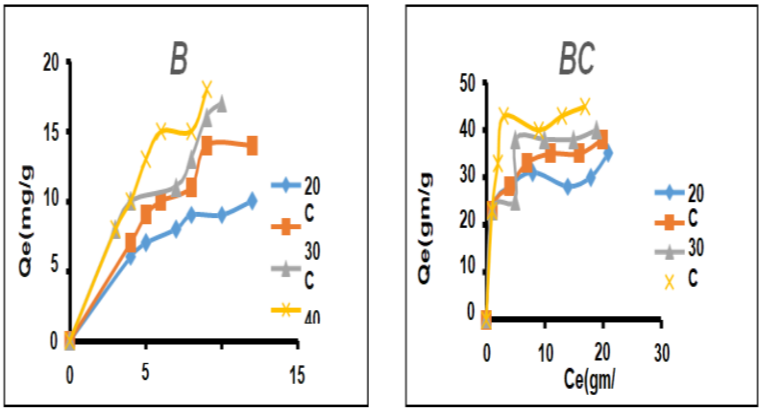

Fig. 5. (a, b) Adsorption isotherms models of (Brilliant Green and Brilliant Cresyl Blue) on Siliceous Rocks powder at different temperature.

The general scheme of adsorption isotherm of (BG) on SRP surface pointing out that was of (S2) class according to Giles classification where the orientation of the adsorbate particles on the surface is bevel vertical [18]. While adsorption isotherm of (BCB) on SRP surface pointing out that was of (L2) class according to Giles classification as the orientation of the adsorbed particles on the bound surface has a horizontal shape [18].

Depend Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{q_m K_e} + \frac{C_e}{q_m}$$

Ce/Qe Vs Ce was plotted as shown in figure (6). Langmuir constant were calculating for BG, BCB dyes as shown in Table (2).

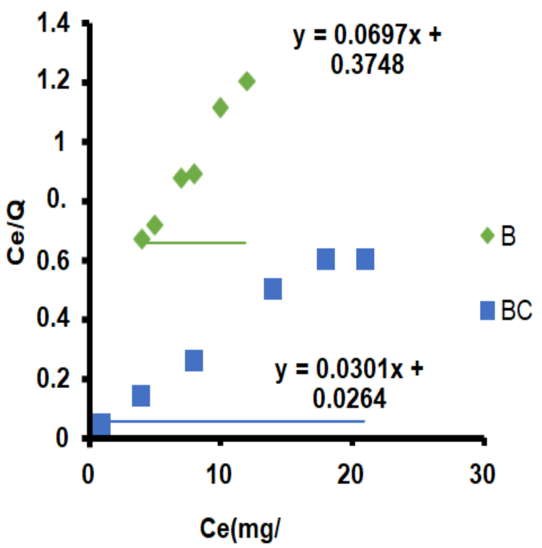

Fig. 6. Linear application of Langmuir equation

Table 2. The value of Langmuir constant (K_L, a) for adsorption of (BG, BCB) dyes on SPR

20C°			
Dyes	***KL(L/mg)***	***a(mg/g)***	***R^2***
BG	***0.1859***	***14.3472***	***0.982***
BCB	***1.1402***	***33.2225***	***0.9746***

--Depend Freundlich equation.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e,$$

where K_F, n= Freundlich constant

LnQe Vs LnCe was plotted as shown in figure (7); Freundlich constant were calculate for (BG, BCB) dyes as shown in Table (3).

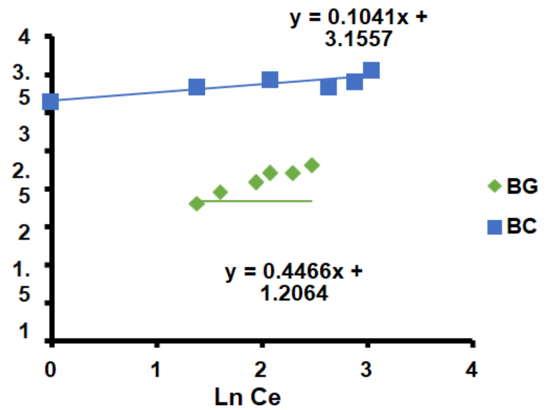

Fig. 7. Linear application of Freundlich equation

Table 3: The value of Freundlich constant (k_F, n) for adsorption (BG, BCB) dyes on SPR

20 °C			
Dyes	*KF*	*n*	*R^2*
BG	*3.3414*	*2.2391*	*0.9604*
BCB	*23.4694*	*9.6061*	*0.7454*

The adsorption process on this surface was studies at different temperatures, the results showed that the adsorption of all dyes Brilliant (BG, BCB) on surface increased with increased temperature (Endothermic process).

The value of (ΔH) calculated by using Vant Hoff- Arrhenius equation "LnXm Vs Inverted temperature (1/T) was plotted as show in (figure 8) and (Table 4)

Table 4. The value of LnXm, T for (BG, BCB) dyes on SPR

T(K)	BG		BCB	
	Xm (mg/g) When Ce = 8 (mg/L)	LnXm	Xm (mg/g) When Ce= 12 (mg/L)	LnXm
293	9	2.197	27	3.295
303	11	2.397	34	3.526
313	13	2.564	37.5	3.624
323	15	2.708	41	3.713

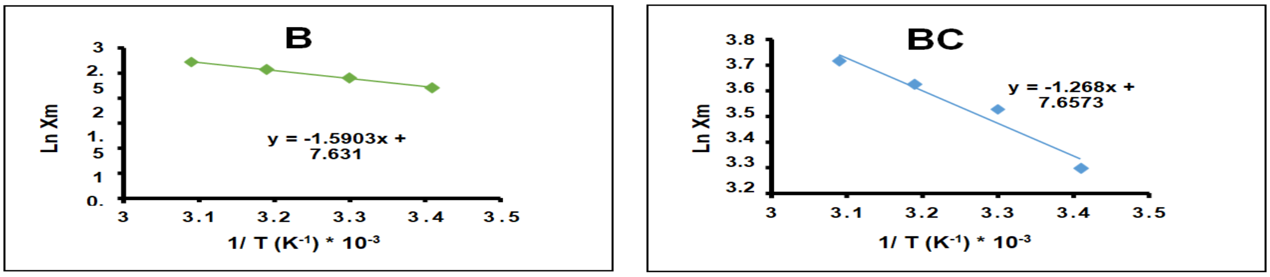

Fig. 8. (a, b) Vant Hoff curves for adsorption of (BG, CBC) dyes on the surface

The value of (ΔG, ΔS) were calculated as shown in Table (5), depending on following equations:

$$\Delta G^{\circ} = RT \ \ln \ K_c,$$

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

Table 5. The values of the thermodynamic functions of the dyes at (20 C°)

Dyes	ΔH(J/mole)	ΔG(J/mole)	ΔS(J/mole.K)
BG	13.2217	-286.91	1.0243
BCB	10.542	-1975.42	6.7780

The positive values of (ΔH, ΔS) while (ΔG) were negative for (BG, BCB) dyes it indicates the spontaneous of adsorption and that the dyes molecules rearrange themselves on surface differently within the solution [19].

Effect of Salt

The Adsorption Process was studied at different concentration of NaCl sait as shown in Figure (9).

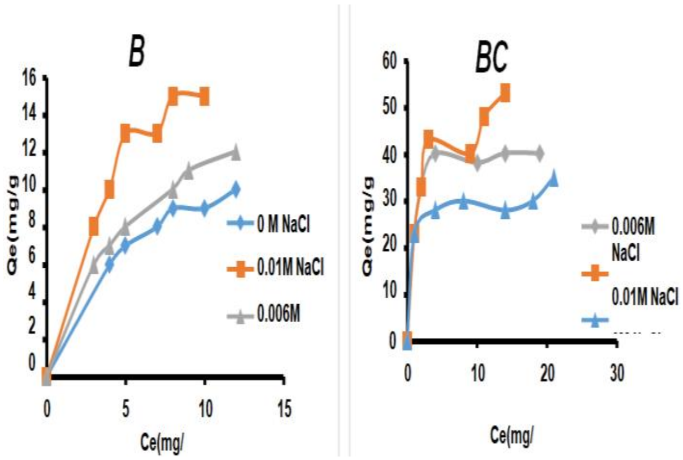

Fig. 9. Effect of salt on adsorption at (20 C°) of (BG, BCB) dyes on SRP

The salt effect on adsorption of two dyes at (20C°) it was found the adsorption increased by the presence of salt. Adsorption of dyes on the surface can be explained according to Imbibition process As the impregnation process swells the surface powder to remove permeable pressure The saline solution has thus changed the geometry of the pores of the surface powder, meaning that the increase or The decrease in the adsorption process is affected according to any change in the surface shape [20]

Adsorption Kinetic

1. Largergreen equation used to studie Kinetic by dyes (BG, BCB)

$$\ln (q_e - q_t) = \ln q_e - k_{ad}$$

where qe and qt are the adsorption capacity at equilibrium and at time (t) respectively (mg/L). Ked: the rate constant of pseudo firs- order kinetic adsorption (min^{-1}).[21]

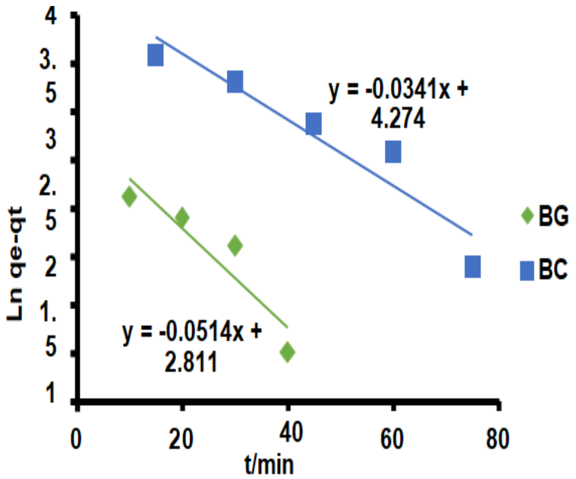

Fig.10. The adsorption pseudo firs- order kinetic of the (BG, BCB) dyes on the surface

Table.6. value the rate constant adsorption for dyes on the SRP

Dyes	*Kad (min^{-1})*
***Brilliant* Green**	***0.0514***
Brilliant Cresyl Blue	***0.0341***

2. The second-order equation model

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t,$$

ked: the rate constant of pseudo second - order kinetic adsorption $(mg/L)^{-1}$. min^{-1} [22]

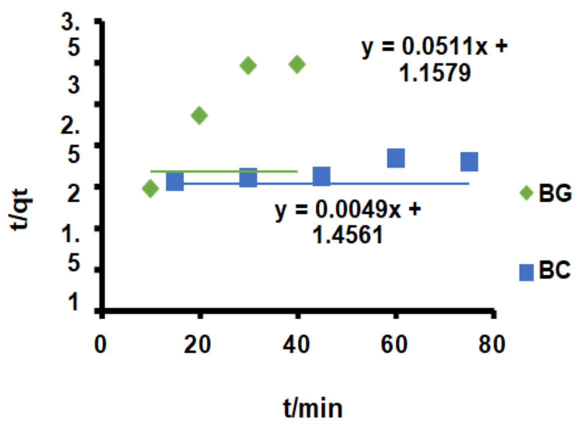

Fig.11. The adsorption pseudo second - order kinetic of the (BG, BCB) dyes on the surface

Table.7. value the rate adsorption for dyes on the SRP

Dyes	*Kad $(mg/L)^{-1}$. min^{-1}*
Brilliant Green	***0.0022***
Brilliant Cresyl Blue	***0.000016***

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