

**FULL PAPER**

# Removal of some brilliant dyes by poly acrylic acid hydrogel beads

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The current work discusses the removal of brilliant dyes. These dyes were Brilliant Cresyl Blue (BCB) and Brilliant Green (BG) by the use of poly acrylic acid hydrogel beads (PAA). We examined the adsorption isotherms and found that the factors preferring it are temperature and salt, shaking effects, wet PAA, (BCB) and (BG) follows Freundlich equation more than other equations. Based on the results, there is a positive correlation between adsorption of dyes (BCB and BG) and temperature (Endothermic process). We calculated the thermodynamic functions ( $\Delta G$ ,  $\Delta S$ , and  $\Delta H$ ). The ion strength effects on the adsorptions at (20 °C) increased adsorption if the salt concentrations is high. We treated the kinetics outcomes based on Lagergren Equation for the first-order and the second-order equations. The kinetics experimental data show that the adsorptions were the pseudo first-order change based on the changing conditions.

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**KEYWORDS**

Brilliant Cresyl Blue; brilliant green; poly acrylic acid hydrogel beads; adsorption.

**Introduction**

Organic dyes used in many various industries such as oil industries, coloring of photography, dyeing, textile industry, and different fields, all of which lead to pollute water [1]. Dyes are very visible even if the concentrations are lower than 0.005 mg/l. dyes like Brilliant Cresyl Blue (BCB) and brilliant green (BG) have highly color intensity, brilliance, and highly visible [2]. A BCB dye is utilized for smearing the reticulum in small erythrocytes (reticulocytes). This kind of cells has commonly used for studies of various biological systems [3]. BG dye is utilized for different aims such as biological stains, dermatological factors, and an addition to chicken feeds for preventing the formation of parasites and fungi [4,5]. Likewise, it is commonly used in textile dyeing and printing of paper [6,7]. There were many

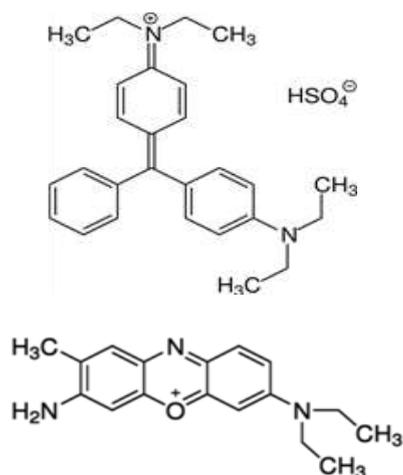
treatments including adsorption [8], precipitation, and coagulation [9]. The ion exchanges [10] co-precipitations/adsorptions [11], etc. established for removing pollutants from an aqueous solution. The adsorption approach is the commonly utilized cause of its flexibility in operations and designs plus the easy desorption of the adsorbent [12]. Adsorption is a little promising alternative to that aim, particularly utilization of cost-effective sorbents. A super absorption of three dimensional polymers was utilized to function like absorbents to the dyes from the water and others aqueous solution, such as polyacrylamide polyacrylic acids and their derivatives with functional groups (like an amide, carboxylic, and hydroxyl) as an absorbent to remove dyes by the interaction between the these groups and dyes [13] Polyacrylic acid (PAA) formed hydrogel networks can absorb more than five to ten

hundreds times of their weight in the water, so they are considered as the basis of a materials class named super absorbents. Super absorbent polymers are compounds with the ability of absorbing water and swelling to several times their original weight and size. The super absorption polymers are used widely in the personal hygiene products [14]. In this search, the possibility of using PAA hydrogel beads to remove BCB and BG from an aqueous solution was examined through conducting batch adsorption studies.

## Experimental

### Materials

We used (BCB), (BG), and NaCl provided by (Fluka) and deionized water. Figure 1 displays the dyes structure.



**FIGURE 1** (a,b) Structures of BCB and BG

Commercial poly acrylic acid hydrogel beads were used to remove brilliant Cresyl blue. Figure 2 depicts pol acrylic acid before and after swelling in water.



**FIGURE 2** Form and size of gel bead before (A) and after (B) swelling

## Methods

1- The UV-Vis spectroscopy techniques were used to find the absorption for the concentrations. The wavelengths of absorption were (621) nm for brilliant Cresyl blue and (625) nm for brilliant green.

2- The contact time is examined to find the required time for the equilibrium between the adsorbent and the adsorbate, several certain concentrations are mixed with (0.025 gm) of PAA in shaking water bath at 20 °C. The solution samples were in various sequences and times to obtain various concentrations with time by passing.

3- Adsorption isotherms are used to obtain the removal isotherms of the dyes solutions, (0.025 gm) of the surface six round flasks weighed put to each (50 mL) flask of dyes (BCB) and (BG) with some concentrations. We put these flasks in a water bath at (20 °C). The adsorption quantities were calculated by following equation [15]:

$$Q_e = \frac{(C_o - C_e)V}{m}$$

$Q_e$ = The quantity of adsorbate (mg/g).

$V$ = Solution volume (L).

$C_o$  = The initial concentrations (mg/L).

$C_e$ = The equilibrium concentrations (mg/L).

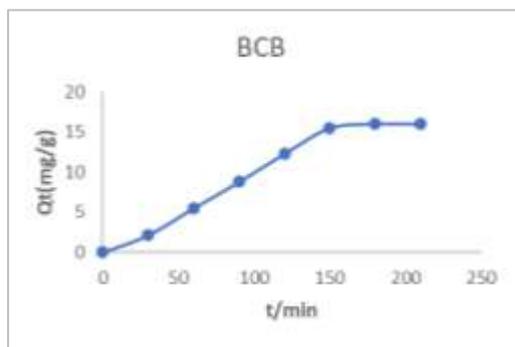
$m$ = The mass of the surfaces (g).

The previous step was repeated at various temperatures for following up the dyes adsorption on the surface at different temperatures.

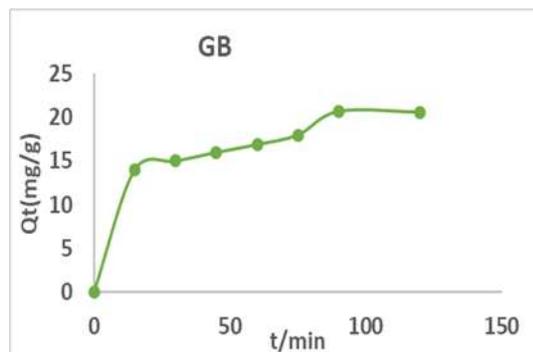
## Results and discussion

### Effect of contact time

As a function of time the increase of removal, the result shows the contact time to BCB and GB dyes at (180 min) and (90 min), respectively as displayed in Figures 3 and 4.



**FIGURE 3** Contact time impact on BCB (temperature 20 °C, concentrations 30 ppm, rotations per minute=85 rpm, equilibrium time=180 min)



**FIGURE 4** Contact time impact on GB (temperature=20 °C, concentration=10 ppm, rotations per minute=190 rpm, equilibrium time=90 min)

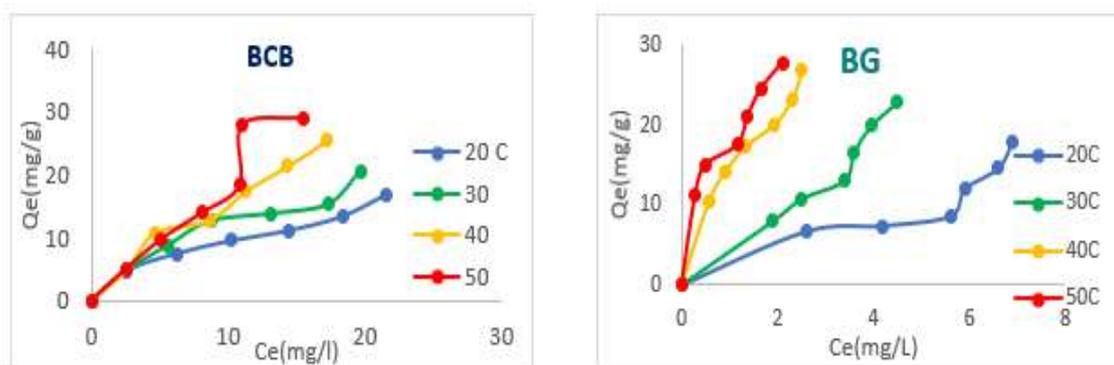
### Adsorption isotherms

The adsorbed quantity ( $Q_e$ ) was calculated for equilibrium Concentration.  $Q_e$  vs.  $C_e$  was plotted to show the general scheme of adsorption isotherm, as indicated in the following figures.

The general scheme of the adsorption isotherm of BCB and BG on PPA pointing out that was (S3) class in accordance with Giles

classification, where the orientation of the adsorbate particles on the surface is vertical.

The linear plotting shape of the adsorption equations (Langmuir, Freundlich, and Temkin) demonstrated that the results were more applicable to Temkin and Freundlich equations, as illustrated in Figures 6, 7, and 8.



**FIGURE 5** (a,b) Adsorption isotherms models of BCB and BG dyes on PPA at different temperatures

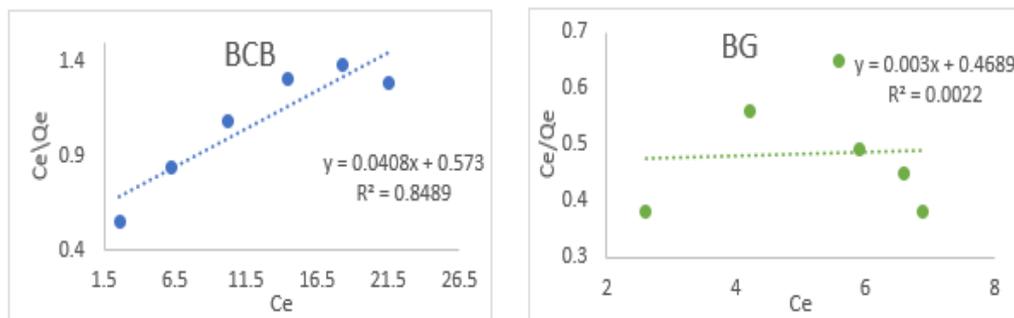


FIGURE 6 (a,b) The application of linear Langmuir equation

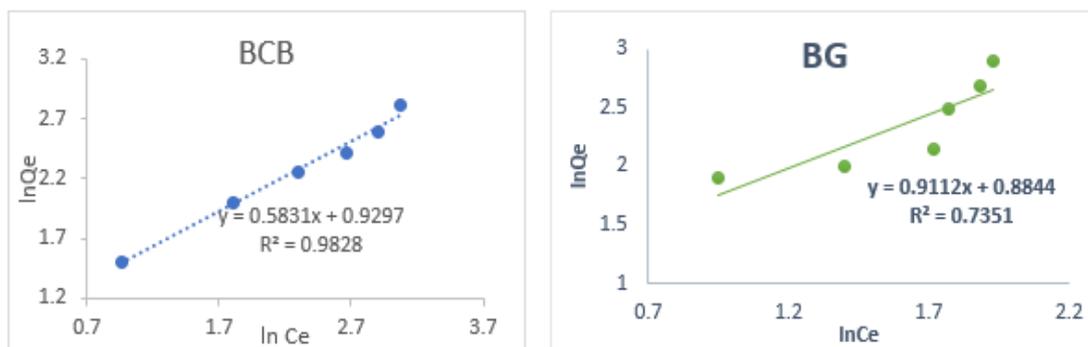


FIGURE 7 (a,b) The application of linear Freundlich equation



FIGURE 8 (a,b) The application of linear Temkin equation

**Thermodynamic studies for removal**

The adsorption quantity increased when temperature increased (Endothermic process). The ( $\Delta H$ ) is measured by Vant Hoff-Arrhenius equations.

$$\ln Q_{max} = \frac{-\Delta H}{RT} + \text{Constant} \dots \dots 1$$

Where,  $Q_{max}$  = Maximum adsorbed quantity.  
 R = Gas constant.  
 T = Temperature.

$\ln Q_{max}$  vs. inverted temperature ( $1/T$ ) was plotted, as displayed in Figure 9.

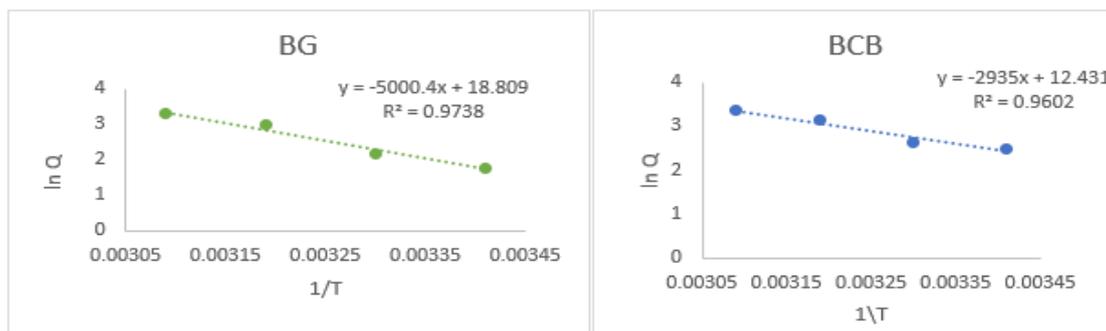


FIGURE 9 (a,b) Vant Hoff curves for BCB and BG dye adsorption on the PAA

Table 1 represents the measured ( $\Delta H$ ,  $\Delta G$ , and  $\Delta S$ ), according to:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \dots\dots\dots 3$$

$$\Delta G = -nRT \ln \frac{Q_e}{C_e} \dots\dots\dots 2$$

TABLE 1 The dye thermodynamics at different temperatures

Dyes	$\Delta H(\text{KJ/mole})$	$\Delta G(\text{J/mole})$	$\Delta S(\text{J/mole.K})$
BCB	+24.401	293	+543
		303	+173
		313	-1112
		323	-1770
		293	-2676
BG	41.573+	303	-3788
		313	-6239
		323	-7086

The positive and negative values are for ( $\Delta H$ ) ( $\Delta G$  and  $\Delta S$ ), respectively, meaning that the process is endothermic, spontaneous at most temperatures, and that the adsorbent molecules arranged on the surface [16], and that there is an association of adsorption and absorption [17].

The adsorption was studied in (0.006 M, 0.01M) sodium chloride solution. To test the proposed removal efficiency, the samples of tap water were used to prepare BCB, BG, and remove them with the same surface and conditions, revealing the effectiveness of this method for all samples, as demonstrated in Figure 10.

The ion strength effect

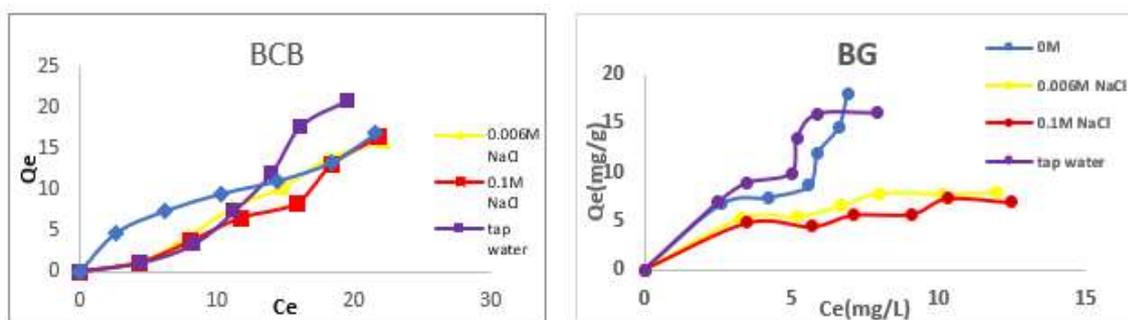
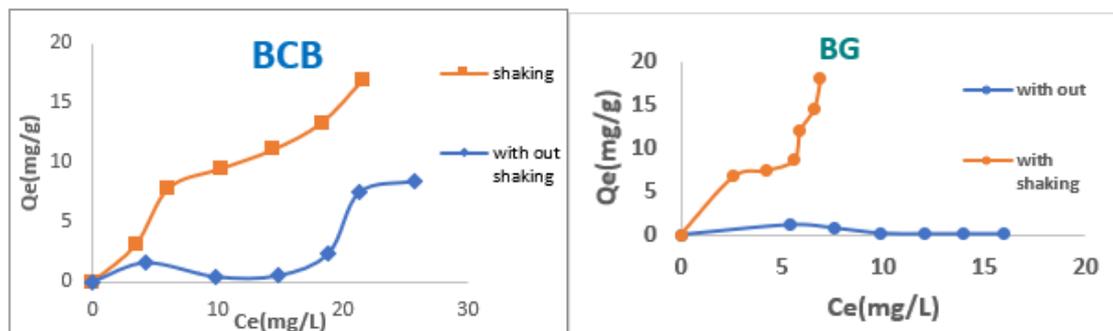


FIGURE 10 (a,b) Removal of prepared dyes with tap water and salt at T=293 K

*Shaking effect*

The shaking rate is the main factor influencing the adsorption process of dyes

because it is related to the diffusion mobility of dyes molecules to the adsorbents PAA surface [18]. The shaking Effect was studied, as shown in Figure 11.



**FIGURE 11** (a,b) Shaking effect on adsorption at T= 293K

*Effect of using wet PAA*

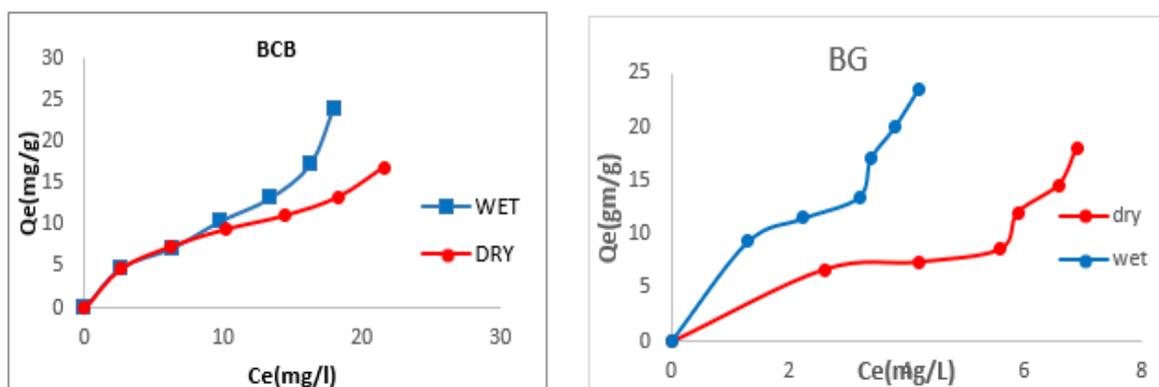
The percentage of dyes removal increases when using wet PAA instead of dry, as depicted in Figure 12.

*Effect of initial dyes concentration*

Removal percentage was estimated by varying dyes concentration. A 50 mL solution of BCB, BG was used at T=293K. The solutions were left to equilibrium time and the residual BCB, BG concentration was determined. The results in (Table 2, Figures

4 and 5) are revealed the removal percentage of dyes higher at low concentration unlike a high concentration. At a low concentration, the maximum capacity of PAA does not reach because its ability to absorb big quantity of dyes and the residual concentration is low. However, PAA at a high concentration reaches the maximum capacity, so the residual concentration is high. The removal percent is studied as follow:

$$\% \text{ removal} = \frac{\text{initial conc.} - \text{residual conc.}}{\text{initial conc.}} \times 100\% \dots\dots 4$$



**FIGURE 12** (a,b) Effect of using wet PAA and dry at T=293K

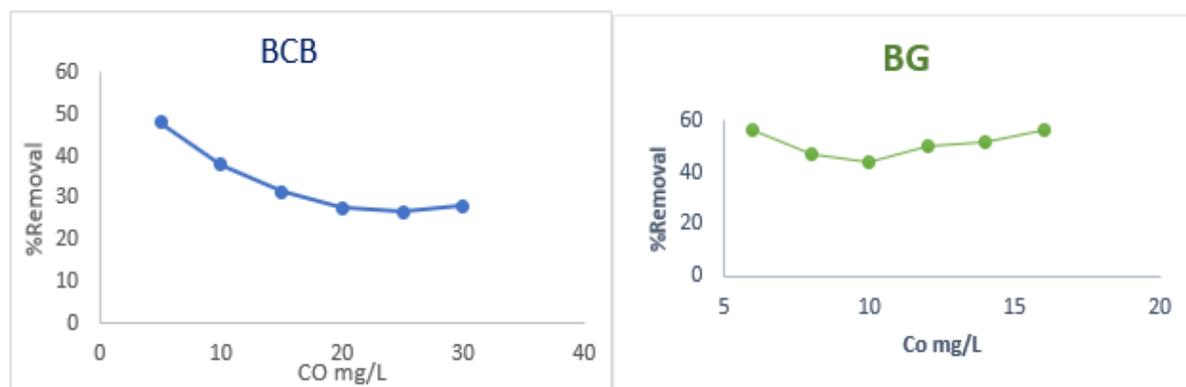


FIGURE 13 (a,b) The removal percentage at T=293K

### Adsorption kinetic

The kinetics of the removal process were studied on BCB and BG according to:

1-Largergreen Equation

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

Where,  $q_e$  and  $q_t$  are the equilibrium adsorption capacities at times ( $t$ ), respectively (mg/L).  $k_{ad}$  is the ratio constants of the pseudo first-order kinetic adsorptions ( $\text{min}^{-1}$ ) [19].

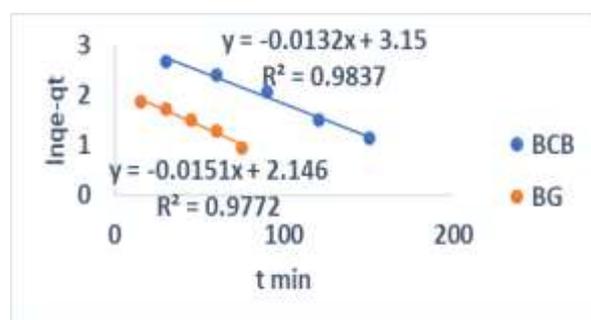


FIGURE 14 The adsorption of the pseudo first-order kinetic of the (BCB and BG) dyes on PAA

TABLE 2 Value adsorption of the ratio constants for dyes on PAA

Dyes	$K_{ad}(\text{min}^{-1})$
BCB	0.0132
BG	0.0152

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

### The second-order equation

$k_{ed}$  is the ratio constant of the pseudo second-order kinetic adsorption ( $\text{mg/L})^{-1} \cdot \text{min}^{-1}$  [20].

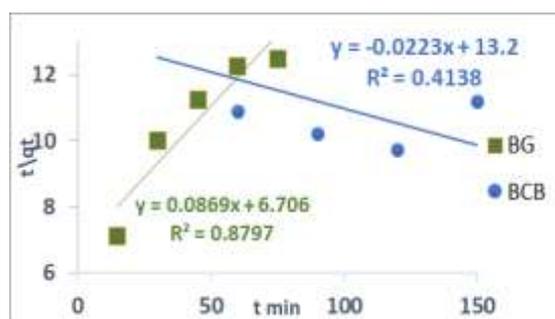
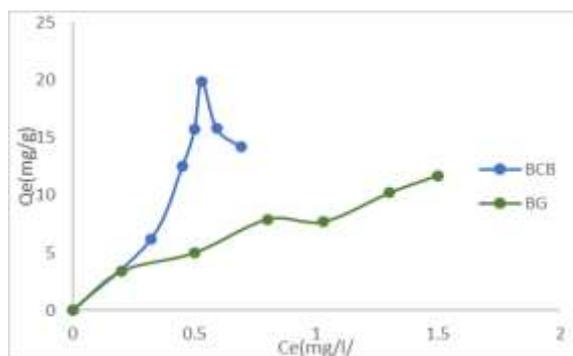


FIGURE 15 The adsorption of the pseudo second-order kinetics of the (BCB and BG) dyes on the PAA

The result showed that the removed of BCB, BG dyes by PAA obeys the first order reaction.

### Isotherm of desorption

For practical application, the dyes adsorbed by PAA need to be desorbed with ease and is reusable again following the regeneration reparation. Furthermore, we examined the PAA polymer desorption by the batch experimental techniques. Also, we obtained the value of the desorbed dyes. The results show the recovery% and the capacity rose with the rise of the dyes concentrations, as demonstrated in Figure 16.



**FIGURE 16** The desorption of (BCB and BG) from PAA at T= 343K from PAA at T= 343K

## Conclusion

polyacrylic acid hydrogel beads (PAA used in this study to remove some Brilliant dyes, the adsorption isotherms and the factors affecting the adsorption process (concentration, temperature, ionic strength and shaking rate) were studied. The results obtained were as follows:

The removal process was studied at different temperatures (293K,303K,313K,323K), and the results showed that the removal of dyes (BG, BCB) on the surface increases with increasing temperature. (BG), (BCB) are obeyed with the Freundlich isotherm. The effect of ionic strength was studied using sodium chloride salt and it was found that the removal process decreases in the presence of salt. When preparing dyes with normal Tap water, the removal process will be more efficient than if prepared with distilled water. The effect of wet beads was studied and the results showed that using a wet surface leads to an increase in the adsorption process of dyes. The effect of shaking was studied and the results indicated an increase in the adsorption process when shaking was used. The thermodynamic functions were calculated. The adsorption kinetics of dyes were studied on the surface of polyacrylic acid beads. It was found that the adsorption process is compatible with Lager green equation of first order and incompatible with second order equation. The desorption

process of dyes was studied at a temperature of (343K) and it was found that it was possible to recover part of these dyes.

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## Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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