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THERMODYNAMIC AND KINETIC ANALYSIS OF BASIC GREEN-4 DYE REMOVAL FROM AQUEOUS SOLUTIONS USING ADSORPTION TECHNIQUE

Saja S. Al-Taweel[1*], Khalid Waleed S. Al-Janabi[2] and Hasan M. Luaibi[3]

[1]Chemistry Department, College of Science, University of Al-Qadisiyah, Diwaniyah - 58002, Iraq.
[2]Chemistry Department, College of Education for Pure Sciences, Ibn Al-Haitham, University of Baghdad, Baghdad - 10053, Iraq.
[3]Department of Environmental Sciences, College of Energy and Environmental Sciences, Al-Karkh University of Science, Baghdad - 10081, Iraq.

Abstract

In this work, a local sunflower husk (SFH) was used as a natural surface for removing Basic Green-4 (BG4) dye, as a water-soluble pollutant. The effect of initial concentration, contact time, the mass of surface of the dye with the SFH as well as the medium temperature was studied.

The application of Langmuir, Freundlich isotherms on the collected data of the adsorption process found to harmonize to Freundlich equation more than that of Langmuir. However, the adsorbed mass of BG4 dye showed a direct increase with the increase of SFH mass and equilibrium was achieved within a 60min window.

The interaction of BG4 with SFH surface was spontaneous and exothermic. The empirical kinetic outcomes at ambient temperatures were applied to pseudo 1st and 2nd order equations. However, the process has found to follow the rate of pseudo 2nd order, while the intraparticle diffusion was considered as a step in the mechanism of adsorption.

Key words: Sunflower husk, Green-4 dye, Freundlich, adsorption, Langmuir

Introduction

Wastewater is a major source of water pollution since it contains different kinds of environmental, and industrial pollutants (Al-Janabi *et al.,* 2011; Crini and Lichtfouse, 2019). One of the most common environmental pollutants is dyes which are widely spread and commonly be found in industries discharges (Al-Janabi *et al.,* 2012) like paper rubber, textile, dye, motor oils (Abdul Kareem and Al-Janabi, 2018) and plastic manufacturing industries (Ramaraju, Manoj Kumar Reddy and Subrahmanyam, 2014; Teng, San Wong and Low, 2014). The chemical nature and the type of functional groups of dyes, make them carcinogenic and mutagenic agents for the environment and the aquatic habitat even when they exist in low concentrations (Jain *et al.,* 2007). The origin of synthesis and the complex chemical structure of dyes make the process of dye removal from water resources as a complicated process (Elmoubarki *et al.,* 2015).

Different techniques were used for the treatment and control of chemical pollutants (Al-Janabi, 2016), not limited to; sedimentation, coagulation, ion exchange, oxidation, foam flotation, and adsorption techniques (Franca *et al.,* 2010; Sharma, Saikia and Das, 2014). The adsorption techniques are considered one of the most preferred approaches used in the treatment of water pollution, due to the simplicity of the method, equipment that used, affordability, as well as the availability of adsorption surfaces locally (Kar, Smith and Subramanian, 2009). The widely used surface in wastewater treatment is activated carbon prepared from different natural sources. Other types of cheap and natural adsorption surfaces were also used, like, wheat husk (Sivakumar *et al.,* 2012), palm leaf (Uddin *et al.,* 2009), coconut shells (Ardejani *et al.,* 2008; Tanyildizi, 2011), lemon peel, date waste and coffee waste(Liang *et al.,* 2014).

***Author for correspondence :** E-mail : saja.al-taweel@qu.edu.iq

The aim of this research is to work out the capacity of the SFH sorbent to seizure aqueous pollution such as Basic Green-4 dye (BG4). Thermodynamic and kinetic parameters were studied in addition to the mechanism of the adsorption.

Materials and Methods

UV-Vis. Spectrophotometer, Shimadzu. PC 1650, Japan**.**

Malachite Green (Basic Green-4) (BG4) dye, Henan DaKen Chemical Co. (99%), China (Fig. 1).

Standard solutions of BG4 dye: A set of BG4 dye standard solutions of different concentrations (10–200 ppm) were prepared in distilled water.

Preparation of SFH sorbent bed: SFH powder was washed with distilled water and dried for 2 hr under sunlight then overnight in an oven at 60°C.

Effect of mass

An exact mass of the SFH in the range of (0.05-0.2g) were mixed with a 10ml of BG4 solution (100 ppm), were used and the adsorption experiment was done at 25˚C.

The adsorption isotherm

The isotherms of BG4 adsorption was performed by shaking 0.05g of SFH into 10ml dye in the concentrations of (10–200 ppm). After 60 min of shaking at pH = 5.4, the mixture was centrifuged for 30min at about 3000 rpm and the supernatant analyzed spectrometrically at l_{max} = 617 nm to quantify BG4 dye (Fig. 2).

The amount of BG4 adsorbed was obtained using equation (1) (Bencheikh Lehocine, 1989; M. Dharmendirakumar, G.Vijayakumar *et al.,* 2015):

$$q_e \quad \frac{v\,C_o \quad C_e}{m} \qquad (1)$$

Where; q_e is the adsorbed mass of the dye (mg/g) on a certain mass of the sorbent bed of SHF m (g), V (L) is the volume of BG4 solution, while C_o and C_e (µg/ml) is the startup concentration of BG4 and at equilibrium, respectively.

The adsorption process and the value estimation of the thermodynamic functions were performed at temperatures ranging from 25 to 45˚C.

Kinetic Studies

The contact time of the adsorption process was tested on a thermostatic shaker by mixing 0.05g of SFH into 10 ml BG4 solutions (100 ppm), at 25°C. The residual concentration of dye was determined at different durations, the removal dye percentage was calculated as follows (Blázquez *et al.,* 2010):

$$\%\,\mathrm{Re}\,moval \quad \frac{C_o \quad C_e}{m} \quad 100 \qquad (2)$$

Effect of ionic strength

Different concentrations of sodium chloride (0.05-0.25µg/mg) were used to determine the influence of the ionic-strength on the adsorption of BG4 dye.

Results and Discussion

Effect of SFH mass

The influence of SFH mass on the quantity of BG4 adsorbed was studied. It was shown that the quantity adsorbed decreased, as the mass of SFH increased from 0.01 to 0.2g, (Fig. 3). The surface area of any surface, so the sum of active sites that is free for adsorption is increased as the mass of surface increased (Lakshmipathy and Sarada, 2015). While (Fig. 4) showing the adsorption of BG4 onto SFH at 25˚C.

The amount of BG4 adsorbed on the SFH surface, increased as the concentration of dye increased. The driving force of concentration gradually proportional directly with increasing the concentration of dye and hence increase the mobility of the molecules in the liquid phase

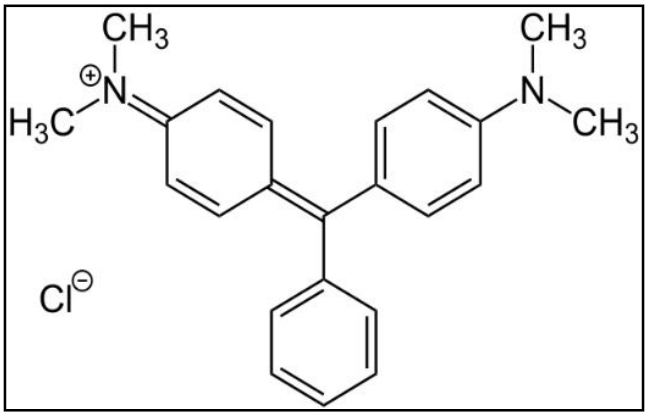

Fig. 1: The chemical structure of the BG4.

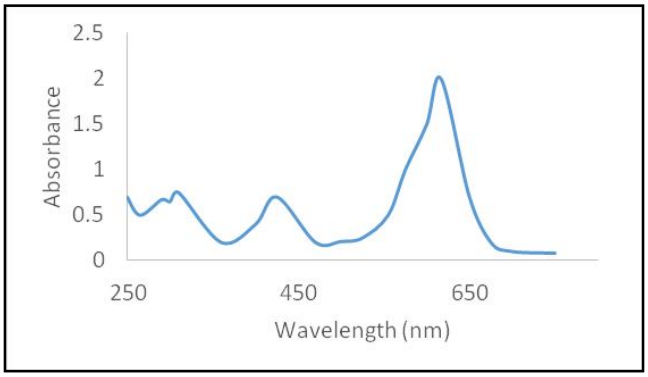

Fig. 2: UV-Vis Spectrum of BG4 dye exhibit an absorbance maximum at l_{max} = 617 nm.

(Tongpoothorn *et al.,* 2019).

Adsorption isotherm

Generally, the models of Langmuir and Freundlich controls the adsorption mechanism (Ge *et al.,* 2006). The results show that adsorption of BG4 dye on SFH does not follow Langmuir isotherm ($r^2 = 0.137$) while it well represented by Freundlich equation:

$$q_e \quad \log K_f \quad \frac{\log C_0}{n} \tag{3}$$

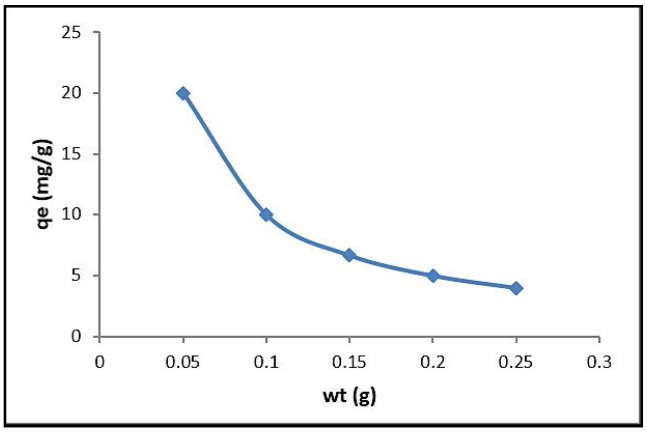

Fig. 3: Effect of SFH mass on the quantity of BG4 adsorbed at 25°C.

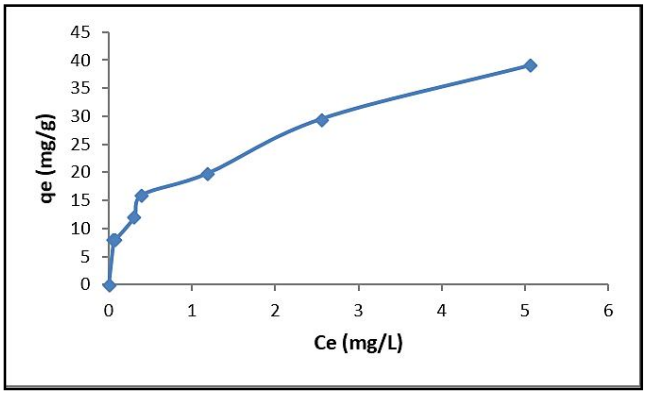

Fig. 4: Adsorption isotherm of BG4 on SFH at 25°C.

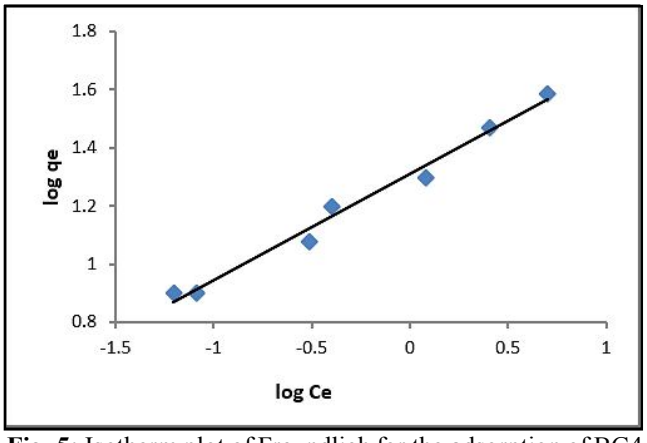

Fig. 5: Isotherm plot of Freundlich for the adsorption of BG4 on SFH.

where: K_f and n are the experimental constants of Freundlich.

The Freundlich constants and the correlation coefficient ($K_f = 21.37$, $n = 2.74$, $r^2 = 0.983$), were obtained from linear plot, (Fig. 5).

Thermodynamic of the adsorption process

35°C, 25°C

A decrease in the adsorption of BG4 on SFH with increasing the heat from 25°C to 45°C, means it is an exothermic adsorption process (Fig. 6). This is expected as an increase in temperature weakens the attraction forces of BG4 molecules with the sorbent surface (Suteu and Malutan, 2012).

The equations (4-6) were used to calculate the functions of (ΔH, ΔG, and ΔS)

$$InXm \quad \frac{}{RT} \quad cons\tan t \tag{4}$$

$$G \quad RT\ In\ K \tag{5}$$

$$G \quad H \quad T \quad S \tag{6}$$

The adsorption of BG4 dye on SFH has a negative value of free energy and entropy (Table 1). This refers to the spontaneity of the adsorption process and to the uniform distribution of dye molecules on the SFH surface(Valizadeh *et al.,* 2016).

Kinetic analysis

The rate of BG4 removal increase with time as appears from Figure 7.

Adsorption process on the solid surfaces occurs firstly on the adsorbent external surface until equilibria. The removal rate of the dye out of the aqueous medium is governed by a molecular diffusion of BG4 on the adsorbent internal surface. While the inner side has higher attraction towards adsorbent molecules. Thus, the content of BG4 adsorbed by the SFH surface is increased (Alghamdi *et*

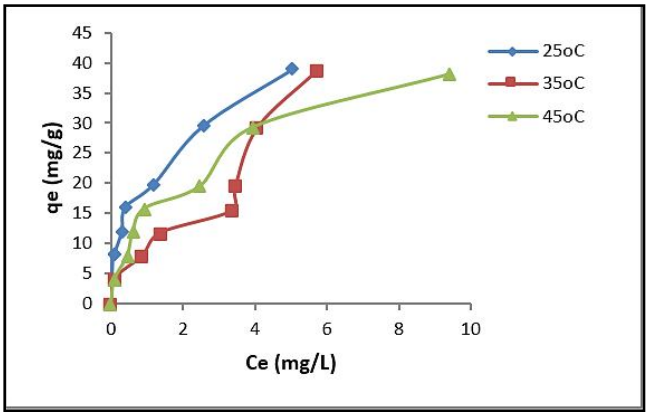

Fig. 6: Temperature effect on adsorption of BG4 dye.

Table 1: Thermodynamic functions of BG4 adsorption on SFH.

ΔH(*kJ/mol*)	ΔG(*kJ/mol*)	ΔS(*J/(mol .K)*)
-29.323	-41.594	-41.190

al., 2019).

The adsorption mechanism and kinetics of dye were evaluated by applying pseudo 1st order and pseudo 2nd order equations. The pseudo 1st order kinetics is given by the (equation 7) (Hsieh *et al.,* 2004).

$$In\ q_e \quad q_t \quad In\ q_e \quad k_1 t \tag{7}$$

As: q_e and q_t were the amount in (mg/g) of BG4 that adsorbed at equilibria and at the time t (min.) respectively, k_1 is the rate constant of the pseudo 1st order model.

k_1 for the adsorption of BG4 dye on SFH was worked out from the slope of the plot in equation (7) and (Fig. 8).

The linear form of the pseudo-second-order model is (Hsieh *et al.,* 2004):

$$\frac{t}{q_t} \quad \frac{1}{h} \quad \frac{1}{q_e}\ t \tag{8}$$

As: h is the rate of startup adsorption as $h \quad k_2 . q_e^2$,

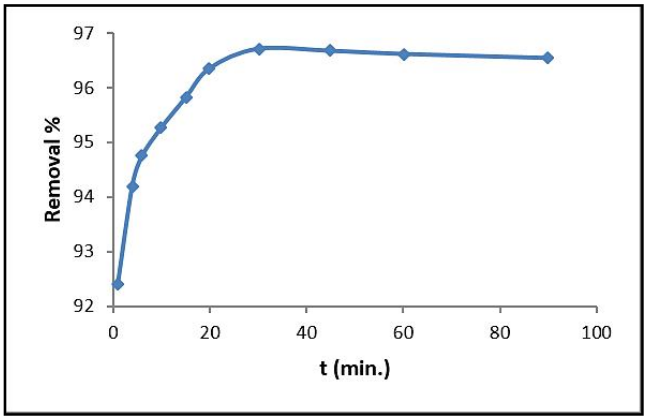

Fig. 7: The relation between the removal percentage of BG4 and time of contact at 25°C.

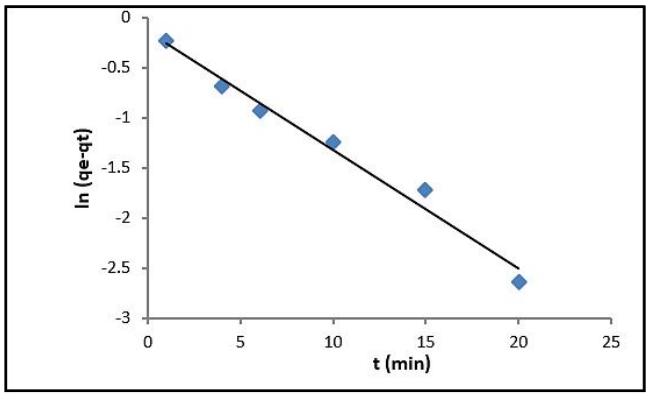

Fig. 8: Linear plot of pseudo 1st order kinetic of BG4 adsorption.

k_2 is the rate constant of pseudo 2nd order.

A straight line resulting from plotting $\frac{t}{q_t}$ versus t

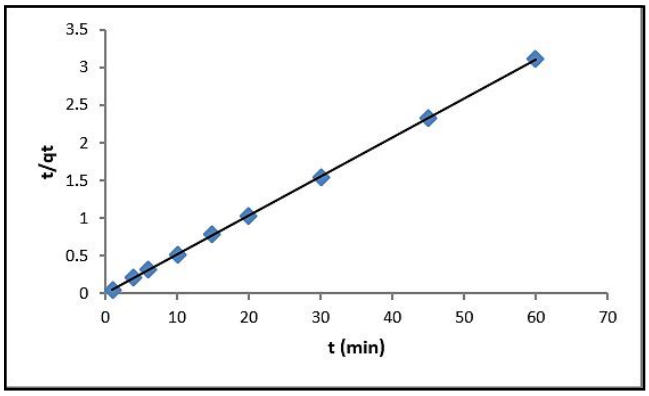

Fig. 9: Pseudo 2nd order kinetic of BG4 adsorption.

where the constants of the pseudo 2nd order can be acquired (Fig. 9).

The kinetic constants of BG4 adsorption on SFH. As indicated in Table 2 the correlation coefficient of pseudo 2nd order is bigger than the 1st order kinetic, and the value of q_e is fit with the experimental q_e value at 25°C. This suggests that the adsorption process of BG4 on the SFH surface obeys the 2nd order kinetics and the mechanism of the process may be determined by intraparticle diffusion (Al-Kadhi, 2019).

The experimental kinetic data were analyzed by intraparticle diffusion kinetics to calculate the rate-determining step of adsorption process:

Table 2: Kinetic constants for adsorption of BG4 dye on SFH at 25°C.

T (K)	Pseudo 1st order			Pseudo 2nd order			
	k_1 (min^{-1})	q_e (mg/g)	r^2	k_2 (g/(mg .min))	q_e (mg/g)	hx10 ² (mg/(g .min))	r^2
298	0.117	1.151	0.978	0.492	19.379	1.851	1.000

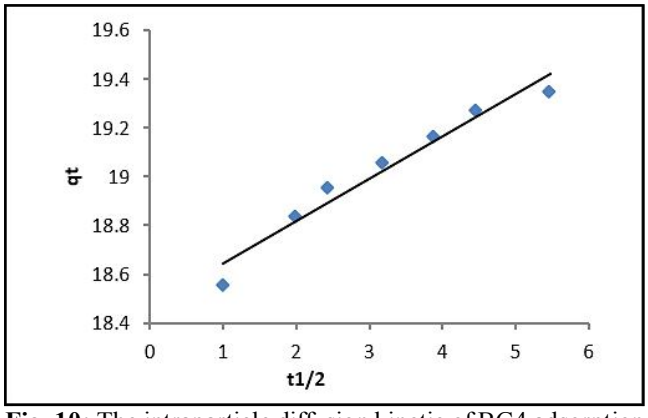

Fig. 10: The intraparticle diffusion kinetic of BG4 adsorption at 25°C.

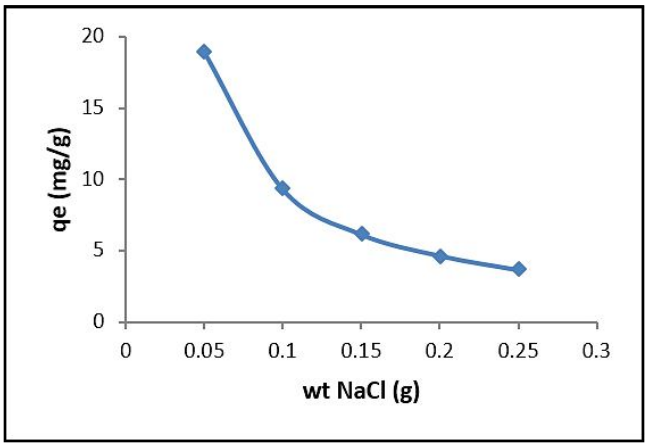

Fig. 11: The relation between the quantity of BG4 adsorbed and the weight of salt Conclusions.

$$q_t \quad k_d t^{1/2} \quad C \tag{9}$$

As: k_d *in* $\frac{mg}{g.\sqrt{\min}}$ is the rate constant of intraparticles.

The correlation of q_t against $t^{1/2}$ exhibited high linearity (Figure 10). However; k_d, C and r^2 were 0.174, 18.467 and 0.953, respectively. Nevertheless, the trend line does not go through the point of origin which conclude that the step of intraparticle diffusion might not be the controlling step in the adsorption mechanism. In addition, the adsorption process may include boundary layer effect as appear from the value of constant C (18.467) (Mohammadi, Daemi and Barikani, 2014; AL-TAWEEL, 2014; NAS, 2019; Sarma, Gupta and Bhattacharyya, 2019).

Effect of ionic strength

The results (Fig. 11) show that the quantity of BG4 adsorbed was decreased with increasing the quantity of NaCl, which can be attributed to the competition of Na^+ ions with dye on the active sites of SFH surface (Veli and Alyüz, 2007).

Conclusion

SFH surface has a high capacity to capture BG4 molecules from their aqueous solutions. The adsorption outcome of BG4 dye was well obeyed Freundlich isotherm and the thermodynamic parameters exhibited that adsorption of BG4 dye by SFH was spontaneous and exothermic in nature. The adsorption process follows Pseudo second-order kinetics at 25°C, and the intraparticle diffusion kinetics shows that more rate-controlling steps that control the adsorption process.

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