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ISOTHERM, KINETIC AND THERMODYNAMIC STUDIES ON THE ADSORPTION BEHAVIOR OF DISPERSE BLUE 165 DYE ONTO CHITOSAN AND PHOSPHOGYPSUM

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ABSTRACT

Wastewater is environmentally damaged by textile industry due to dyes which are an important class of pollutants. This research explores the possibility of using the biopolymer chitosan and phosphogypsum a by-product of treating phosphate ore as adsorbents for the removal of disperse blue 165 from aqueous solution. Chitosan and Phosphogypsum were characterized by Fourier transform infrared spectroscopy and X-ray diffraction. Optimum adsorption conditions were selected by varying the adsorbent dose, solution pH, initial dye concentration, and contact time. The results show that the removal of disperse blue 165 increases with increasing initial dye concentration and the equilibrium contact time were 60 min and 30 min for chitosan and phosphogypsum respectively. The adsorption isotherms were examined and the Langmuir model gives the best fit. Adsorption capacities were 103.09 $mg.g^{-1}$ for chitosan and 6.79 $mg.g^{-1}$ for phosphogypsum. Dynamic adsorption studies show that the adsorption reaction was well represented by the pseudo-first-order kinetic process for both adsorbents. The adsorption behavior was also tested using thermodynamic parameters.

INTRODUCTION

Industrial effluents have become an issue of increasing worldwide concern due to environmental pollution that they cause. In fact, effluents discharged from textile industries contains toxic chemical mixtures due to textile dyes which are one of the worst pollutants of water bodies .Therefore, dye effluents must be treated before discharge to minimize the threat to the environment [1-2].

Several physical, chemical and biological techniques have been used to treat dye laden wastewaters [3-4]. Among the methods available, the adsorption process occupies a prominent place due to its high efficiency and can produce high-quality water [5-6].

Many adsorbents have been used for the removal of dyes from wastewater. Recently, the attention has been focused on new, economic, easily accessible and highly efficient adsorbents. In this study, two adsorbents were used: Phosphogypsum which is a by-product of treating phosphate ore with sulfuric acid to produce fertilizers and Chitosan is a modified natural biopolymer derived from deacetylation of chitin, and mainly obtained from crustacean shells of pawn, crab, shrimp or lobster. It acts as an efficient adsorbent for all classes of dyes because of the amino functional groups [7, 8, 9].

The purpose of this study was to evaluate the suitability of using Phosphogypsum and chitosan for the adsorption of disperse blue 165. The influence of several parameters (contact time, sorbent amount, dye concentration, pH and temperature) on the adsorption capacity was evaluated and discussed. The adsorption dynamics were scrutinized using pseudo-first order and pseudo-second order models. The Langmuir and Freundlich isotherm models were tested to analyze the adsorption process

MATERIALS AND METHODS

Dye stuff

Disperse dye used in this study was Disperse blue 165 (DB165) which is from a textile factory in Morocco and was of commercial quality. It was chosen because of its known toxicity due to the presence of amines in the dye [10]. The structure of DB 165 dye and its properties are given in Figure1 and Table 1 respectively.

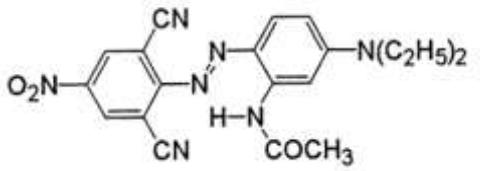

Figure 1. Molecular structure of DB 165

Table 1: Properties of DB 165

Commercial Name	Resolin Blue BBLS (1.8%)
Molecular Formula	$C_{20}H_{19}N_7O_3$
Molecular Weight	405.41
Type	Azo dye
λ max (nm)	540

Adsorbents

The adsorbents used in this study are PG and CHT. The PG is from the region of El Jadida in Morocco. It has a grey color, damp (5%), fine-grained powder, silty-sand materials. It is mainly composed of $CaSO_4$, $2H_2O$ with small amounts of phosphate, sand, and clay. CHT was purchased from sigma-aldrich MO, USA with more than 75% degree of deacetylation.

Adsorption experiments

An adequate amount of dye was dissolved in distilled water to prepare various solutions with different initial dye concentrations (20, 50, 70 and 100mg.l^{-1}). The pH of the solutions was adjusted to a given value ranging from 4 to10 by addition of 0.1M HCl or 0.1M NaOH and was measured using a pH meter. The adsorption experiments were carried out at different temperatures (293, 303, 313, 323 and 333 K). After the desired contact time, samples were withdrawn from the mixture using a micropipette and centrifuged for 7 min at 4600 rpm. Once centrifuged, the supernatant is analyzed to determine the concentration which is calculated according to the Beer Lambert's law .The absorbance was read in the range of visible wavelengths (340nm-825 nm) using a spectrophotometer Jasco (V-630).

The adsorption capacity values at equilibrium q_e mg.g^{-1} and time q_t (mg.g^{-1}) and adsorption percentage (%R) were calculated using the following equations:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{C_0 - C_e}{W} \times V \quad (2)$$

$$q_t = \frac{C_0 - C_t}{W} \times V \quad (3)$$

Where C_0,C_e ,C_t are the initial dye concentration , the concentration at equilibrium and the dye concentration at time (t) respectively . W(g) the amount of adsorbent and V(l) the volume of dye solution.

RESULTS AND DISCUSSION

Characterization of the adsorbents

Analysis by X-ray Diffraction

The XRD patterns of PG and CHT are shown in Figure2 they were obtained using an X-ray Diffractometer (X'Pert Pro PANalytical). The samples were scanned from 6° to 60° (2θ). In the figure 2b the PG was composed mainly of calcium sulphate dihydrate $CaSO_4.2H_2O$ [11,12,13] .The spectrum of CHT (Figure 2a) showed two peaks, one at 2θ= 10° and another at 2θ= 21°which were assigned to (020) and (110) [14]

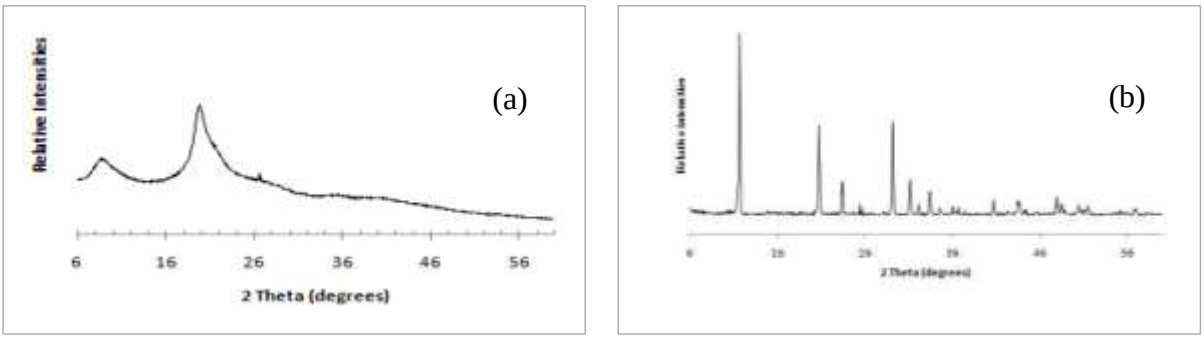

Figure2. XRD patterns of (a) CHT and (b) PG

Analysis by FT-IR spectroscopy

The infrared absorption spectra of PG and CHT were analyzed using a FT-IR spectrophotometer (Alpha Burker) at a range of 400–4000cm^{-1}. The spectrum of CHT (Figure 3a) shows peaks appearing between the ranges of 3200 cm^{-1} to 3500 cm^{-1} that are due to –OH and -NH stretching bands. The bands at 1150cm^{-1} and 1034 cm^{-1} corresponds to C-O-C [15].

The IR absorption spectrum (Figure 3b) shows bands characteristics of PG. Sulfate groups bending were observed at 650 cm^{-1} and 2300 cm^{-1} . The bands appearing at 3500 cm^{-1} and 1600 cm^{-1} are designed H_2O [16].

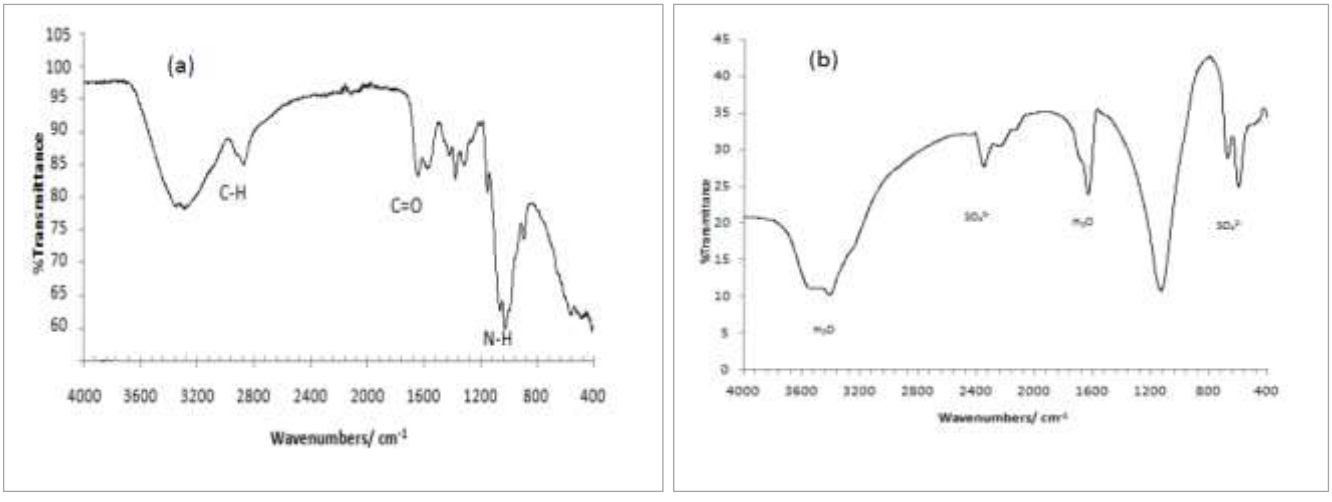

Figure3. FT-IR spectra of (a) CHT and (b) PG

Factors affecting adsorption of dye

There are many factors influencing dye adsorption such as solution pH, temperature, and initial dye concentration. Optimization of such parameters will contribute in the development of dye removal treatment process. In the next section, some of the factors affecting adsorption of dyes are discussed.

Effect of initial dye concentration and contact time

Figure4 Shows the effect of the DB165 solution concentration on adsorption onto the PG and CHT adsorbents. In these experiments, the amounts of PG and CHT were constant at 1g and 50mg respectively in 100 mL of dye solution, while the dye concentration was varied from 20 to 100 mg.l^{-1} with different time intervals.

The effect of initial dye concentration depends on the relation between DB 165 concentration and the available sites on the adsorbents surface [17]. Figure4 show that the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface [18]. Moreover, the capacity of the adsorbents increases with increasing initial concentration of the dye and this may be due to the high driving force for mass transfer at a high initial dye concentration [19].

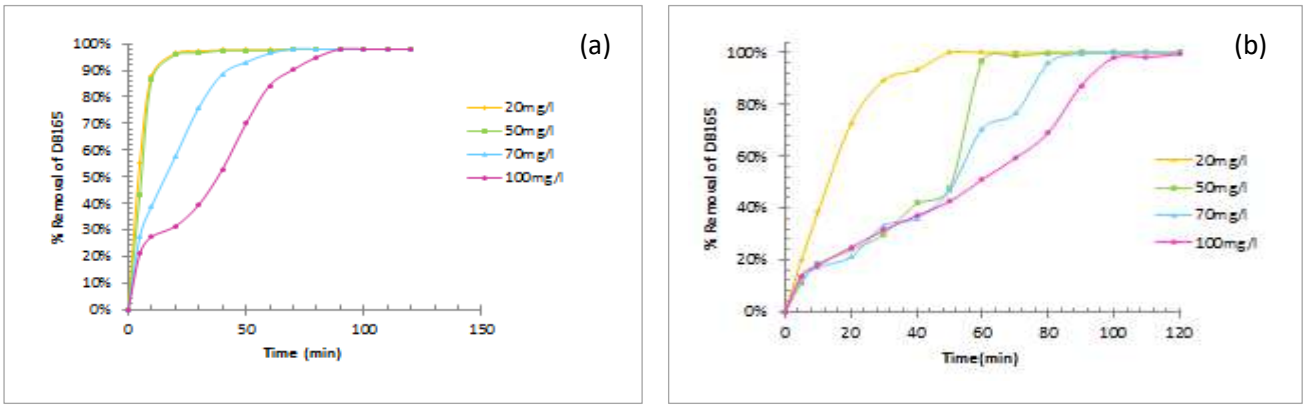

Figure 4.Effect of contact time and initial dye concentration on the adsorption of DB 165 onto (a) PG and (b)CHT

Effect of adsorbents dose

In order to evaluate the adsorbent dose effect on the removal of DB 165 dye , the adsorption experiments were carried out by varying the adsorbent amounts from 500 mg to 2g/ 100 ml for PG and 20 mg/100ml to 70 mg/100 ml for CHT.

The results show that the adsorption percentage of DB165 increases with increasing PG amount up to 10g.l^{-1} (Figure 5a) and an amount up to 0.5g.l^{-1} for chitosan. It can be explained by the availability of more adsorption site.

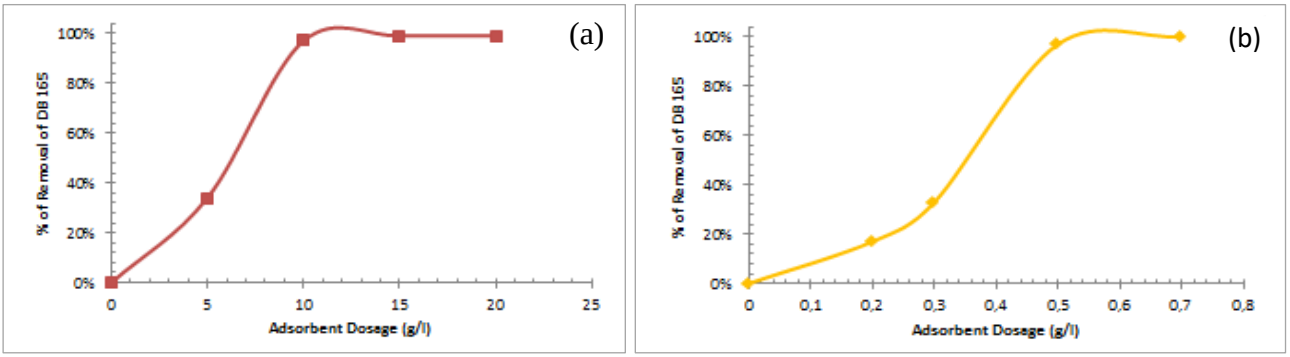

Figure 5. Effect of adsorbent dose on the adsorption of DB 165 by (a) PG and (b)CHT (experimental condition initial dye concentration: 50mg.L^{-1}, temperature: 293 K, contact time: 30 min for PG and 60 min for CHT

Effect of pH

Figure 6 shows the variations in the DB 165 removal from wastewater at different solution pH. It is observed that the removal of DB165 dye decreased up to 95% for PG and 85% for CHT when the pH was increased from 4 to 10.this can be due to the instability of azo group present in the studied dye at high pH [20].

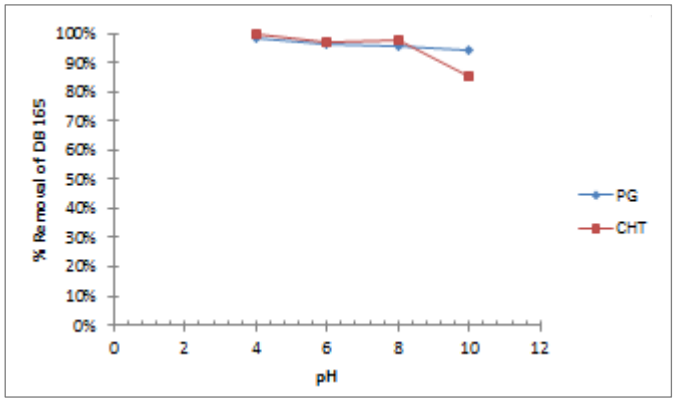

Figure 6. Effect of pH on DB 165 removal by PG and CHT initial dye concentration: 50mg.l^{-1}, temperature: 293 K, contact time: 30 min for PG and 60 min for CHT

Effect of temperature

The effect of temperature on the removal of DB 165 by CHT and PG is shown in Figure7.Experiments were carried out at different temperatures (293 – 333K) with constant amount of PG (1g/100ml) and CHT (50mg/100ml) and constant concentration (50mg/l) of dye. It is apparent from the results that the increase in temperature has a negative effect on the adsorption of CHT, which leads to the conclusion that the sorption process of CHT is of exothermic nature. The removal of DB 165 by PG increases with increasing temperature. That may due to the endothermic nature of the interaction between the adsorbate and the adsorbent.

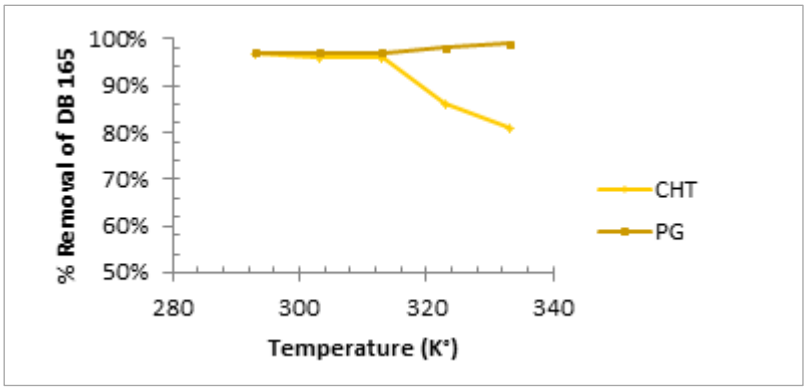

Figure 7. Effect of temperature on DB 165 removal by PG and CHT initial dye concentration: 50mg.l-1, pH=6, contact time: 30 min for PG and 60 min for CHT

Kinetic studies

A kinetic study was performed to understand the adsorption mechanism and to scale-up the efficiency of the adsorption process. Two kinetic models were proposed in the analysis of the sorption data of DB 165 onto PG and CHT: pseudo-first order model (Figure.8I) and pseudo second-order model (Figure.8II).

The linear form of pseudo first order equation is given by [21]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) t \quad (4)$$

The linear form of pseudo second order model is given by [22]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

The kinetic parameters are summarized in Table 2 .Based on the correlation coefficients (R^2) the adsorption kinetic data is best described by the pseudo-first-order equation for both PG and CHT (Eq. 4)

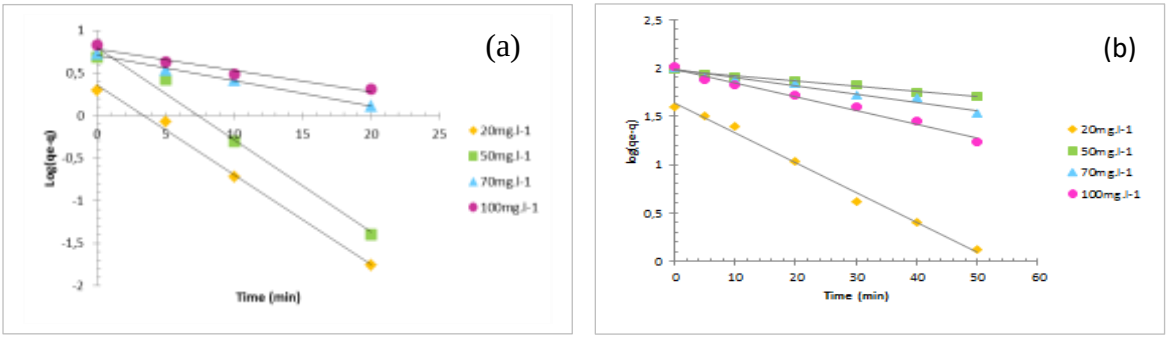

Figure 8.I: Pseudo-first-order plots for adsorption of DB 165 onto (a) PG and (b)CHT.

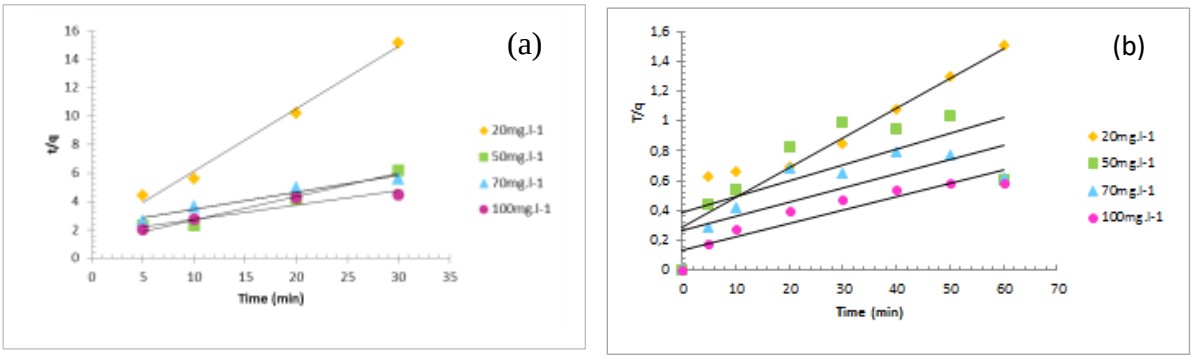

Figure 8.II: Pseudo-second-order plots for adsorption of DB 165 onto (a) PG and (b) CHT.

Table 2: Kinetic parameters for the adsorption of DB 165 onto PG and CHT.

			Pseudo-First Order			Pseudo-Second Order		
Adsorbent	**C ($mg.L^{-1}$)**	**Q_{exp}**	**Q_{calcul}**	**K**	**R^2**	**Q_{calcul}**	**K**	**R^2**
PG	20	1.98	2.28	0.2425	0.9942	2.09	0.2616	0.9837
	50	4.86	4.79	0.2494	0.9997	5.63	0.0653	0.9178
	70	5.34	5.14	0.0691	0.9948	5.90	0.0338	0.8518
	100	6.71	6.07	0.0583	0.9626	7.12	0.0230	0.8598

CHT	20	40.13	43.82	0.0713	0.9921	50	0.0013	0.923
	50	98.26	94.66	0.0126	0.9801	94.33	0.0002	0.434
	70	99.73	95.94	0.0198	0.9642	104.16	0.0003	0.5809
	100	102.66	97.02	0.0327	0.9839	111.11	0.0005	0.863

Adsorption isotherm

Adsorption isotherm describes the interaction between the adsorbent and the adsorbate molecules. So as to scrutinize the adsorption isotherm, two equilibrium isotherm models were investigated in the present study: Langmuir and Freundlich.

Langmuir isotherm

Langmuir isotherm describes the formation of a monolayer of dye molecules on solid surface and assumes that the adsorption realized on a homogenous surface and there was no interaction between the adsorbed molecules and the adsorbent. [23]

The linear form of the Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (6)$$

Where C_e ($mg.l^{-1}$) is the concentration of DB165 in solution at equilibrium, q_m ($mg.g^{-1}$) represents the maximum adsorption capacity and q_e ($mg.g^{-1}$) the equilibrium adsorption capacity and K_L is a constant of Langmuir reflecting the energy of adsorption.

From Table 3 we can see that the maximum adsorption capacity of PG and CHT was found to be 6.79 ($mg.g^{-1}$) and 103.9 ($mg.g^{-1}$) respectively, and from correlation coefficients we perceive that the equilibrium data fit well with the Langmuir isotherm which may be due to homogeneous distribution of sites on the PG and CHT surface [24].

The characteristics of the Langmuir isotherm can be represented by dimensionless constant separation factor or equilibrium parameter R_L.

$$R_L = \frac{1}{(1+K_L C_0)} \quad (7)$$

The values of R_L are 0.080 and 0.057 for PG and CHT respectively which are between 0 and 1 indicating that the adsorption of DB165 onto PG and CHT are favorable [25].

Freundlich isotherm

The Freundlich isotherm model describes the interaction between adsorbate molecules and adsorbents with multilayer adsorption on heterogeneous surfaces [26].
The Freundlich equation is given by:

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log K_F \quad (8)$$

Where Ce is the dye concentration in solution at equilibrium ($mg{\cdot}l^{-1}$); q_e is the amount of adsorbed dye at equilibrium ($mg{\cdot}g^{-1}$); K_F ($(mg.g^{-1})(L.mg^{-1})1/n$) and n are constants incorporating factors affecting the adsorption process by adsorption capacity and adsorption intensity, respectively.

Table 3: Isotherm parameters for the adsorption of DB 165 onto PG and CHT.

Isotherm model	Parameters	PG	CHT
Langmuir	Q_m (mg.g^{-1})	6.79	103.9
	K_L (L.mg^{-1})	0.569	0.822
	R^2	0.9849	0.9983
Freundlich	k_F(mg.g^{-1}(L.g^{-1})$^{1/n}$)	2.93	14.75
	N	4.097	5.924
	R^2	0.7596	0.3912

Thermodynamic studies

Thermodynamic parameters, namely the Gibbs free energy (ΔG), the enthalpy (ΔH) and the adsorption entropy (ΔS) onto CHT and PG were determined from the Langmuir isotherms at different temperatures using Van't Hoff equation:

$$\Delta G° = -RTlnK_D \quad (9)$$

$$lnK_D = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (10)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (11)$$

Where R is the universal gas constant (8.314 J/kmol.k), T is temperature in kelvin (K), and K_D (L/mol) is the adsorption equilibrium constant. For PG the negative values of the enthalpy and the free energy indicate the exothermic and spontaneous nature of the process, respectively, which coincides with the previous findings in this paper and for CHT the positive value of ΔH^0 show the endothermic nature of the adsorption and it may also designated the adsorption process is physisorption. The positive value of ΔS indicates an increased in the degree of freedom and randomness at the solid liquid interface throughout the adsorption process [27].

Table 4: Thermodynamic parameters for the adsorption of DB 165 onto PG and CHT

Adsorbent	ΔG° KJ mol^{-1}					ΔH° KJ/mol	ΔS°J mol^{-1} K^{-1}
	293	303	313	323	333		
PG	-25.28	-26.32	-28.36	-29.75	-31.70	-3.32	0.058
CHT	-15.97	-14.77	-13.91	-10.02	-8.72	8.31	0.022

CONCLUSION

The present work has investigated the dynamic adsorption process of DB 165 on PG and CHT. The experimental data indicate that both adsorbents were shown to be promising adsorbents for the removal of dyes from aqueous solutions. The initial dye concentration, pH , contact time and temperature are parameters influencing adsorption process. The highest adsorption capacities obtained are 6.79 mg.g^{-1}and 103.09 mg.g^{-1} for PG and CHT respectively. For the equilibrium analysis, the Langmuir and Freundlich isotherms models were applied. It was

shown that the obtained data fitted the Langmuir isotherm model and the adsorption follows pseudo-first order kinetics for PG and CHT.

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