Equilibrium and Isotherm Modeling of Toxic dye Adsorption onto Modified Apricot Stone

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Abstract. In the present study, adsorption of toxic dye Diret red 28 (acid benzidinediazo-bis-1- naphtylamine - 4- sulfonique) from aqueous solution was investigated using activated carbon synthesized with Phosphoric Acid activation.

The synthesized adsorbent was analyzed using BET, FT-IR and SEM techniques. The BET analysis showed that the area provided by the synthesized activated carbon was 88.01 m^2/g. The adsorption isotherms of Toxic dye onto ASAC are determined and correlated with common isotherms equations.

The smaller RMSE values obtained for the Langmuir and Dubinin-R models indicate the better curves fitting, the monolayer adsorption capacity of toxic dye is found to be 32.85 mg/g at temperature 25 °C and 23.42 mg/g at temperature 65 °C at pH 13.

The adsorption of toxic dye was carried out using a batch system and the effects of pH, contact time, adsorbent dosage, initial concentration and temperature on the adsorption capacity of synthesized adsorbent were investigated.

Kinetics studies proved that for both metals, the kinetic data follows the pseudo second order kinetic model. In addition, the thermodynamics studies proved that the adsorption process of toxic dye could be considered spontaneous and endothermic.

Keywords. Apricot Stone, Direct Red 28, Kinetic, Isotherm, Adsorption, Thermodynamic

INTRODUCTION

Dyes are colored compounds, which are widely used in textiles, printing, rubber, cosmetics, plastics, leather industries to color their products results in generating a large amount of colored wastewater. Mainly dyes are classified into anionic, cationic, and non-ionic dyes.

Among all the dyes using in industries, textile industries placed in the first position in using of dyes for coloration of fiber (Reisch, 1996).

Dyes are chemical compounds that attach themselves to fabrics or surface shells to impart color. Depolarization of wastewater from textile and manufacturing industries is a major challenge for environmental managers (Ho and Chiang, 2001) as dyes are water-soluble and produce very bright colors in water with acidic properties.

It has been projected that textile and manufacturing industries are using more than 10,000 commercially available (worldwide) dyes and the consumption of dyes in textile industry is

more than 1000 tones/year and about 10-15% of these dyes are discharged into waste streams as effluents during the dyeing processes.

Dyes are mainly derived from natural sources without any chemical treatment (Kadolph, 2008) such as plants, insects, animals and minerals.

Dyes derived from plant sources are indigo and saffron, insects are cochineal beetles and lac scale insects, animal sources are derived from some species of mollusks or shellfish, and minerals are ferrous sulfate, ochre.

Industries such as textile, printing, paper, carpet, plastic, and leather use dyes to provide color to their products. These dyes are always left in industrial waste and consequently discharged into the water body (Crini, 2006; Ong et al., 2007).

Dyes release into wastewater from various industrial outlets, such as paper, food coloring, cosmetics, leather, pharmaceutical, dyeing, printing, carpet industries etc.

The textile manufacturing and dyeing industries utilize more quantities of a large number of dyes and release these dye pollutants into environment as wastewater effluents.

These dyes are highly toxic and even carcinogenic to microbial populations and mammalian animals hence these are needed to remove from the water effluents before they are released into water bodies.

Dyes are stable to light and not biologically degradable; they are resistant to aerobic digestion and signify one of the difficult groups to be removed from the industrial wastewater (Doulati Ardejani et al., 2007).

The apricot stone used in the present study was prepared by chemical and physical activation this study was carried out with the aim to optimize conditions such as initial dye concentration, pH, particle size, contact time, adsorbent dosage, agitation speed and temperature.

Besides this, the equilibrium adsorption data were fitted to various equations to obtain constants related to the adsorption phenomena.

Equilibrium and kinetic analysis were conducted to determine the factors controlling the rate of adsorption, the optimization of various parameters in dye recovery and to find out the possibility of using this material as low-cost adsorbent for dye removal.

EXPERIMENTAL

Analytical grade reagents are used in all experiments. Basic dye (C.I. Direct Red 28) (99 %) is purchased from Merck Company the chemical structure and Uv spectrum are represented in figure 1.

In this work, required activated carbon was prepared by a conventional method carbonization and chemical activation with phosphoric acid as follows:

Apricot stones obtained from Boumerdes region in Algeria, are air-dried, crushed and screened to obtain two fractions with geometrical mean sizes ranging from 63 to 2.5 mm. 100 g of the selected fraction are impregnated with concentrated H_3PO_4 and dried in air.

Then, it is activated in a hot air oven at 250 °C . The carbonized material is washed with distilled water to remove the free acid until the pH reaches 6.8 and dried at 105 °C.
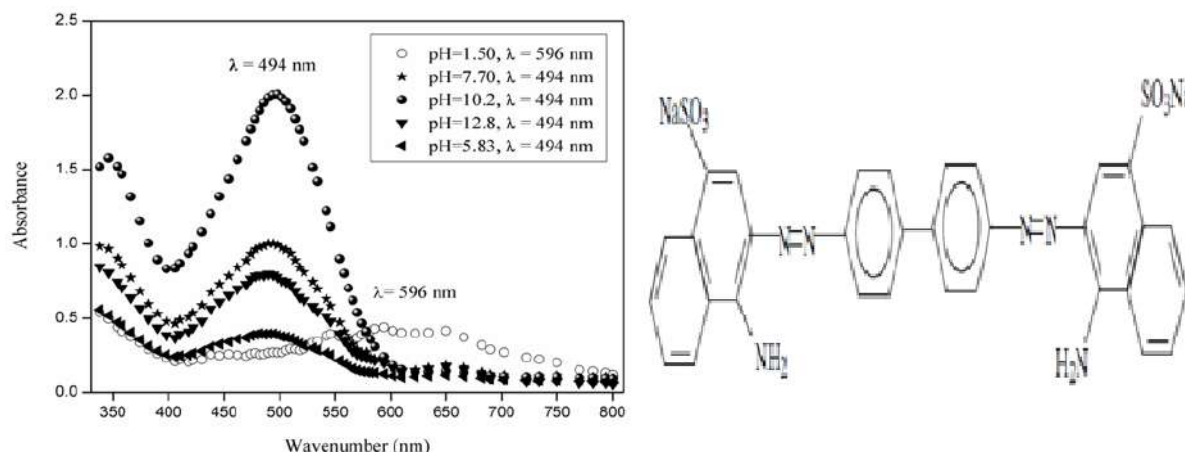
Fig.1. Chemical structure and Uv spectrum of Direct Red 28.

Batch mode adsorption studies

The effects of the experimental parameters such as the initial (C.I. Direct Red 28) concentration (40-100 mg/l), pH (2-14), adsorbent dosage (1-10 g/l), Agitation speed (100-1200 rpm) and temperature (298-338 K) on the adsorptive removal of CR ions is studied in a batch mode of operation for a specific period of contact time (0-60 min).

The (C.I. Direct Red 28) solutions are prepared by dissolving the accurate amount (C.I. Direct Red 28) (99 %) in distilled water, used as a stock solution and diluted to the required initial concentration. pH is adjusted with HCl or NaOH. The (C.I. Direct Red 28) content in the supernatant was measured spectrophotometrically on a Perkin Elmer UV-visible spectrophotometer model 550S at wavelength of 494 nm.

The amount of (C.I. Direct Red 28) ions adsorbed by activated carbon q_t (mg/g) is calculated by using the following equation (A1):

$$q_t = \frac{(C_0 - C_e) \cdot V}{m} \qquad (1)$$

Where C_o and C_t are the initial concentration and concentrations (mg/l) at any time respectively of the basic dye, V the volume of solution (L) and m the mass of the activated carbon (g).

Error functions

Within recent decades, linear regression has been one of the most viable tool defining the best-fitting relationship quantifying the distribution of adsorbates, mathematically analyzing the adsorption systems and verifying the consistency and theoretical assumptions of an isotherm model.

Due to the inherent bias resulting from the transformation which riding towards a diverse form of parameters estimation errors and fits distortion, several mathematically rigorous error functions (Root Mean Square Error (RMSE) equation (2), the Sun of Error Squares (SSE) equation (3) and Chi-Squares (X^2) equation (4) have lately drastically been addressed and confronted

$$RMSE = \sqrt{\frac{1}{N-2} \cdot \sum_1^N (q_{e,exp} - q_{e,cal})^2} \quad (2)$$

$$SSE = \frac{1}{N} \sum_{n=1}^{\infty} \left(qe_{cal} - qe_{exp}\right)^2 \qquad (3)$$

$$X^2 = \sum_1^N \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \qquad (4)$$

Where, $q_{e(exp)}$ (mg/g) is the experimental value of uptake, $q_{e(cal)}$ the calculated value of uptake using a model (mg/g), and N the number of observations in the experiment (the number of data points). The small the RMSE values, the better the curve fitting (Abbas et al., 2014).

RESULTS AND DISCUSSION

Characterization of the prepared ASAC
The composition of native Apricot stone NAS and ASAC determined by X- fluorescence FX are summarized in table 1.
The FTIR spectra of the adsorbent display a number of absorption peaks, indicating that many functional groups are present in the adsorbent (Abbas et al., 2015).

Table 1. Composition of NAS and ASAC.

Oxides	NAS (%)	ASAC (%)
SiO_2	0.963	0.326
Al_2O_3	0.413	0.075
Fe_2O_3	0.092	0.025
CaO	0.303	0.264
MgO	0.138	0.096
MnO	0.001	0.003
Na_2O	0.079	0.049
K_2O	0.120	0.118
P_2O_5	0.056	0.698
TiO_2	0.009	0.004
Cr_2O_3	0.001	0.003
SO_3	0.063	0.037
ZnO	0.001	0.001
CuO	0.008	0.009
NiO	0.002	0.002
P.E	97.58	98.32
Total	99.83	100.03

P.E: Loss on Ignition

Effect of analytical parameters
The effect of particle sizes on the acid dye adsorption by ASAC is examined. Significant variations in the uptake capacity and removal efficiency were observed at different particles sizes, indicating that the best performance is obtained with lower particle sizes (315-800 µm) is subsequently used in all adsorption experiments.
The pH of the DR 28) solution plays an important role in the adsorption process. It is evident that the percentage of acid dye removal increases consistently with decreasing pH (Fig.2).
The surface charge of the adsorbent is positive when the medium pH is under the pH_{zpc} value and negative for pH ions is favored. The pH(zpc) of ASAC is 7.05 and the surface charge of ASAC is negative at higher pH. As the pH decreases, the number of positively charged sites increases and favours the adsorption of CR ions by electrostatic attractions.
The effect of the stirring speed on the CR dye adsorption capacity onto the prepared ASAC. The maximum uptake was obtained for a stirring speed of 300 rpm. Such moderate speed gives a good homogeneity for the mixture suspension.
The adsorption capacity of CR increases with time and attains a maximum value after 40 min and thereafter, it reaches a constant value indicating that no more CR ions are further removed from the solution.

The equilibrium time works out to be 40 min.
Thus changing the initial concentration of acid dye from 50 to 100 mg/l, the adsorbed amount increases from 10.08 to 34.51 mg/g (Fig.3).

This may be attributed to an increase in the driving force of the concentrations gradient with increasing the initial basic dye concentration in order to overcome the mass transfer resistance of CR ions between the aqueous and solid phases. For the first stage of batch adsorption experiments on ASAC.
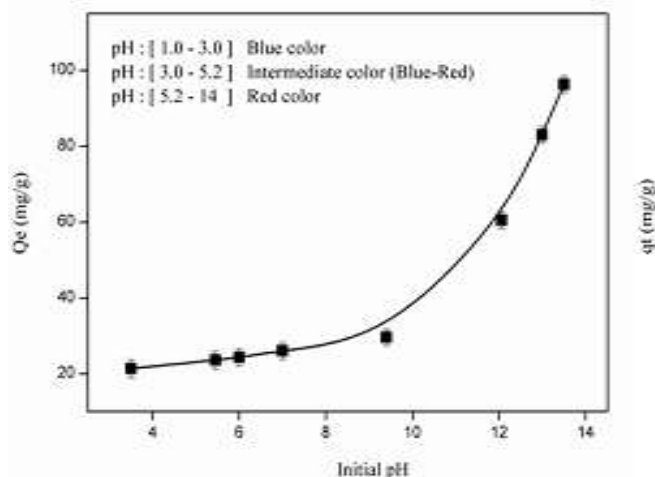

Fig.2. Effect of pH on the Direct Red 28 adsorption of Direct Red 28 onto ASAC.
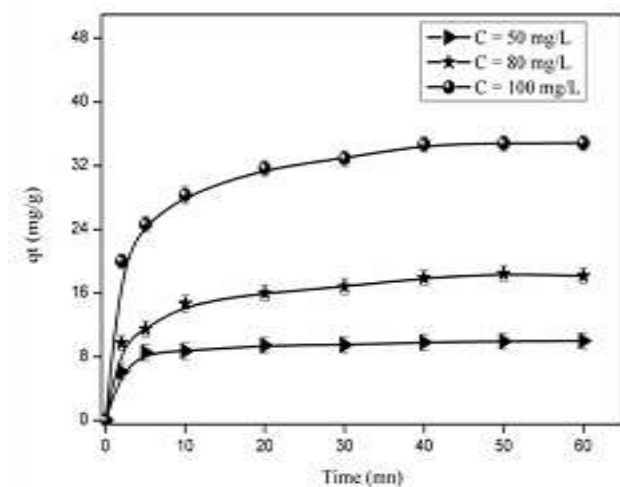

Fig. 3. Effect of contact time on the adsorption onto ASAC.

The effect of adsorbent dosage on the acid dye adsorption by ASAC is examined. Significant variations in the uptake capacity and removal efficiency are observed at different adsorbent dosages (1 to 10 g/l) indicate that the best performance is obtained with an adsorbent dosage of 1 g/l. The optimum conditions are listed in table 2.

Table 2. Optimum parameters for the isotherm model.

Parameters	Optimum condition
Time (mn)	40
Agitation speed (rpm)	300
Adsorbent dosage (g/l)	1
Particle sizs (µm)	300-800

Adsorption isotherms models

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration.

Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration. Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents.

Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Temkin, Elovich, Dubinin–Radushkevich) have been formulated in terms of three fundamental approaches.

Langmuir adsorption isotherm

Langmuir adsorption isotherm, originally developed to describe gas–solid-phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different bio-sorbents.

In its formulation, this empirical model assumes monolayer adsorption, with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites.

In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy, with no transmigration of the adsorbate in the plane of the surface. Graphically (Fig.4a, 4b), it is characterized by a plateau, an equilibrium saturation point where once a molecule occupies a site, no further adsorption can take place.

Moreover, Langmuir theory has related rapid decrease of the intermolecular attractive forces to the rise of distance.
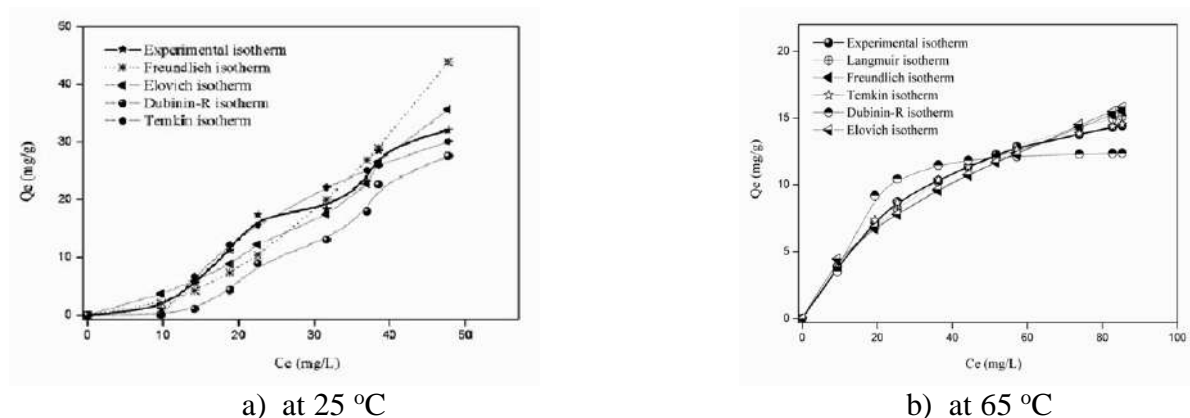

a) at 25 °C   b) at 65 °C

Fig.4. Adsorption Isotherm.

The assumptions of Langmuir equation include the followings:

a) Maximum absorption occurs when the adsorbent surface is covered by a single molecular layer of soluble material.

b) The absorption energy is fixed and identical at all the points.

c) The molecules of adsorbed material cannot move in the adsorbent surface.

The essential features of the Langmuir isotherm can be expressed in (4).

$$Qe = \frac{Qm. \, K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (5)$$

Where C is the concentration of soluble material in the steady state mg/l. Q_m is the maximum absorption capacity (mg/g) and K_L is Langmuir equation constant (l/mg).

Terms of dimensionless constant called separation factor which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (6)$$

Where K_L is the Langmuir constant and C_o the initial concentration of the adsorbate in solution.

The values of R_L indicates the type of isotherm:

Irreversible : $(R_L = 0)$,
Favourable : $(0 < R_L < 1)$
Linear : $(R_L = 1)$
Unfavourable : $(R_L > 1)$.

In this study, the R_L values are less than 1, confirming that the adsorption process is favoured in both the cases as well as the applicability of Langmuir isotherm.

Dubinin–R adsorption isotherm

Figure 5 can be used to describe adsorption on both homogenous and Heterogeneous surfaces. The Dubinin-R linear equation (7) has the following form (Shahwan and Erten, 2004):

$$Lnq_e = Lnq_m - \beta . \varepsilon^2 \quad (7))$$

Where q_m is the Dubinin-R monolayer capacity (mg/g) , β a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows equation (8):

$$\varepsilon = RTLn \left(1 + \frac{1}{Ce}\right) \quad (8)$$

Where R is the gas constant (8.314 J/mol K) and T is the absolute temperature. The constant β gives the mean free energy E of adsorption per molecule of the adsorbate (Lin et al., 2012).

$$E = \frac{1}{\sqrt{2\,\beta}} \quad (9)$$

The magnitude of E is useful estimating the mechanism of the adsorption reaction (Ozcan et al., 2007).

Adsorption kinetics

Kinetic consideration is the first approach to be referred. Here by, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal.

The kinetic study is important for the adsorption process, it describes the uptake rate of adsorbate and controls the residual time of the whole adsorption process.

Two kinetic models namely the pseudo first order and pseudo second-order are selected in this study to describe the adsorption.

The pseudo first order equation (Lagergren et al., 1998) is given in equation (10):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \cdot t \quad (10)$$

The pseudo second order model [15, 16] is expressed by the equation (11):

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{q_e} \cdot (11)$$

Where q_t (mg/g) is the amount of metal adsorbed on the adsorbent at various times t (min), K_1 the rate constant of the pseudo-first order kinetic (min⁻¹), K_2 the rate constant of the pseudo-second order kinetic (g/mg min). The determination coefficient and $q_{e,cal}$ of the pseudo-second order kinetic model are in good agreement with the experimental results (Table 3).

Table. 3. Kinetic parameters for adsorption of CR ions onto ASAC.

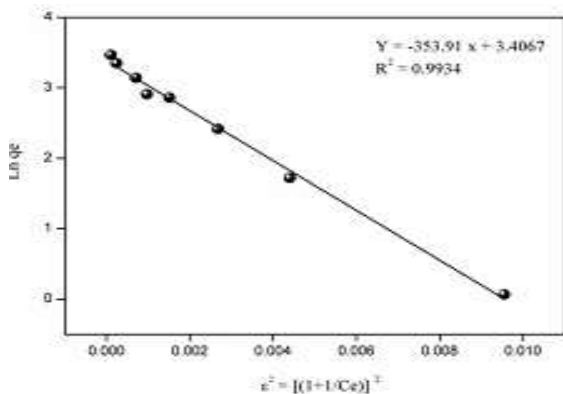| Co (mg/l)	Q_{exp} (mg/g)	Pseudo -First order Kinetic				Pseudo-Second order Kinetic			
		K_1 (mn^{-1})	R^2	Q_{cal} (mg/g)	$\Delta Q/Q$ (%)	K_2 (g/mg.mn)	R^2	Q_{cal} (mg/g)	$\Delta Q/Q$ (%)
50	9.990	0.0755	0.9587	3.1438	217.7	0.0604	0.99962	10.22	2.25
80	18.44	0.1146	0.7780	16.366	12.66	0.0157	0.99822	19.38	4.85
100	34.84	0.1174	0.9364	23.662	47.24	0.0115	0.99918	36.35	4.15

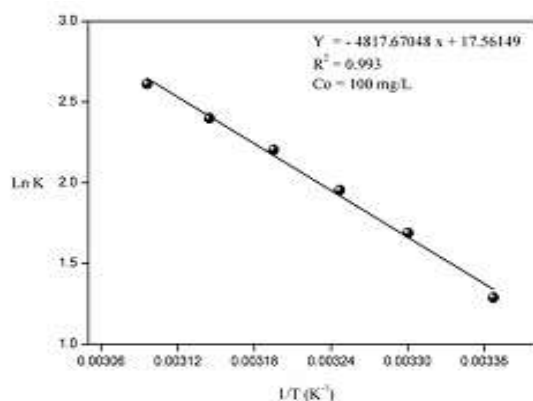Fig.5. Thermodynamic parameters for the CR.

Fig.6. Isotherm Modeling of D-R.

The adsorption capacity of ASAC decrease (21.64 to 7.33 mg/g) with increasing temperature (295 to 323 K), indicating that the adsorption is disfavored at high temperature. Thermodynamic parameters are determined from the following equations (12) and (13) (Abbas et al., 2015).

$\Delta G = - RT\, LnK$ (12)

$\Delta G = \Delta H - T\Delta S$ (13)

The thermodynamic equilibrium constant K for the sorption was determined by Khan and Singh (Ghaedj et al., 2013) by plotting q_e/C_e versus C_e and extrapolating to zero q_e, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J.K^{-1}mol^{-1}). The ΔH and ΔS values obtained from the slope and intercept of Von't Hoff plots of LnK versus 1/T (Fig. 6) and the ΔG values at various temperatures are summarized in table 4.

In order to have an idea about the efficiency of the prepared ASAC, a comparison of basic dye adsorption of this work and other relevant studies is reported. The adsorption capacity of the adsorbent q_{max} is the parameter used for the comparison. One can conclude that the value of

q_{max} is in good agreement with those of most previous works, suggesting that CR could be easily adsorbed on ASAC used in this work. This indicates that the apricot stone, very abundant in Algeria, is a cheap and effective adsorbent for the CR.

Table 4. Thermodynamic parameters for the Direct red 28 adsorption on ASAC.

T (K)	1/T (K^{-1})	(Qe/Ce)= f(Ce)	K	LnK	ΔH^o (KJ/mol)	ΔS^o (J/K.mol)	ΔG^o (J/mol)	
293	0.003413	R^2 : 0.997	0.2326	-1.458			-3538.15	
308	0.003247	R^2 : 0.997	0.2924					
318	0.003145	R^2: 0.994	0.3317	-1.229	10.79254	24.759	-3166.76	
328	0.003049	R^2 : 0.996	0.3733	-1.104			-2919.18	
				-0.985			-2671.58	

CONCLUSION

This study has shown that activated carbon prepared from apricot stone can be employed as effective adsorbent for the removal of CR from aqueous solution. The Dubinin-R and Langmuir isotherms model provided a better fit of the equilibrium adsorption data one. It gave a maximum adsorption capacity of 34.51 mg/g at temperature 25 °C, which decreased up to 23.08 mg/g at 65 °C at 13. The pseudo-second order model proved the best description of the kinetic data. The negative value of ∆G and positive value of ∆H indicate that the adsorption of CR onto ASAC is spontaneous and endothermic over the studied range of temperatures. The positive value of ∆S state clearly that the randomness increased at the solid-solution interface during the CR adsorption onto ASAC, indicating that some structural exchange may occur among the active sites of the adsorbent and the ions.

The adsorption of CR ions by ASAC follows a pseudo-second order kinetic model, which relies on the assumption that chemisorptions may be the rate-limiting step. In chemisorption, the CR ions are attached to the adsorbent surface by forming a chemical bond and tend to find sites that maximize their coordination number with the surface.

This study in tiny batch gave rise to encouraging result, and we wish to achieve the adsorption tests in column mode under the conditions applicable to the treatment of industrial effluents and the present investigation showed that ASAC is a potentially useful adsorbent for the metals, acid and basic dyes.

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