

Kinetic, Batch Equilibrium and Thermodynamic Studies on Adsorption of Congo Red in Aqueous Solution onto Activated Carbon by H₃PO₄ Activation from the Hulls Seeds of *Ziziphus Spina-Christi*.

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ISSN: 2582-3353



Publication details

Received: 02nd Dec 2019

Accepted: 19th Dec 2019

Published: 28th Dec 2019

Abstract: Pollution of the water environment of dyes can cause health risks to humans and environment. The management of these involves the establishment of specific methods. Herein, we demonstrated the adsorption capacity of Congo Red (CR) from an aqueous solution by activated carbon prepared from *Ziziphus Spina-Christi* shells. Prepared activated carbon was characterized by means of Fourier transform infrared (FTIR) spectroscopy and determination of the iodine number, and methylene blue index in aqueous solution. The experimental parameters such as pH of solution, contact time, adsorbent dose, initial concentration of CR and temperature were analyzed. To analyze the adsorption mechanism, Langmuir isotherms, freundlich models, Dubunin-Kaganer-Radushkevich (D-K-R), kinetic models of pseudo-first order, pseudo-second order, Elovich and Intraparticle Diffusion were studied. The adsorbent showed good potential for adsorption at pH 3.0 with an excellent yield of elimination of CR by active carbon (86.23% at 30°C). Adsorption equilibrium was reached after 20 min. Thermodynamic parameters such as $\Delta H^\circ = -5.819 \times 10^{-3}$ KJ/mol, $\Delta G^\circ = -9.082$ at -9.662 KJ/mol and $\Delta S^\circ = 0.029$ KJ/mol proved that adsorption mechanism of CR is possible, with the physisorption, spontaneous and exothermic in the ranges of temperature 30-60°C.

Keywords: Adsorption; kinetic; Congo-Red; activated carbon; *Ziziphus spina-christi*.

1. Introduction

Water is a vital element whose importance at the planetary level is unceasingly pointed out. However, actually the industrial and agricultural activities generate significant pollutions due to large generation of following the residues such as pesticide, dyes, gases, and heavy metals which very often are released to the environment without any control. The quality of drinking water is a powerful environmental determinant of human health. The problems associated with dyes pollution be reduced or minimized by various methods such as precipitation, ultra-filtration, electrode-deposition, solvent extract,^[1,2] electrochemical oxidation,^[3] the ozonation,^[4] and adsorption.^[5] The activated carbon (AC) is the most widely used because of their high adsorption capacity and high stability.^[6] Adsorption is a promising technique due to ease of use and low compared to other applications in the bleaching process cost, especially if the adsorbent is inexpensive and readily available. It is a method that this great advantage and good results in the retention of organic dyes. CR is an anionic dye of the azoic family. It finds application in the textile, cosmetic, food^[7] and tanneries. CR is carcinogenic and can cause irritation, redness and pain of the eyes,

lungs and skin.^[8] Hence, the removal of such dyes from wastewater by adsorption using activated carbon has been in the present work. In testing the efficacy of the present activated carbon for the removal of CR, various reaction parameters were considered (mass of the adsorbent, the pH, the initial content of adsorbate, and the model of sorption kinetics response best describes the process of sorption). The present study aims to use activated carbon from shells of *z. spina* to remove the CR in order to reduce dye pollution.

2. Materials and Methods

2.1. Preparation of Activated Carbon

The cores of *z-spina* were collected from Maroua city, Far North region of Cameroon. After we collect it, it was washed well and finally shells were collected. The shells were then immersed in the hot water for separation of the pulpe of hulls. Once the separation completed, we used mortar to separate the hulls of the almonds. After this operation, the hulls were then washed by distilled water and then dried in the air oven at 110°C for 24 hours. Finally, particle of size lower than 300 μm were obtained.

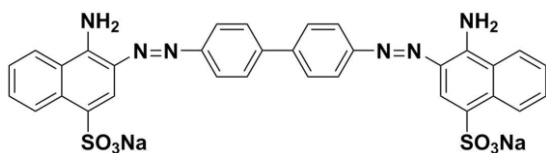


Fig. 1. Chemical structure of Congo-Red.

These fractions of the hulls are impregnated by phosphoric acid (1:1) at ratio from the initial solution of 95% of phosphoric acid, a prepared solution of 25% by dilution, is then mixed with the raw material. The mixture is homogenized with magnetic stirrer for 48 hours. After impregnation, the samples of the hulls of *z. spina* are dried in the oven at 110°C for 24 hours and cooled down to room temperature. Finally, the resultant material was carbonized at 500°C with average activation time of 2 hours in a furnace with a heating rate of 10°C/min and the cooling is done gradually in a desiccators to room temperature.^[9] Once cooling we washed with distilled water and then dried again in the air oven at 110°C for 24 hours. Then we crushed the resultant sample using mortar with a porcelain pestle. The activated carbon having a particle size less than 100 µm was successfully obtained.

2.2. Characterization of the AC

The functional surface groups of the prepared activated carbon were studied by FTIR spectroscopy. The Iodine index gives the indication on the porosity of the prepared activated carbon.^[9] Quantitative characteristic for the activated carbon reveals the mass loss during carbonization.^[9]

2.3. Preparation of CR solution

CR is an anionic dye with a molecular formula $C_{32}H_{22}N_6Na_2O_6S_2$ (Fig. 1). The dye stock solution was prepared by dissolving accurately weighted CR in distilled water to with concentration of 1000 ppm. Experimental solutions were obtained by diluting CR in accurate proportion of required initial concentration.

2.4. Batch Mode Adsorption Study

Adsorption studies were carried out at room temperature (25°C) in a 250 mL reactor. For each experiment, remove 0.02-0.36g of adsorbent was weighed and put in the reactor containing 20mL of concentration ranging from 5 to 35 ppm, and pH increasing from 3 to 12. The mixture was mixed by magnetic stirrer in the time interval of between 3 and 60 minutes. After agitation, the solution was filtered and the residual concentration was determined by UV-visible spectrophotometry. The absorbance was measured at 500nm for the CR, the adsorbed per unit mass of adsorbent (Q_e ; mg/g) in the equilibrium amount of adsorption and the percentage (%R) are given by the following relationship.

$$Q_e = \frac{(C_0 - C_e)V}{m_{cA}} \quad (1)$$

$$\%R = \frac{C_e - C_0}{C_0} \times 100 \quad (2)$$

C_0 : Initial adsorbate concentration in solution (ppm).

C_e : Equilibrium adsorbate concentration in solution (ppm).

m : Dried mass of used adsorbent (mg).

V : Volume of the adsorbate solution (L).

2.5. Adsorption Kinetics Studies

Pseudo first-order, pseudo second-order, intraparticle and fractional power rate equations have been used to model the kinetics adsorption of CR.^[5] A nonlinear regression was used for all these models. All experiment was done in triplicate. The pseudo first-order equation^[10] is generally expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

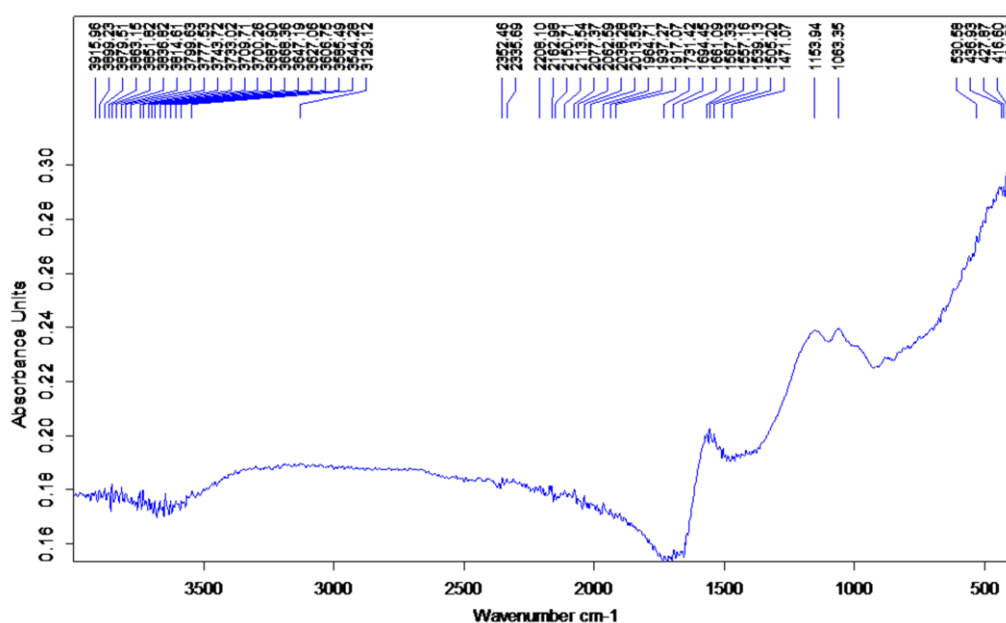


Fig. 2. FTIR spectrum of activated carbon.

Where q_e is the amount of CR adsorbed at equilibrium per unit weight of the adsorbent (mg/g), q_t is the amount of CR adsorbed at any time (mg/g) and k_1 is the pseudo first-order rate (constant/min). The values of $\log(q_e - q_t)$ were correlated with t . From the plot of $\log(q_e - q_t)$ versus t , k_1 and q_e can be determined from the slope and intercept, respectively. The pseudo second-order kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

Where k_2 is the rate constant of the pseudo second-order adsorption equation (g/mg.min). The constants q_e and K_2 can be obtained by plotting t/q versus t in equation (4). Intraparticle diffusion model equation^[11] is generally expressed as:

$$q_t = k_{int}\sqrt{t} + C \quad (5)$$

Where q_t (mg/g) is the amount adsorbed at time t and K_{int} is the intraparticle rate constant (mg/gmin^{1/2}), whereas the larger K_{int} values illustrate a better adsorption mechanism which is related to an improved bonding between ions and the adsorbent particles.

2.6. Adsorption Isotherms

The adsorption isotherm indicates how the molecules distribution occurred between the liquid phase and the solid phase until this process reaches an equilibrium. Analysis of equilibrium adsorption data by fitting different linear isotherm models is an important step to find the suitable model that can be used for design purposes.^[12] The studies of adsorption isotherms are carried out by two well-known isotherms, the Langmuir and the Freundlich adsorption isotherm models. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. While, the Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage.^[11] The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2 .

2.6.1. Langmuir Isotherm

The linear form of the Langmuir isotherm model is given by the following equation:

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

Where C_e is the equilibrium concentration of the adsorbate (CR) (ppm), q_e , the amount of adsorbed per unit mass of adsorbate (mg/g), and Q_{max} and K_L are the Langmuir constants related to the monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively. Where C_e/q_e was plotted against C_e , a straight line with slope of $1/Q_{max}$ was obtained, indicating that the adsorption of the CR on treated *z. spina* produced from treated *z. spina* follows the Langmuir isotherm.

Table 1. Characteristics of the activated carbon from the hulls of *z-spina*.

Parameters	Values
Methylene blue Index	965,5mg/g
Iodine Index	889mg/g
Ph	6,14

2.6.2. Freundlich Isotherm

The well-known logarithmic form of the Freundlich model is given by the following equation:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (7)$$

Where q_e is the amount adsorbate equilibrium (mg g⁻¹), C_e the equilibrium concentration of the adsorbate (CR) and K_f and n are the Freundlich constants, n giving an indication of how favourable the adsorption process and K_f is the adsorption capacity of the adsorbent. K_f can be defined as the adsorption or a distribution coefficient and represents the quantity of dye adsorbed onto treated hulls adsorbent for a unit equilibrium concentration. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.^[12] A value for $1/n$ be low one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption. The plot of $\log q_e$ versus $\log C_e$ gives straight lines with slope of $1/n$ which shows that the adsorption of the CR also follows the Freundlich isotherm.

3. Results and Discussions

3.1. Characterization of the activated carbon

3.1.1. Infrared spectroscopy of adsorbent

The FTIR spectrum (Fig. 2) of adsorbent shows a peak at 1731.42 cm⁻¹ corresponding to the stretching vibration of C=O bond of ketones. The peak at 1661.09 cm⁻¹ indicates the presence of the C=C bond of the aromatic nuclei characteristic and the strong peak at 1471 cm⁻¹ indicates the presence of the stretching vibration of CH₂ bond alkanes. The peak appeared at 1691.45 cm⁻¹ corresponding to the stretching vibration of C-O bond of the carboxylic acids. We observe a peak at 3647.19 cm⁻¹, corresponding to the stretching of the hydroxyl grouping -OH and the hydrogen bonds of alcohols. The peak located at 1505.20 cm⁻¹ indicates the presence of the stretching of N-H bond of secondary amine. Thus, the spectrum suggests the presence of the functional groups like phenol, carbonyl, amine, ether and carboxylic.

3.1.2. Values of some parameters of the characterization of the activated carbon

Table 1 presents values of methylene blue index, iodine index and pH as characteristics of the activated carbon from the hulls of *z-spina*. The value of methylene blue index is 965; 5mg/g shows an important presence of mesoporous.

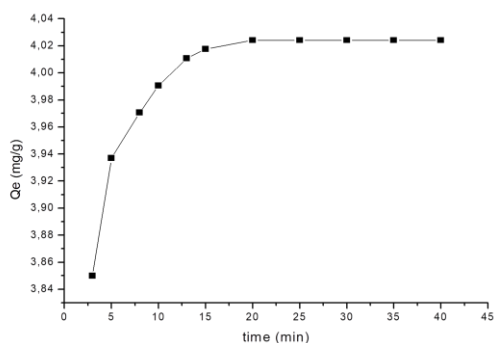


Fig. 3. The effects of contact time on sorbent-sorbate interaction time.

3.2. Effect of Agitation Time

Fig. 3 shows the effects of contact time on sorbent-sorbate interaction time (Conditions: initial concentration of 35 ppm with initial pH for the CR pH=3, 0.04 g of activated carbon; and increasing times of agitation).

From this curve, it comes out that the adsorption of the molecules of CR the Activated Carbon is fast during the first 5 minutes to reach the balance which is 20 min for the CR with adsorbed quantities maximum which are 4.0107 mg/g. The fast speed of adsorption of the first phase (fast phase) can be explained by the fact why at the beginning of the phenomenon, the sites of adsorption are free on the surface of our adsorbent material. Once that the molecules of CR are fixed, they blocks the pores, thus slowing down the speed of adsorption, there is apparition of a plate of saturation, from where the second phase (slow phase). This trend agrees with the report of other investigators.^[13]

3.3. Effect of the amount of adsorbent

The number of slots and available ion exchange for adsorption depends on the amount of adsorbent in the adsorption process. It is apparent from Fig. 4, the amount of CR adsorbed decreases with increasing mass of adsorbent (other parameters constant). From 0.36 g of activated carbon, the adsorbed amount of the dye did not change. This behaviour may be due to the number of adsorption sites, which decreases with the amount of adsorbent to the weight of 0.36g at which the adsorption sites becomes stable.^[8,14] This behaviour can be explained by:

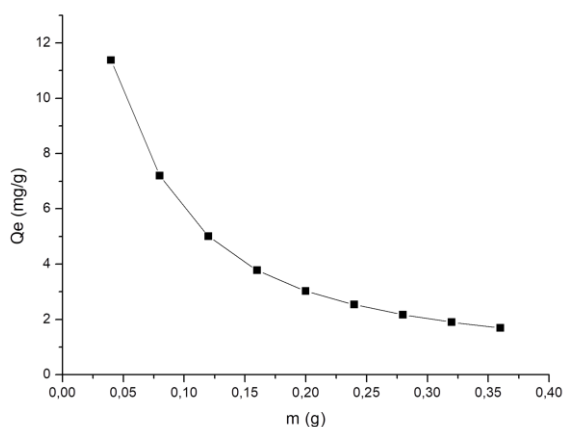


Fig. 4. The effect of carbon dose for the uptake of Congo Red.

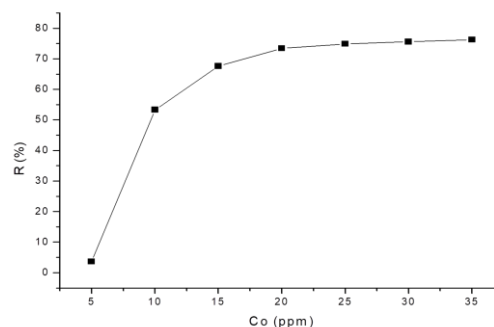


Fig. 5. Influence of Initial Concentration of Congo Red.

- As long as the amount of added adsorbent dye solution is low, the dye cations have easy access to adsorption sites. Uploading adsorbent increases the number of adsorption sites of the dye cations but more difficult to approach these sites because of congestion;
- A large amount of adsorbent creating agglomerations of particles, resulting in a reduction of the total surface area for adsorption, and therefore, a decrease in the amount adsorbed per unit mass of adsorbent.

3.4. Effect of initial concentration

We are seeing an increase in the amount of dye adsorbed at the concentration level ranging from 5 to 35 ppm; the results are presented in Fig. 5. The adsorbed quantities are ranging from 0.09 to 13.33 mg/g. The increase of the amount of dye adsorbed with the initial dye concentration is explained by the fact that the initial concentration supplied significant forces to overcome any resistance of the mass transfer between molecules of the aqueous solution and the surface of the AC. This increase of the amount adsorbed with the initial dye concentration is also due to the fact that increases the collision between the molecules and the dye adsorption sites.^[15]

3.5. Effect of pH of solution

The pH is an important factor in any adsorption study, because it may influence both the structure of the adsorbent and adsorbate, and the mechanism of adsorption. The effect of pH was studied in the range from 3.0 to 12.0 and the results are represented by Fig. 6. It is noted that the adsorbed quantities of CR by the activated carbon generally

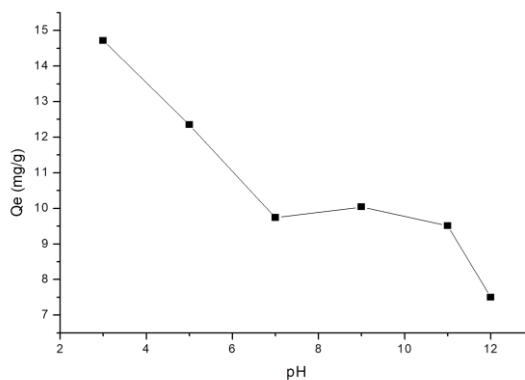


Fig. 6. The effect of pH on CR adsorption by Activated Carbon from *z. spina*.

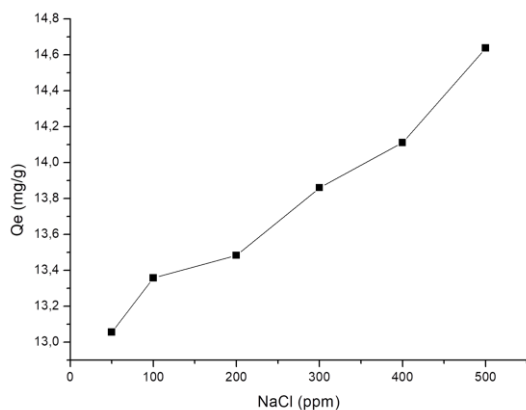


Fig. 7. The effect of the ionic strength of NaCl on the adsorption of the CR by the Activated Carbon.

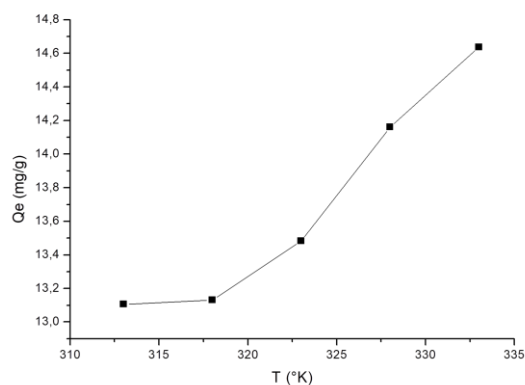


Fig. 8. Effect of temperature on the adsorption of CR by the activated carbon.

are overall weak for the basic zone and the more acid zone (pH=3). The adsorbed quantity is maximum with pH equal to 3.0; and the adsorbed quantity is 14.71 mg/g. This can be explained by the fact why in basic zone, the load of surface of the activated carbon is negative, if the pH is higher than pKa is about 4 for CR, and the ionized shape of this acid (ion phosphate, PO_4^{3-}). There may be repulsion between the surface of the activated carbon and the groupings phosphates (PO_4^{3-}) of CR. This result is in agreement with those observed in the literature.^[16]

3.6. Effect of Ionic Strength

Fig. 7. shows the evolution of the adsorbed quantities of the CR according to the concentration of added electrolyte. The study shows as the addition of the NaCl electrolyte, makes grow to a significant degree the quantities adsorbed as well for the CR. This growth is also a function of the concentration of the electrolyte. This fact that, the addition of the solution NaCl would lead to an increase in the ionic force, which would contribute to the aggregation of the adsorbates supporting the bringing together between the adsorbent and the adsorbate.^[17,18]

3.7. Effect of Temperature

Fig. 8 shows the adsorbed amount of CR as a function of temperature. The temperature is an important variable in the adsorption process. It is noted that the increase in temperature from 40 to 60°C induces an increase in the adsorption capacity. The experimental results show that this parameter positively affects this process by high energy contribution, and to overcome the repulsive forces located at the interfaces of liquid and solid media. So, it is interesting to note that the contribution of the heating has an important role in the kinetics of retention of the dye irrespective of their affinity for the support.^[19,20] It can be concluded that there is an optimum temperature value to promote the adsorption of the dye and the mixture. Result indicates that the adsorption capacity of activated carbon of CR increased with temperature. This may be a result of increase in the mobility of the large dye ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a

swelling effect within the internal structure of the activated carbon enabling large dyes to penetrate further.^[21]

3.8. Adsorption Isotherms

The results obtained show that the isotherm is type II. Isotherm type II features a macroporous adsorbent so the volume is particularly small. It is an isotherm that approximates the mathematical model of Langmuir. The values of all the constants and correlation coefficients R^2 Langmuir, Freundlich, Temkin and DKR are summarized in Table 1. The results obtained show that the Langmuir model best describes the adsorption of CR on the surface of CA because are close to unit. Indeed, the Langmuir model indicates that we have a homogeneous distribution of the adsorption sites on the surface of our CA, more of the adsorption compound is our multi-layer.^[22,23] The essential feature of the Langmuir isotherm is the separation factor defined by Equation 8.^[24] When it has a value between 0 and 1, the adsorption is favorable. The case of CR, $RL = 9.10^{-4}$.

$$R_L = \frac{1}{1 + K_L \cdot X C_0} \quad (8)$$

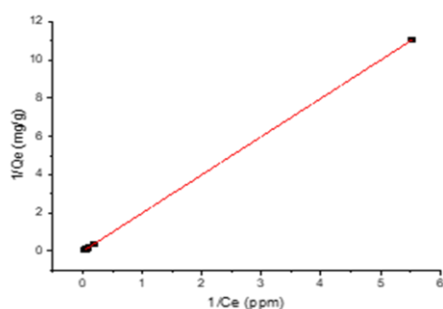
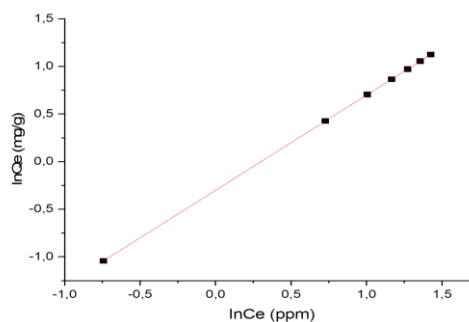
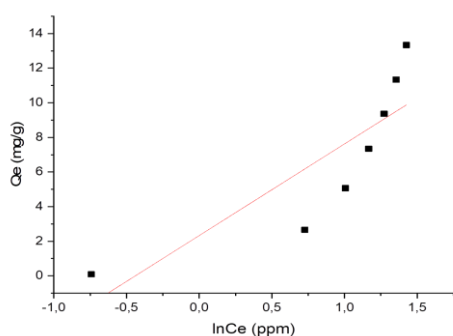
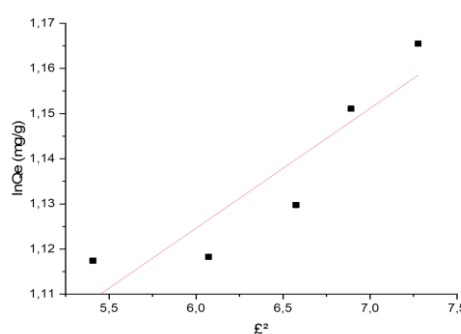
The values of $1/n$ in the Freundlich models are higher than 1. This shows that the adsorption is carried out with great intensity characterized by a heterogeneity between the surface of the boards and the adsorption capacity of the AC high value of n of our molecules dyes is between 1 and 5.^[25] Temkin and DRK models do not define adsorption because they all have correlation coefficients less than 0.90, indicating that adsorptive sites are not uniform at the AC surface. The values of the adsorption energy determined from the D-R-K model gives an indication of the type of adsorption.

3.9. Adsorption kinetics

It arises from Table 2 that the models of Elovich and the intra particulate diffusion cannot be applied to explain the adsorption of the CR because of their low values of the coefficients of correlation R^2 which are all lower than 0.90. However, the coefficient of correlation of the kinetic model of pseudo-first order and pseudo-second order is more about the unit. This result indicates that the kinetic model pseudo-first order and pseudo-second order describes well the experimental results of the adsorption of the CR by the

Table 2. Correlation Coefficients and Constants of Langmuir, Freundlich, Temkin and K-D-R

Model	Langmuir			Freundlich			Temkin		D-R-K					
Parameters	R ²	Q _{max}	K _L	R _L	R ²	N	K _f	R ²	β	K _T	R ²	Q _{max}	B	E
RC	0.999	111.1	9.10 ⁻⁴	0.22	0.998	1,02	10	0.713	8.85	0.078	0.832	8.44	0.233	1.47

**Fig. 9.** Langmuir plot for the CR.**Fig. 10.** Freundlich plot for the R.**Fig. 11.** Temkin plot for the CR.**Fig. 12.** DRK plot for the CR.

activated carbon. The values of the calculated theoretical adsorbed quantities (3.48 mg/g) of the model of pseudo-second order are very close to adsorbed quantities obtained experimentally (4.02 mg/g). The mechanism of adsorption of the CR is thus done according to the assumption of the kinetic model of pseudo-second order in two stages:

- The first is the diffusion of the CR towards the surface of the adsorbent;
- The second is the interaction between the molecules of adsorbates (CR) and surfaces of the adsorbent (activated carbon).

3.10. Calculation of Thermodynamic Parameters Related to Adsorption Process

Thermodynamic parameters, namely free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have an important role to determine spontaneity and heat change of the adsorption process. Thermodynamic parameters were calculated using the following relations:^[26]

$$\Delta G^\circ = -RT \ln K_c \quad (9)$$

The equilibrium constant K_c was calculated using the ratio:

$$K_c = \frac{C_d}{C_e} \ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

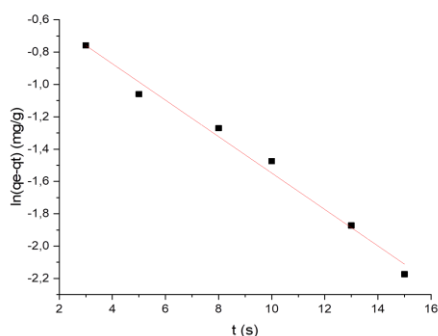
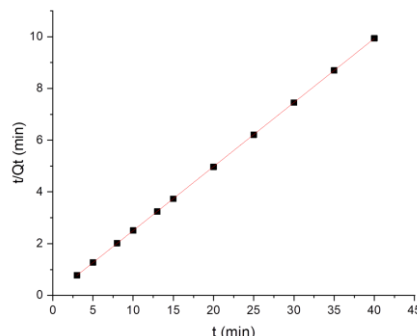
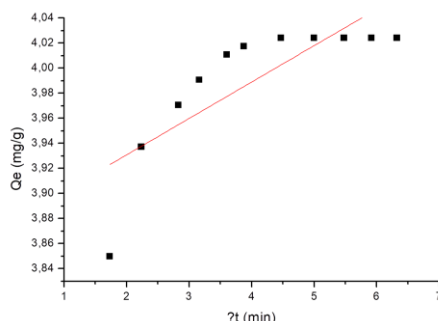
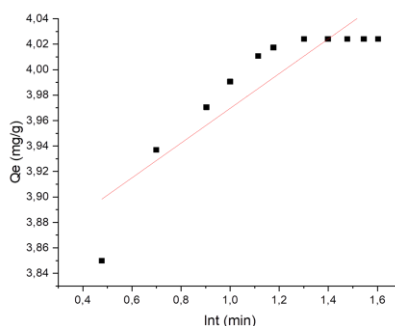
Where K_c is the equilibrium constant, C_d and C_e are concentration of CR above adsorbed and of solution (mg/L) at equilibrium respectively. R is the universal gas constant (8.314J /mol/K) and T is the temperature (K). ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot $\ln K_c$ vs. $1/T$, respectively (From equation 10), ΔG° were determined using $\ln K_c$ values for different temperatures. The Results were summarized in Table. 3. The negatives values of standard energy of Gibbs (ΔG°) of CR indicate that the adsorption is thermodynamic possible and spontaneous. The positives values of standard entropy (ΔS°) show the crescent aspect to interface this solid/liquid during the adsorption of CR dye on active carbon. The positives value of ΔH° indicates the positive nature of the present adsorption phenomenon. Also, the positives value of ΔH° proves the endothermic and physical nature of this retained phenomenon of dye. Furthermore, examination of the values of the standard enthalpy of adsorption (<40 kJ/mol) shows that it is a physisorption.^[27] The Results were summarized in Table. 3.

4. Conclusions

This study confirms that the activated carbon from the hulls of *z. spina* allows the elimination of the CR in aqueous solution. The optimal pH of adsorption of the CR is equal to 3.0. The amount of the adsorbent and the ionic strength has a significant influence on the process of sorption. Absorption balance of CR reached 20 min and

Table 3. Constant Speed and Correlation Coefficients of Kinetic Models

Models	Pseudo-first order			Pseudo-second order			Intraparticualar			Elovich		
Parameters	R ²	K ₁	Q _{cal}	R ²	K ₂	Q _{cal}	R ²	K _{int}	C	R ²	A	B
CR	0.989	0.110	0.261	0.998	2.73	3.48	0.701	0.023	3.350	0.819	467.73	0.094

**Fig. 13.** Plot for First-order for CR.**Fig. 14.** Plot for Second-order for CR.**Fig. 15.** Plot for Intraparticualar for CR.**Fig. 16.** Plot for Elovich for CR.

the percentage of retention is 86.23%, this percentage is favored by concentrated solutions. The Freundlich, Langmuir and Temkin isotherms describes the adsorption processes involved, and the kinetics of dye binding is the best represented by the model pseudo-second order. The negatives values of standard energy of Gibbs (ΔG°) of CR indicate that the adsorption is thermodynamic possible and spontaneous and the negative value of ΔH° proves the exothermic and physical nature of this retained phenomenon of dye. An activated carbon prepared from the hulls of *z-spina* is economic in the treatment of waste water containing CR.

Conflicts of Interest

The authors declare no conflict of interest.

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