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KINETIC AND THERMODYNAMIC STUDY TO REMOVAL OF CONGO RED DYE FROM AQUEOUS SOLUTIONS USING APRICOT SEEDS

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Abstract

The Apricot Seeds as a surface, Low cost and available was used for removing toxic Congo red (CR) dye. The effects of surface weight, contact time, initial dye concentration, PH and the temperature have been investigated, the results showed that the equilibrium time was 50 min, and the highest adsorption capacity (88.858%) was obtained at 0. 05gm of surface used. Isotherms studies for Langmuir, Freundlich, Dubinin and Temkin indicated that adsorption data was best fit with the Freundlich isotherm model. The adsorption kinetic was found best described by pseudo-second-order. The thermodynamic functions ($\triangle G^{\circ}$, $\triangle H^{\circ}$, $\triangle S^{\circ}$) of the adsorption were calculated, which show the adsorption is spontaneous and the adsorption is endothermic.

Key words : Adsorption, Congo red, Apricot Seeds, Thermodynamics and Kinetic study.

Introduction

Water pollution appears in various forms, such as poisoning with organic waste, pesticides or detergents or pollution resulting from food impact or thermal pollution or pollution with oil materials or pollution from factories (Nassar *et al.,* 2015) Dyeing Where the river water is contaminated with excess dyes from factories, including textile factories and others Different pollutants that area to account for here. Wastewater and industrial waste are a source (Tadesse *et al.,* 2015) Head of water pollution sources. It has therefore become necessary to subject them to treatment to reduce organic matter Biodegradable before being released to water sources and that the most important chemical methods used in this area are Chemical oxidation (Wang *et al.,* 2015) Reverse Osmosis (Memon *et al.,* 2015) Ion Exchange (Foroughi-Dahr *et al.,* 2015) Adsorption Adsorption (Ahmed *et al.,* 2015) Adsorption is an effective technique used in purification and separation processes and adsorption has expanded It has aroused the interest of many researchers for its effective role in accomplishing so many purification processes that it is hardly any Today's industry is devoid of adsorption. It is one of the means to remove substances or contaminants of aqueous or alcoholic solutions or a combination thereof and at low or no concentrations or inorganic Membership It has opened new horizons in various fields of science and life. Continuous progress where adsorption has been used as a successful solution in addressing water pollution problems resulting from Industrial wastes, especially industrial and textile factories. Despite the large number of published research (Ahmadi and Shadizadeh *et al.,* 2015) In this area, however, most of them are directed using the same adsorption surfaces, from the beginning of the activated carbon surface.(J. N Murrell *et al.,* 1982) Its wide application to porous clay surfaces Which are required for most adsorption processes. And with a twist Natural analyzes and methods of studying adsorption and the different application needs and expansion, the urgent need emerged The task is to study other porous solid surfaces that are no less important than previous surfaces, especially if they are Charcoal, zeolite, aluminum oxide and animal charcoal (charcoal) (Amir *et al.,* 2017) These surfaces are naturally cheap like wood (coal) silica gel (Ahlam *et al.,* 2014, Amir and Abduliah 2018).

Do not give high adsorption capacity when working as adsorption surfaces. So It has become necessary to develop and deepen more to obtain surfaces or materials with high adsorption capacity and cost Recent studies

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have used some types of polymers Economic development Manufactured as natural acrylic tissue including cellulose. Cotton which has shown high efficiency as mazah surfaces Adsorbents in adsorption processes (Amir and Abduliah 2019).

Materials and Methods

UV-Visible (Shimadzu, Jaban 1700) was used to measure the dye concentration. The PH of all aqueous solution was recorded by PH meter 7110wtw, Germany. The temperature was controlled using isothermal water bath shaker (BS-11, Korea)

Adsorbents preparation

Prepare by taking a large amount of apricot seeds available in the local markets as nature waste as they were washed With distilled water to get rid of impurities and then dried at 100 ° C for 60 minutes to remove moisture after adsorbed dye. Grind well with an electric grinder and then sieve with a 100 µm sieve.

Preparation of congo red dye

Congo red dye is water soluble (λ max 497nm). A standard solution (1000 mg/L) was prepared by dissolving 1g of congo red dye in 1L of D1 water. The experimental solution were prepared by diluting the standard solution of dye with DI water to give the appropriate concentration of the desired solutions (10-50) ppm and the solutions are left for 24 hours in order to homogenize. Dilute (0.1 M) HCl and (0.1 M) NaOH was used for pH adjustment. The UV-Visible spectrometer used to determination calibration curve for congo red dye λ max (497 nm).

Results and Discussion

Determine the equilibrium time

Adsorption of congo red dye by adding 10ppm of dye solution to 0.02 gm of apricot seeds surface The results were shown in Fig. 1. The removal increases with time to reach the equilibrium time 50 min at which the highest amount of dye adsorption occurs. The amount of adsorbent increases with time to provide a large number of active sites on the adsorption surface where molecules travel. The dye from the solution to the surface is characterized by the effect of the hydrogen bonding forces that occur between the active sites of the dye and the surface. When the equilibrium state is reached in the said time, the active sites in the surface are occupied by molecules.

Effect of adsorbent weight

The effect of apricot seeds on the adsorption capacity of congo red dye was studied. Different weights were taken from 0.01 to 0.05gm, and it was noted that the adsorption capacity of the dye is affected by the weight of the Adsorption is increased by increasing the surface area, the highest capacity is obtained Adsorption (85.288%) at 0.05 g, as shown in Fig. 2.

Effect of pH

The effect of the acidic function on the adsorption of the congo red dye on the surface of apricot seeds was studied by changing the acid function in different concentrations of the congo red dye within the range (10-50ppm) while maintaining constant temperature at 25^0C and equilibrium time (50min) as the results are shown in Fig 3.

Adsorption Isotherm

Information given by Isotherm adsorption is important. It gives an idea of how molecules are distributed between the liquid phase and the solid phase when adsorption reaches equilibrium. The adsorption isotherms of the congo red dye were studied at concentrations (10-50 ppm) and different temperatures (20, 25, 30, 35, 40°C) to four different isotherms namely: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms respectively. All adsorbents of adsorption to the congo red dye indicate that they are S type by Giles classification. The S-type isotherm is based on the assumptions of Isotherm Freunndlich, which include that the adsorbent surface is not homogeneous. This property is general due to the different locations of adsorption are unsaturated and energy differences.

Langmuir Adsorption Isotherm

The Langmuir model assumes that the effective sites obtained by adsorption are almost uniformly distributed (Homogenous), where the area of any site on the surface is fixed and the distribution of energy on the surface is uniform and adsorption It is evident that adsorption is monolayer (Amir and Donia 2018).

The linear formula of the Langmuier equation is :

$$Ce/Qe = 1/K_L\, q_{max} + (1/q_{max})\, Ce \quad (3)$$

Where Ce is the equilibrium concentration of dye (mg/L); q_{max}, Qe are the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g) and capacity at equilibrium (mg/g), respectively; and K_L is Langmuir constant (L/mg), linear relationship of (Ce/Qe) versus (Ce) gives a straight line of slope 1/qmax and intercept ($1/K_L$ qmax) Fig 4. For the Langmuir model, the maximal value of adsorption q_{max} was negative, which reflects the inadequacy of this model for explaining the adsorption process, although it shows a good linearity compared with other models a dimensionless constant separation factor of Langmuir

Table 1: The calculated adsorption parameters of the four used isothermsm.

Freundlich			Langmuir				
R^2	1/n	K_F	R^2	qmax	R_L	K_L	T (°C)
0.9724	0.409	4.246	0.9948	-7.993	-0.364	-0.3741	20
0.9818	0.385	4.507	0.9753	7.293-	-0.324	0.4080-	25
0.9938	0.376	5.693	0.9853	- 7.153	-0.311	- 0.4209	30
0.9917	0.374	5.222	0.9743	- 7.137	-0.295	- 0.4382	35
0.9918	0.386	4.905	0.9488	-6.640	-0.267	-0.4732	40
Temkin			**Dubinin (DKR)**				
R^2	B	KT	R^2	E	qmax	β	T (°C)
0.8426	0.968	31.697	0.9292	1.367	4.004	0.934	20
0.8838	1.411	34.622	0.9449	1.360	4.146	0.925	25
0.9063	1.937	35.55	0.9629	1.387	4.205	0.963	30
0.9032	3.258	35.698	0.9306	1.364	4.01	0.930	35
0.9232	4.271	38.197	0.9792	1.281	4.381	0.821	40

Table 2: Kinetics parameters for adsorption Congo red dye on apricot seeds.

pseudo-second –order			pseudo-first -order					
R^2	K_2 g.mg^{-1} min^{-1}	q_e(calc.)	R^2	K_1 min^{-1}	q_e(calc.)	q_e (exp.)	T(c^0)	
1	0.9148	5.3078	0.9501	0.0003	1.0259	5.3574	20	C_0 = 10 (ppm)
1	1.2938	5.3304	0.9904	0.0002	1.0215	5.3797	25	
1	1.87	5.347	0.9624	0.0001	1.0169	5.3894	30	
1	2.7319	5.3475	0.8934	0.00009	1.0149	5.3967	35	
1	3.1773	5.3734	0.9656	0.00008	1.0120	5.4113	40	

Table 3: Values of thermodynamic functions for adsorption Congo red dye apricot seeds.

40 °C	35 °C	30 °C	°C 25	20°C	Thermodynamic Function	Co (mg/L)
0.2362					H △ kJ.mol^{-1}	50ppm
-7.2733	-7.0406	-6.7867	-6.5899	-6.4251	G △ kJ.mol^{-1}	
0.02399	0.02362	0.02317	0.02290	0.02273	S △ kJ.mol^{-1} K^{-1}	

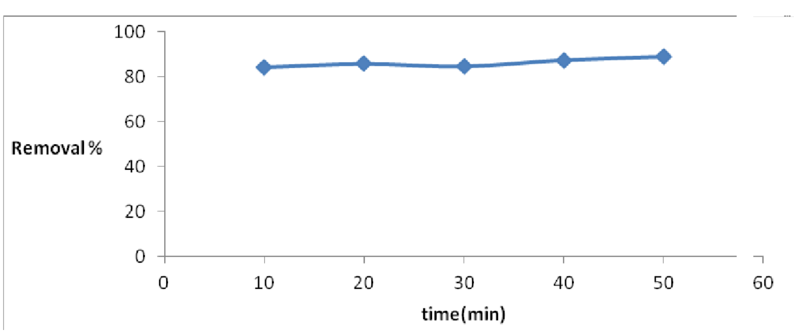

Fig. 1: Equilibrium time of the Congo red dye on.

isotherm (R_L) was also calculated using equation (Amir and Sara 2017).

$$R_L = 1 / (1+K_L C_0) \quad (4)$$

Where C' is the initial concentration of Congo red dye solution (mg/L) and K_L (L/mg).

Freundlich Isotherm

It is considered one of the most important isothermic equations used when the surfaces are not homogeneous, potential energy changes are irregular due to the occurrence of adsorption sites at varying levels of energy. Developed a Friendlich equation to represent the change in the amount of adsorbent (Qe) in the unit area or mass of the adsorbent with pressure or concentration of equilibrium (Ce) Write the Friendlich equation as follows (Amir and Donia 2019).

$$Qe = K_F \, Ce \, 1 / n \quad (5)$$

Qe: Weight of adsorbed material in mg / g

Ce: Concentration at equilibrium in mg / l

K_f : the Friendlich constant it is a measure of adsorption capacity

n : a constant value that expresses adsorption affinity and depends on the type of surface and the nature of the adsorbent and temperature.

Taking the algorithm of both sides of the equation (5) becomes as follows :

$$\ln Qe = \ln kF + 1 / Ln \, Ce \quad (6)$$

When plotting lnQe vs. LnCe we get a linear relationship with a slope of (1 / n) and an intersection lnKf as shown In the Fig. 5. The Freundlich constant (K_F) decreasing with increasing the temperature, that is an indication for exothermic.

Temkin isotherm

The Temkin isotherm in the linear form has been used as the following equation (Aseel and Karim 2018).

$$Qe = B \ln K_T + B \ln Ce$$
(7)

Where Q is the quantity of the substance adsorbed in mg / g

Ce: Concentration at equilibrium in units of g / l or mg / l

R : is the gas constant 8.314 J. mol^{-1}.deg^{-1}

T: temperature in unit K

B, K_T are the constants of Timken where B = RT / b are calculated from the slope and intercept respectively of curve between the

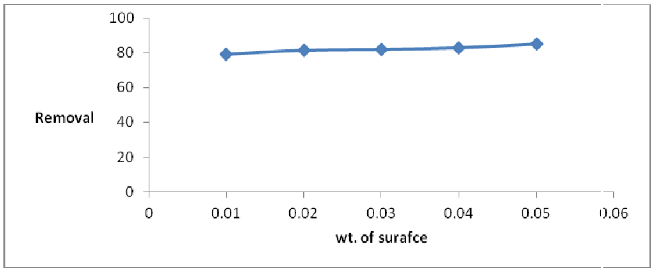

Fig. 2: Adsorbent weight of congo red dye on apricot seeds.

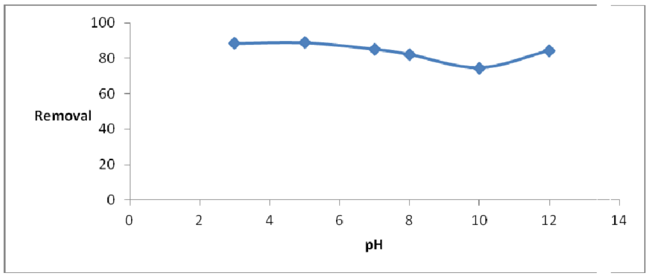

Fig. 3: Effect of' PH on the adsorption of congo red dye on apricot seeds.

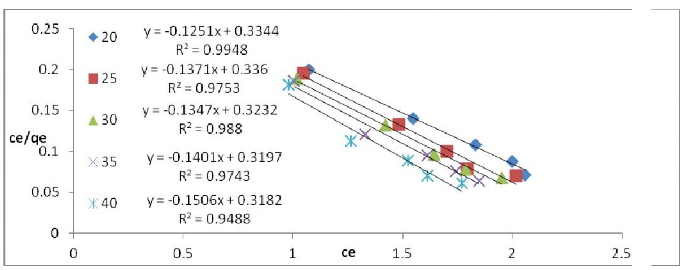

Fig. 4: Isotherm Langmuir for congo red dye on apricot seeds.

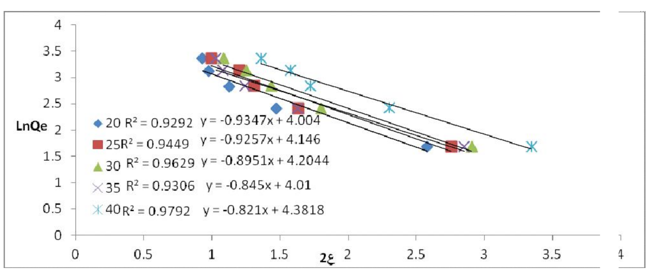

Fig. 5: Isotherm Freundlich for congo red dyes on apricot seeds.

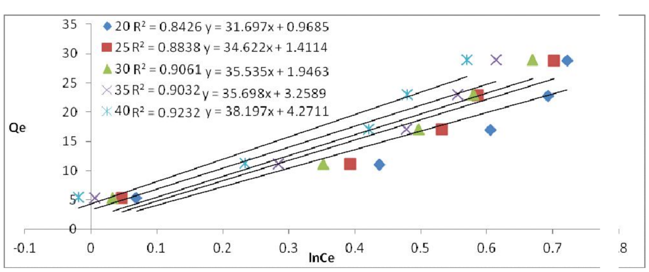

Fig. 6: Isotherm Temkin for congo red dyes on apricot seeds.

Qe and ln Ce as in Fig. 6.

Dubinin Isotherm (DKR)

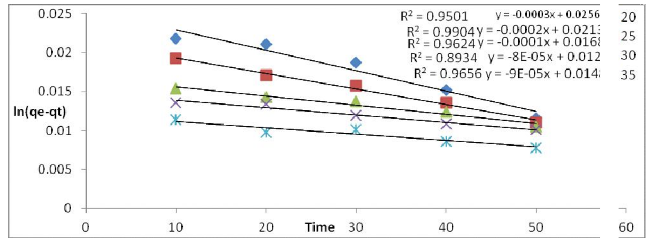

Fig. 7: Isotherm Dubinin for congo red dyes on apricot seeds.

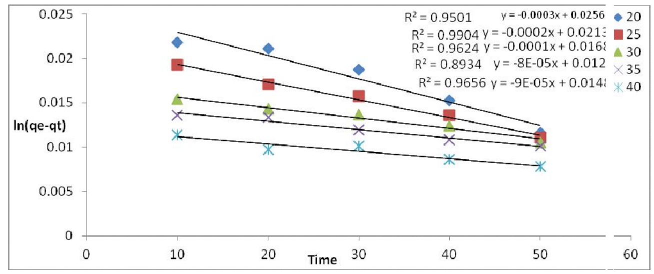

Fig. 8: Plot of pseudo-first order model of Congo red dye on apricot seeds.

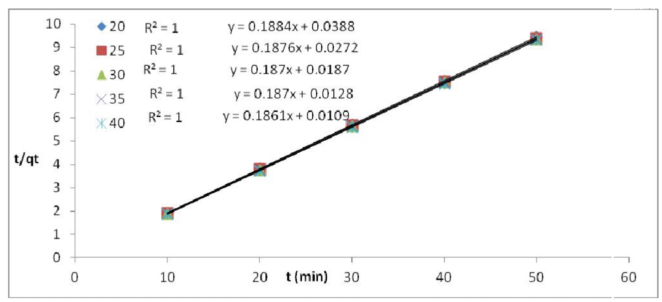

Fig. 9: Plot of pseudo- second order model of Congo red dye on apricot seeds.

Radushkevich (DKR) model proposed by Dubinin, which does not assume a homogenous surface of sorbent. It is applied to determine the adsorption mechanism (physical or chemical). The linear form of (DKR) is as follows (Amir and Abduliah 2018).

$$\ln Q_e = \ln q_{max} - \beta\varepsilon^2 \quad (8)$$

Where q_{max} is the maximum sorption capacity (mg/g), β is the activity coefficient related to mean sorption energy (mol^2/J^2), and ε is the Polanyi potential defined as:

$$\varepsilon = RT \ln (1+ 1/Ce) \quad (9)$$

Where R is the gas constant (KJ/mol. K). The slope of the plot of lnqe versus ε^2 gives β and the intercept yields the sorption capacity q_{max}, as shown in Fig 7. Prediction of the adsorption mechanism (physical or chemical) can be done by calculating the value of the mean sorption energy, E (J/mol), from the following equation(Amir and Abduliah 2019).

$$E = (-2\ \beta)^{-0.5} \quad (10)$$

The values of β, q_{max}, E and R^2 as a function of temperature are listed in (Table 1). If the values of E were less than 8 KJ/mol, the mechanism maybe a physical adsorption, while E values between 8-16 KJ/mol assumes the adsorption to be controlled by ion exchange, and E greater than 16 KJ/mol presume a particle diffusion mechanism (chemical process). It can be observed that the values of E may be physical (electrostatic) in nature.

Study of thermodynamic variables

The values of thermodynamic functions are very important in the interpretation of many interactions (especially the process of adsorption) in terms of their direction and the nature of the forces controlling them, as well as they give a good description of the nature of the regularity of molecules in different systems resulting from molecular interventions of all kinds. The enthalpy value ($\triangle H$) is a direct measure of the interference forces between the emitted molecule and the surface of adsorbent. The results of the thermodynamic functions are shown in (Table 3). Thermodynamic values ($\triangle S^o$, $\triangle G^o$, $\triangle H^o$) were calculated $\triangle G^o$ values were calculated from equation (Amir and Donia 2019).

$$\triangle G^{\circ} = \text{“ } RT \ln K \quad (11)$$

That's where K : equilibrium constant

The amount of heat associated with the adsorption ($\triangle H$) was calculated by plotting $\text{In}X_m$ versus (1 / T) from slope get ($\triangle H$) according to the equation:

$$\ln Xm = \text{—}dH / T + K \quad (12)$$

It was found that the adsorption of the congo red dye on the surface of apricot seeds is spontaneous and through a Gibbs relationship, the change in the entropy ($\triangle S$) can be determined from the following relationship:

$$\triangle G = \triangle H - T\triangle S \quad (13)$$

Adsorption Kinetics

The kinetic study was performed on adsorption of the eosin dye using the batch method at 10ppm concentration and in a range of thermal degrees (293-313K). The following equation was applied (Ghosh *et al.,* 2002) :

$$\ln (qe - qt) = \ln qe - k_1 t \quad (14)$$

$$t/qt = 1/k_2qe^2 + (1/q_e)\, t \quad (15)$$

Where qe (mg/g) is the equilibrium sorption capacity and qt (mg/g) is the amount of dye adsorbed at time t (min), k_1 (min^{-1}) is the rate constant pseudo first-order and k_2 rate constant pseudo second -order (g/mg.min). Values of k_1 and k_2 were obtained from the slope of the plot of ln(qe-qt) vs. time and t/qt versus time respectively. as shown in Fig. (8 and 9). The adsorption kinetic parameters are indicated in (Table 2). The correlation coefficients of the liner curves of both kinetics shows that the process more likely follows a second order kinetics.

Conclusions

Through this study, it was concluded that the apricot seeds have a high efficiency as a low cost, available and harmless surface adsorbent. The adsorption process is influenced by h surface weight, contact time, primary concentration, pH and temperature, also showed that adsorption is subjected to freundlich isotherms and is possible in degrees Low heat. and also q_{max} were very close to the q_{exp} for the pseudo –second order rate kinetics, The Freundlich constant (K_F) decreasing with increasing the temperature, that is an indication for exothermic. E < 8KJ/mol indicates the physical force influence. Thermodynamic studies have shown that adsorption is heat-emitting and spontaneously. It was found that the pseudo –second order model might have followed by the adsorption process as supported by correlation coefficients of the linear plots.

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