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Efficient Removal of Congo Red Dye from Aqueous Solution using a Biosorbent derived from *Phoenix Dactylifera* Seeds: Exploring Kinetic and Thermodynamic Parameters

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ABSTRACT

In this research work, *Phoenix dactylifera* seeds (PDS) was used as an adsorbent for the removal of Congo red dye from aqueous system. Congo red (CR), a typical anionic diazo dye is very difficult to remove from aqueous solutions because of it thermal physicochemical and optical stability which is due to it aromatic structure. Therefore, the removal of CR from aqueous solutions using low cost and sustainable biosorbent is highly necessary. The adsorbent was characterized using Fourier transform infrared spectroscopy (FTIR). The effect of various adsorption parameters such as initial dye concentration, adsorbent dosage, contact time, pH and temperature were optimized for maximum sorption of dye. It was found that percentage removal of the CR dye decreases as pH increases from acidic to basic region. Freundlich and Langmuir isotherms were applied for the interpretation of experimental data. The Langmuir isotherm model was found to give best fit for the adsorption with maximum adsorption capacity of 51.245 mg g^{-1}. The thermodynamic parameters such as Gibb's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were found to be −4.38 kJ/mol, 54.9 kJ/mol and 0.1836 kJ/mol/K respectively. The kinetic studies showed that the adsorption was best described by pseudo-second order kinetic model. The results of thermodynamic studies inferred that adsorption of CR onto *Phoenix dactylifera* seeds was highly feasible, spontaneous and endothermic.

Keywords: Adsorption, Biosorption, Congo red, Isotherms, *Phoenix dactylifera* seeds

INTRODUCTION

The fabric industry plays a vital role in the global economy. Asia accounts for the largest user of dye materials at about 92%, considering every type of dye and pigments manufactured, this would amount to close to over 90,000 tons (Mathur *et al*., 2003). China is the largest exporter of dye materials. Worldwide, on yearly basis, over 1,000,000 tons of synthetic dyes are manufactured for human consumption, and of which over 155,000tons are released into the habitat in wastewaters (Zollinger 1987). This release is as a result of the fact that during the dyeing process, not all dye molecules bind to the fabric. Depending on the class of the dye, the losses in wastewaters may vary from 5.5% for basic dyes to as high as 54% for reactive dyes, culminating in severe contamination of surface and underground waters in the environment of dyeing industries (Ghorai *et al*, 2014). Globally, over 350,000 tons of textile dyes are released in textile industrial effluent annually (Jin *et al*. 2007).

Generally, dyes are toxic chemical substance because, they affect living creatures in the water discharged as effluent into the surroundings (Ghaedi *et al*., 2013). The presence of synthetic dyes in industrial effluents decreases light penetration in water bodies and in turn affect the photosynthetic activities of the aquatic habitat, thereby leading to drastic shortage of food source for the aquatic organisms (Annadurai *et al.*, 2002). The presence of dye – constituted effluents in water bodies can drastically reduce the amount of dissolved oxygen in it, depending on the concentration of dye in the effluents (Nekouei *et al*., 2015). This could pose a great threat to the aquatic lives. Furthermore, dye-containing effluents increase biochemical oxygen demand within the environment (Ahmad *et al.*, 2014). Depending on the length of exposure and concentration, dyes can cause severe chronic health effects on living organisms. Long exposure to dyes may cause acute allergic dermatitis, skin irritation, cancer, mutation, etc (Nethaji *et al*., 2011).

Congo red is a direct diazo dye which often metabolized into benzidine. It causes allergic reaction in living organisms depending on the length of exposure (Hameed, 2009). It is toxic, harmful when inhaled or ingested and can potentially cause skin rashes. In some cases, it can result to kidney failure, and cancer (Miyah *et al.*, 2017). Hence, removal of this dye from wastewater systems is of paramount importance.

In order to safeguard the environment especially the aquatic lives, manufacturing industries are required to treat and render their industrial effluents harmless before dumping them into the water bodies (Mafra, 2013).

Conventional methods such as electrochemical oxidation, ion exchange, photo-degradation, chemical precipitation, electro-dialysis, ultra-filtration membrane separation etc. have been broadly employed overtime for the treatment of various grades of dye concentrations in wastewater systems (Gupta *et al.*, 2009). However, due to various difficulties associated with many conventional processes, adsorption process has been developed by many researchers as a moderate and cheaper alternative method (Pathania *et al*., 2014).

Adsorption is a popular separation technique among researchers in terms of simplicity of design, initial cost, insensitivity to toxic substances, ease of operation and capacity to render a sludge free cleaning operation (Kannan and Sundaram, 2001).

Recently, agricultural wastes have been broadly utilized for the adsorption of pollutants such as organic dyes, phenols, heavy metals and chlorophenols found in varied amounts in the effluents of the cosmetics, leather, paper, textile and dye manufacturing industries which are directly released into the water bodies (Dogan *et al*., 2007). Natural biosorbents such as banana peel, rice husk, wheat shell, orange peel, castor seed shell, soy meal hull, sawdust etc. have been widely employed for the adsorption of dyes from aqueous systems (Ansari *et al.,* 2010). Many of which are found to be efficient and environmental – friendly.

The aim of the present research work is to investigate the effects of contact time, initial dye concentration, pH, and adsorbent dose on the efficiency of the removal of Congo red dye from aqueous solutions using biosorbent derived from date seeds (*Phoenix dactylifera*). The experimental data obtained were evaluated using the pseudo-first-order and pseudo-second-order kinetic model, thermodynamic parameters and isotherm models (Langmuir and Freundlich). The chemical structure of Congo red dye is given in Figure (1).

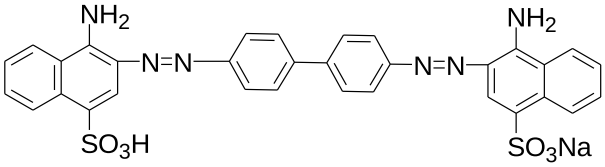

Figure 1: Chemical structure of Congo red dye

MATERIAL AND METHODS

Reagents and their preparation

Congo red dyes were collected from the Industrial Chemistry Laboratory, Bayero University Kano, Kano state, Nigeria. The sodium hydroxide (Heda Chemicals Private Limited, India) and sulphuric acid (Aarti Industries Limited, India) were obtained from the Chemistry Laboratory, Federal University Dutse, Jigawa State, Nigeria. All reagents employed in this research work were of analytical standard and high purity. Double distilled water was also used throughout the research work. The stock solution of the dye was made by dissolving 500 mg of Congo red dye in 1000 mL of double distilled water. Dye concentration and absorbance value during the experiment was determined at maximum wavelength of 590 nm using UV-vis spectrophotometer respectively.

Adsorbents collection and their preparation

Phoenix dactylifera seeds were obtained from Shuwarin village, Kiyawa Local Government Area of Jigawa State, Nigeria. The collected date seeds from the farm were allowed to dry for about two and a half months and the biomaterial was repeatedly washed with distilled water, which was then filtered off and dried in an oven at 90 °C overnight. The dried PDS obtained was crushed using a food processor. The crushed date seeds were then screened using sieves in the range of 1mm. The sieved particles were then stored in a desiccator until required.

Instrumentation

A UV–visible spectrophotometer (Infitek model SP-MUV5600, China) was used for the determination of dye concentration. The pH measurements were made using a pH meter (Kalstein model YR0125, France). Characterization of biosorbent was done using Fourier transform infrared spectrophotometer (Agilent technologies-Cary 630, Malaysia).

Characterization of Adsorbent

The FTIR spectra of PDS was conducted using Fourier transform infrared spectrophotometer. The samples were prepared using KBr disc method. The PDS was thoroughly mixed with KBr, powdered and a disc was formed as a result of the applied pressure. The absorption spectra were recorded in the range from 4000 to 400 cm^{-1}. A UV–visible spectrophotometer was used for the determination of dye concentration.

Characterization of PDS is necessary to understand the chemistry of the pore spaces on the adsorbent layer.

Batch Adsorption Experiment

The adsorption of dye onto PDS was carried out using batch adsorption experiments. The batch adsorption experiments were performed using sample bottles which contain the required amount of biosorbent and 50 mL of CR dye solution with th e initial concentration of 15mg/L. The resulting solution mixture was homogenized until equilibrium is attained, which was then filtered afterwards. To monitor variation in absorbance, small portion of the mixture were withdrawn into a cuvette at different intervals of time (20-170 minutes). All the experiments were conducted at room temperature and duplicated to ascertain the accuracy of data obtained. The pH of each solution was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. The mixtures were then agitated in an incubator shaker at 120 rpm and at 30-60°C until equilibrium was reached and the resultant mixtures were filtered. The equilibrium concentrations of dye in the solutions were measured at 497nm using UV-visible spectrophotometer. The adsorption capacities of the adsorbent and percentage removal of the dye at different intervals of time and at equilibrium were obtained from equations (1) and (2) respectively.

$$q_e = (C_o - C_e)\frac{V}{M} \qquad (1)$$

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \text{ x } 100 \qquad (2)$$

where C_o and C_e are the initial and equilibrium concentration of CR (mg/L), V is the volume of dye solution (L) and M is the mass of biosorbent (g). The experimental conditions were varied at initial dye concentration of 15 mg/l, adsorbent dosage of (200–1700 mg), pH of (2−12), temperature of (30-60°C) and contact time of (20–170 min).

Equilibrium Isotherm

The adsorption isotherms show the amount of dye adsorbed onto biosorbent and the equilibrium concentration of dye in solution at a given temperature (Panthania *et al.*, 2014). The relationship between equilibrium concentration and dye uptake can be obtained using Freundlich and Langmuir isotherms.

Langmuir Isotherm

The Langmuir isotherm is valid for adsorption at homogenous surface containing a finite number of biosorption or identical sites. The model assumes uniform distribution of energy level of adsorption onto the surface of the adsorbent and no transmigration of adsorbates in the plane of the surface (Barka *et al.*, 2011). The linear form of the Langmuir's isotherm model is given by equation 3 (Langmuir. 1918):

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \qquad (3)$$

Langmuir adsorption parameters can be determined by transforming the Langmuir equation, which is in linear form by the plot between C_e/q_e versus C_e (Eq 3) over the entire concentration range. Where q_e is the amount of CR adsorbed in mg/g of the adsorbent, C_e is the concentration of the dye solution at equilibrium (mg/L). Q_m and b are Langmuir constants related to the maximum adsorption capacity (mg/g) and the adsorption energy between the adsorbate and adsorbent (mg/L). The essential features of the Langmuir isotherm can be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant known as equilibrium parameter or separation factor (Foo, 2012).The values of R_L calculated from equation 4 show the nature of the isotherm as indicated in Table (1).

$$R_L = \frac{1}{1+bc_o} \qquad (4)$$

Where C_o is the initial concentration and b is the constant related to the energy of adsorption (Langmuir constant).

Table 1: Essential Features of the Langmuir Isotherm Separation factor (R_L)

Values of R_L	Type of Isotherm
$R_L > 1$	Unsuited
$R_L = 1$	Linear
$0 < R_L < 1$	Suited
$R_L = 0$	Bad

(Usman *et al.*, 2019)

Freundlich Isotherm

Freundlich isotherm is an empirical equation (5) which is employed effectively to study the heterogeneity of adsorption with non-uniform distribution of energy level (Zhao *et al.*, 2011). Freundlich isotherm describes reversible adsorption and is not restricted to the formation of monolayer. The amount of dye adsorbed per unit weight of adsorbent versus the concentration in the fluid in equilibrium is the empirical equation proposed by Freundlich (Gupta *et al.*, 2012):

$$\text{In}q_e = \text{In}K_f + \frac{1}{n}\text{In}C_e \qquad (5)$$

Where K_F and n are, Freundlich constants; q_e is the weight adsorbed per unit weight of adsorbent; C_e = concentration of dye at equilibrium. The constant K_F is an approximate indicator of adsorption capacity (mg/g), while 1/n is a function of the strength of adsorption respectively in the adsorption process. The values of K_F and n can be obtained from the plot of $\text{In}q_e$ *versus* $\text{In}C_e$. $\text{In}K_f$ and 1/n are equal to the intercept and slope of the plot respectively. The magnitude of the term (1 / n) gives an indication about the favourability of the sorbent/adsorbate systems (Malik, 2004).

Adsorption kinetics

Adsorption kinetics is employed to elucidate the mechanism of adsorption. Two kinetic models namely the pseudo first order and pseudo second-order are usually selected to describe the mechanism of adsorption.

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. The rate expression for pseudo-first order reaction can be described in equation (6) (Usman *et al.*, 2019):

$$\text{Log } (q_e - q_t) = \log q_e - \frac{k1t}{2.303} \qquad (6)$$

where q_e and q_t are the amount of dye adsorbed onto sorbent at equilibrium and time t (min) respectively. k1 (min^{-1}) is the rate constant of pseudo-first order adsorption. The value of k_1 and $\log q_e$ can be calculated from the slope and intercept of $\log (q_e - q_t)$ *versus* t respectively.

RESULTS AND DISCUSSION

Characterization of Adsorbent

The linear form of pseudo-second order can be presented as in equation (7) (Usman *et al.*, 2019):

$$\frac{t}{q_e} = \frac{1}{k2q_e^2} + \left(\frac{1}{q_e}\right)t \qquad (7)$$

where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg g^{-1}), k_2 is the overall rate constant of pseudo-second order sorption (g mg^{-1} min^{-1}). A plot of t / q_e against t gives a linear relationship, from which the value of q_e and k_2 can be determined from the slope and intercept respectively.

Thermodynamic Studies

In order to evaluate the thermodynamics of the dye removal process by PDS biosorbent, thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were analyzed (sadiq *et al.*, 2016). K_{ad} is used as the equilibrium constant because of its dependence on temperature. The following equations (8-11) were used to estimate the thermodynamic parameters.

$$K_{ad} = \frac{qe}{Ce} \qquad (8)$$

$$\Delta G^o = -RT \ln K_{ad} \qquad (9)$$

$$\text{In}K_{ad} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (10)$$

$$\Delta G = \Delta H^o - T\Delta S \qquad (11)$$

where q_e is the concentration of CR at equilibrium onto PDS (mg/L), R is the universal gas constant (8.314 J/mol K), and Ce is the CR concentration at equilibrium in the solution (mg/L). The values of ΔH and ΔS were determined from the slope and intercept of plot $\ln K_{ad}$ versus 1/T.

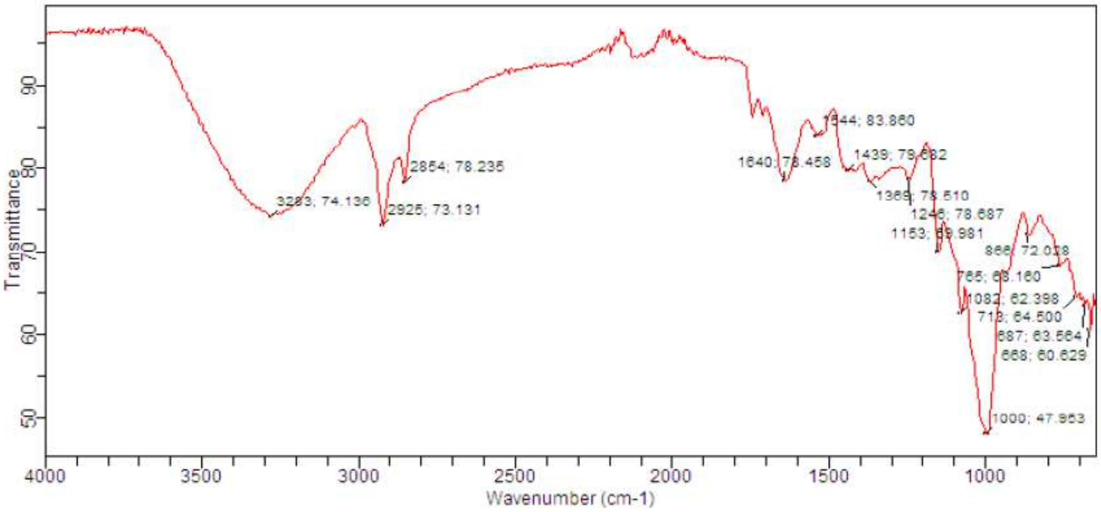

Figure 2: Fourier Transform Infra – Red (FTIR) Spectral of PDS before Sorption of CR

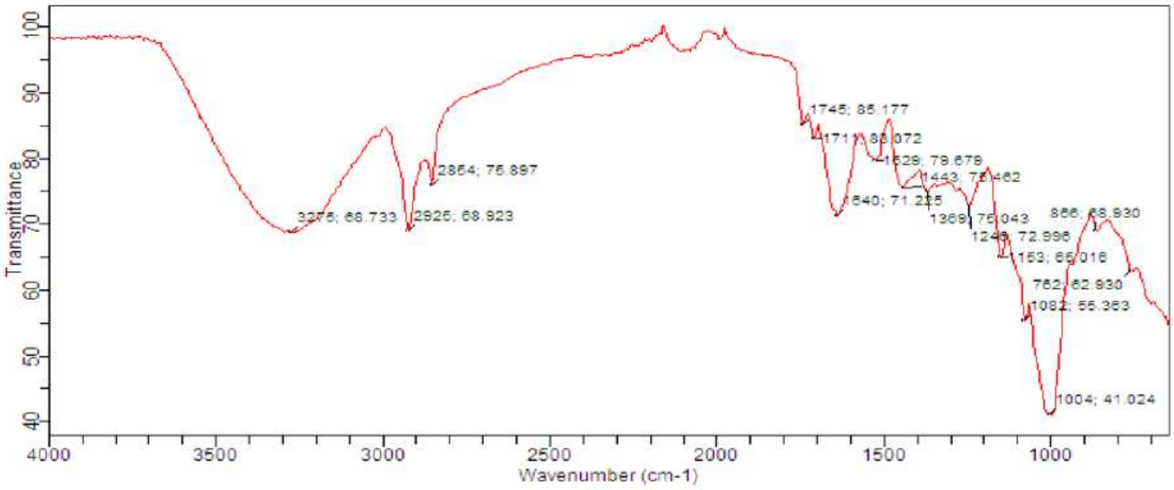

Figure 3: Fourier Transform Infra-Red (FTIR) Spectral of PDS after Sorption of CR

Table 2: Fourier Transform Infra-Red spectral characteristics of PDS before and after Sorption

Band position (cm^{-1}) Before adsorption	Band position (cm^{-1}) After adsorption	Suggested assignments
3283	3275	O-H or N-H broad vibrations
2923 and 2854	2923 and 2854	C-H stretching vibrations
1640 and 1544	1745 and 1711	C=O stretching vibrations of COOH, -COOR- or C=C
1439	1443	C-C stretching vibrations
1153	1153	C-N stretching vibrations
1082	1082	C-O stretching vibrations
1000	1004	C-O stretching vibrations
-	1529	C-C stretching vibrations
-	930	C-O stretching vibrations
-	1369	C-C stretching vibrations
-	1246	C-N stretching vibrations

(Usman *et al*., 2019 and Panthania *et al*., 2016**)**

Figure 2 and 3 show the FTIR spectrum of PDS before and after sorption of CR while table 2 show the band positions and the suggested assignments (functional groups) for each spectral of PDS before and after sorption of CR. Due to the level of interaction of the functional groups on the surface of adsorbent with Congo red dye, the peaks have moved to higher or lower wavelengths and new peaks which belongs to the adsorbate (or breaking of original bands) has appeared. The shifting of bands to higher frequencies suggests increase in bond strength, while a shift to lower frequencies indicates decrease in bond strength or bond weakening (Melo *et al*., 2010) The peaks at 3283 cm^{-1} shifted to 3275 cm^{-1}, while peaks at 1000 cm^{-1} shifted to 1004 cm^{-1}, 1439 cm^{-1} shifted to 1443 cm^{-1} and 1544 cm^{-1} shifted to 1745 cm^{-1} respectively after the sorption of Congo red onto *Phoenix dactylifera* seeds (Table 2). In Congo red-loaded *phoenix dactylifera* seeds (Figure 3), appearance of new peaks at 1529 cm^{-1} and 930 cm^{-1} was as a result of the introduction of new functionalities on the surface of adsorbent (Panthania *et al*., 2016).

The results of the effects of different operational parameters on the sorption of CR dye onto PDS were discussed as follows;

Effect of Adsorbent Dosage

The adsorbent dosages determine the capacity of adsorbent for a given initial concentration of the adsorbate (Kyzas *et al*., 2012). The effect of PDS dosage on the adsorption of Congo red dye was varied from 200 to 1700 mg at 15 mg/l concentration of the adsorbate. Figure 4 illustrates the effect of adsorbent dosage on the sorption of Congo red dye. It was evident that Congo red dye removal increased proportionately with adsorbent dosage and that is due to the availability of more active sites and greater surface area (Yu *et al*., 2010). After 700 mg of adsorbent loading, there was no significant removal of Congo red dye observed. This may be due to the conglomeration of adsorbent particles, as there is significant decrease in effective surface area (Barka *et al*., 2011, Pathania *et al*., 2016). Therefore, 700mg was chosen as the optimum adsorbent dosage for further study.

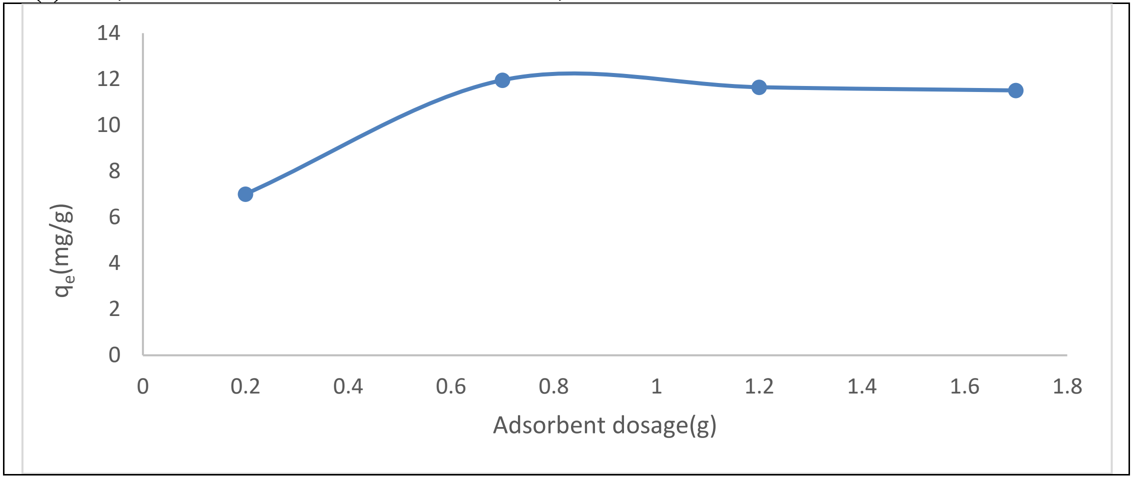

Figure 4: Effect of Adsorbent dosage (g) against Adsorption capacity q_e (mg/g)

Effect of Contact Time

The effect of contact time on the sorption process was investigated at 15 mg/l dye concentration from 20 to 170 minutes. 1000 mg adsorbent dosage was utilized for this experiment. Figure 5 shows the effect of contact time on the removal of CR dye. The adsorption efficiency increased from 46.7 to 87.7%, as the contact time varied from 20 to 170 minutes. The sorption process decreased after 120 minutes. So, based on results, 120 minutes was taken as equilibrium time in the sorption process. This may be as a result of rapid or spontaneous adsorption of Congo red dye by the surface of adsorbent, followed by slow diffusion of ions from the surface to the adsorption sites in the micropores which are less accessible (Wang *et al*., 2011).

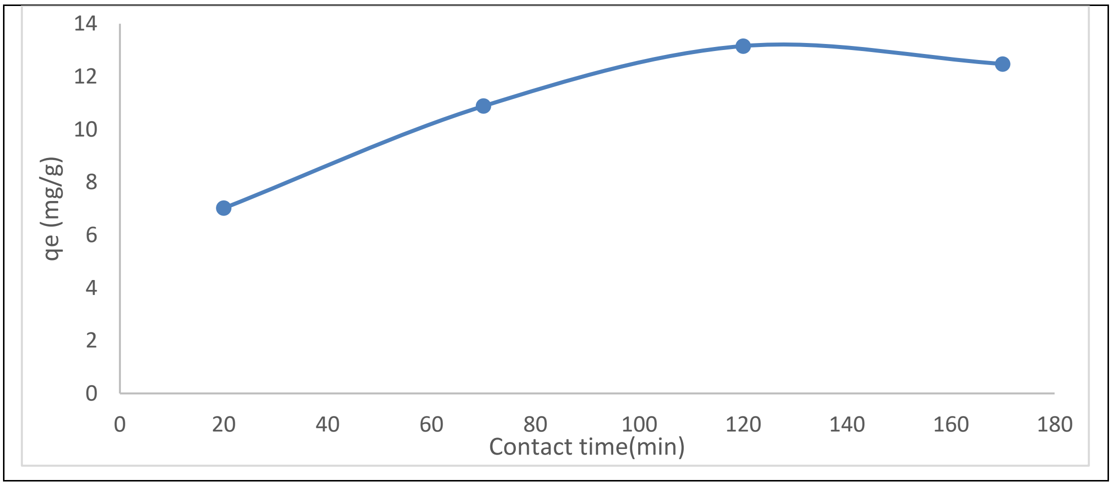

Figure 5: Graph of Contact time(min) against Adsorption capacity q_e (mg/g)

Effect of pH

The pH of dye solution is an important parameter for the complete sorption of CR dye onto the adsorbent (Amel *et al*., 2012). The effect of pH on the sorption process was studied between pH range of 2 to 12. Figure 6 illustrates the effect of pH on the sorption of CR dye onto the adsorbent (*Phoenix dactylifera* seeds). Maximum removal of 81.7% CR dye occurred at pH 2.0 which is then followed by significant decrease in % removal with increasing pH. It can be assumed that at pH 2.0, there is increase in the hydrogen ion concentration in the system which enables the surface of the adsorbent to acquire more positive charge by absorbing the hydrogen ions in the solution system (Oladoja *et al*., 2008). This implies that, at low pH, there is high electrostatic attraction between the positively charged surface of the adsorbent and Congo red dye (anionic dye molecule) resulting to maximum sorption of dye. Meanwhile, at higher pH, CR anions completely detached away from the negatively charged surface of the adsorbent, hence decreasing the sorption of dye (Pereira *et al*., 2010).

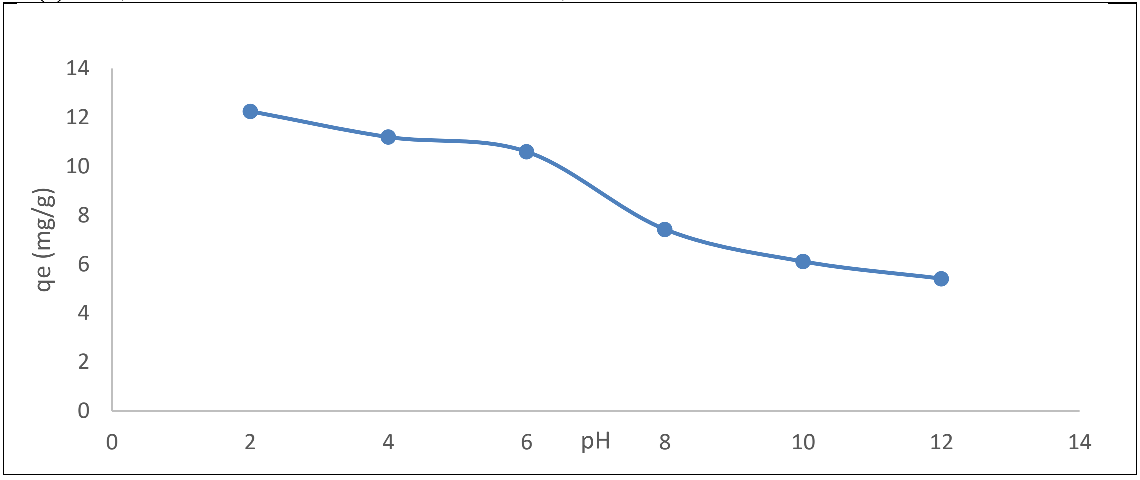

Figure6: Graph of pH against Adsorption capacity q_e (mg/g)

Effect of Temperature

Temperature has pronounced effect on the overall sorption of dye because equilibrium capacity of adsorbent to adsorb the adsorbate changes with temperature. The effect of temperature determines whether the ongoing adsorption process is endothermic or exothermic (Feng *et al*., 2012). The effect of temperature on the sorption process was carried out under the following operational parameters: dye concentration (15 mg/L), sorbent dosage (1000 mg), contact time (170 min) and pH of solution (2.0). Figure 7 shows that the removal of Congo red dye increased with increasing temperature and maximum adsorption was achieved at 60°C, indicating that the sorption process is endothermic in nature (Chamathy *et al*., 2001). It was very clear that percentage removal increased from 61.1% to 78.8% with increasing temperature indicating that the adsorption process is feasible. This could be due to the increase in the rate of diffusion of adsorbate molecules across the external layer and internal pores of the adsorbent particle (Huang *et al*., 2009).

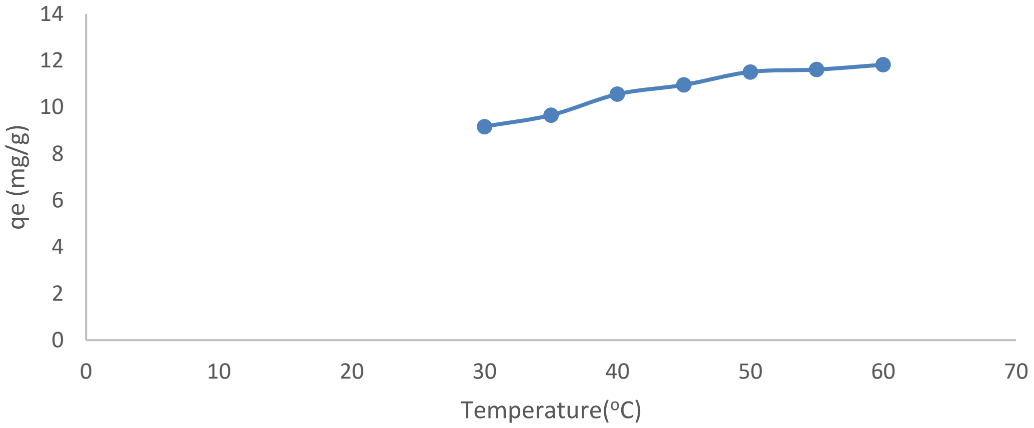

Figure7: Graph of Temperature against % Removal

Adsorption Isotherms

Langmuir Isotherm

The Langmuir isotherm shows that; adsorption takes place at homogeneous sites with the formation of monolayer. It shows that there is uniform energy distribution throughout the surface of the adsorbent (Bharathi, 2012). Figure 8 shows Langmuir isotherm from which the value of the maximum adsorption capacity (Q_m) and adsorption energy (b) were obtained. The maximum sorption capacity (Q_m) was found to be 51.245mg/g. The higher value of correlation coefficient, R^2 (0.9994) indicates a favorable adsorption as shown in Table 3. It implies a monolayer formation and uniform distribution of CR on the surface of adsorbent.

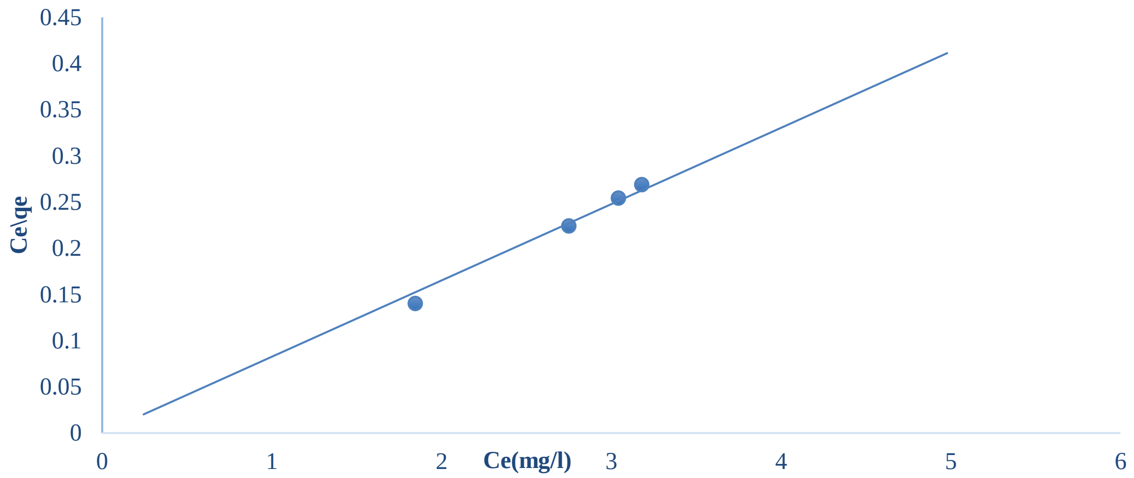

Fig. 8: Langmuir isotherm model for the sorption of CR dye onto PDS

Freundlich Isotherm

This is an empirical equation which is used for heterogeneous sorption of energy system. It shows a non – uniform distribution of energy throughout the surface of adsorbent (Noroozi, 2008). The values for different parameters were obtained from the linear correlations of lnq_e versus lnC_e (Figure 9). From Freundlich isotherm, adsorption capacity (k_f), adsorption strength (n) and R^2 were found to be 42.8233, 8.1813 and 0.9952 respectively as shown in Table 3. It is confirmed that the value of $n > 1$ shows a favorable adsorption (Ghaedi *et al.*, 2013). The value of 1/n is known as heterogeneity factor which ranges between 0 and 1. For more heterogeneous surfaces, the value of 1 / n must be close to 0. The value of the correlation coefficient (R^2) shows that Langmuir model is better fitted for the adsorption than Freundlich model. Table 3 shows the summary of isotherm model parameters for the sorption of CR dye onto PDS.

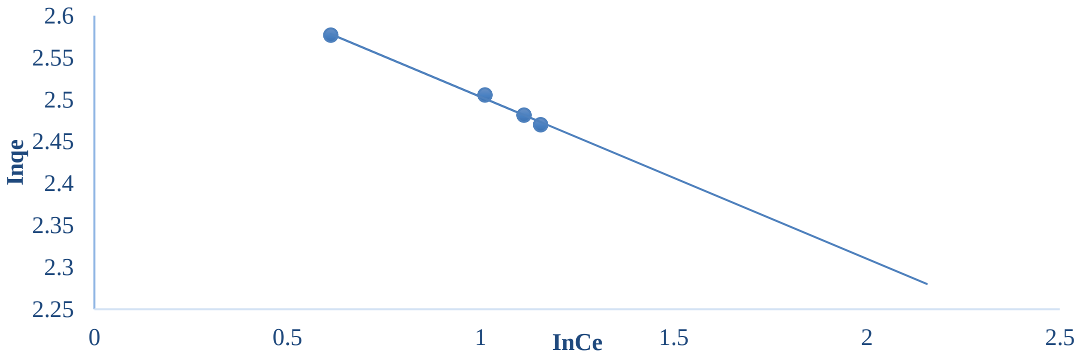

Figure 9: Freundlich isotherm model for the sorption of CR dye onto PDS

Adsorption Kinetics

Kinetics models are important parameters for the evaluation of the time required for the removal of dye and the mechanisms involved in the adsorption process (Lin *et al*., 2011). The pseudo-first order and pseudo-second order kinetic models were tested for the adsorption of CR onto the PDS and the results were shown in figure 10 and 11 respectively. The values of q_e (13.3689), R^2(0.9998) and k_1(0.0874) obtained from the pseudo – second order kinetic are higher as compared to those obtained from pseudo – first order kinetic model q_e (7.2028), R^2 (0.9669) and k_1 (0.01497) as shown in Table 4. So, from the correlation coefficient (R^2) obtained from the two kinetic models (pseudo-first and second order), it is evident that the adsorption of CR dye onto PDS follows the pseudo-second order kinetic model (Figure 11). Thus, this indicates chemisorption could be the rate - determining step for the adsorption (Miyah, 2017). Table 4 shows the summary of kinetic parameters for the sorption of CR onto PDS.

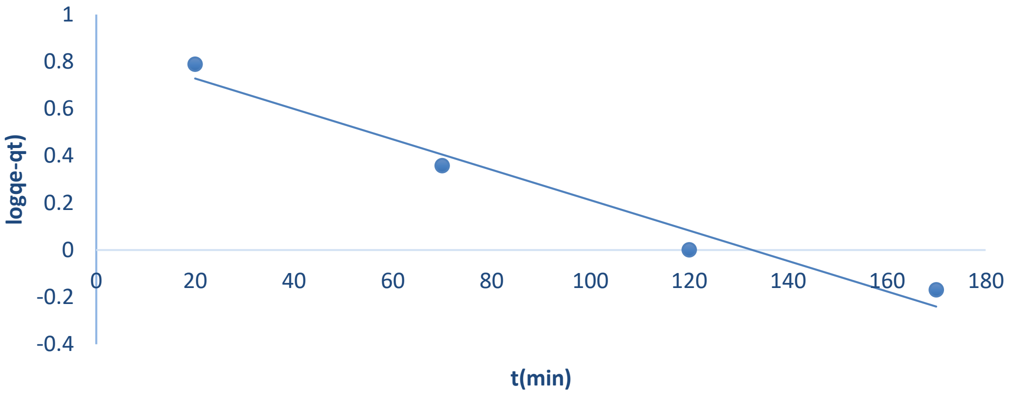

Fig. 10: Pseudo – first order kinetic model

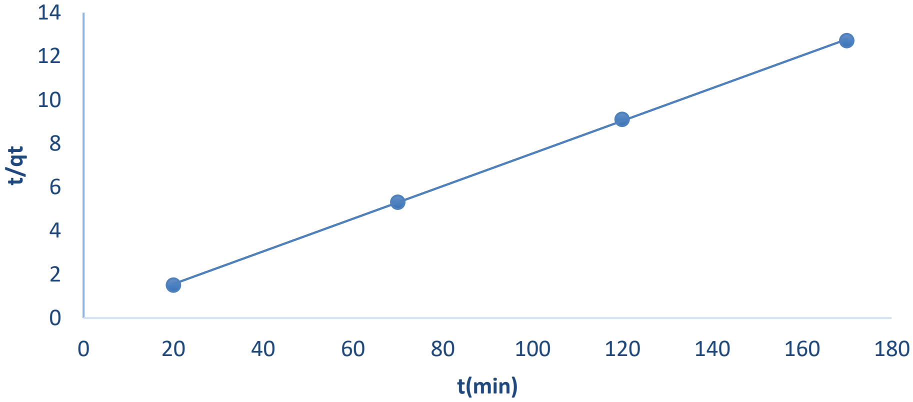

Fig. 11: Pseudo – second order kinetic model

Adsorption Thermodynamics

The negative value of Gibbs free energy (ΔG) indicated that the sorption process was feasible and spontaneous in nature and the degree of spontaneity increased with temperature (Fig. 12). The positive value of ΔH (54.9 kJ/mol) indicated that the sorption of CR onto PDS was endothermic as shown in table 5. Further, the positive value of ΔS (0.184 KJ mol^{-1} K^{-1}) inferred . an increase in the freedom of adsorbate ions and randomness at the solid–liquid interface during the sorption of CR onto PDS (Sadiq *et al*., 2016). Table 5 shows the thermodynamic parameters for the biosorption of CR onto PDS at different temperatures while table 6 shows the adsorption capacities of various biosorbents for the removal of CR with different experimental conditions as compare to the present study.

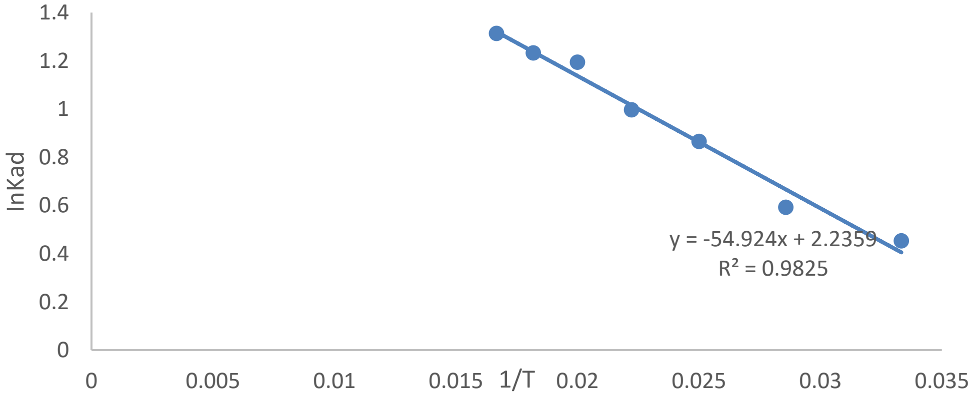

Fig. 12: Plot of lnK$_{ad}$ against 1/ T for the removal of CR by PDS

Table 3: Summary of isotherm model parameters for the sorption of CR dye onto PDS

Parameters	Langmuir isotherm	Parameters	Freundlich isotherm
Q_m(mg g^{-1})	51.245	K_f	42.233
R^2	0.9994	R^2	0.9952
b(l/mg)	14.775	n	8.1813
R_L	0.0174		

Table 4: Summary of kinetic parameters for the sorption of CR onto PDS

Parameters	Pseudo-first order	Parameters	Pseudo-second order
q_e(mg g^{-1})	7.2028	q_e (mg g^{-1})	13.3689
R^2	0.9669	R^2	0.9998
K_1(min^{-1})	0.01497	K_2 (g mg^{-1} min^{-1})	0.0874

Table. 5: Thermodynamic parameters for the biosorption of CR onto PDS at different temperatures

Adsorbent	Temperature(K)	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS (kJ/ (mol K)
PDS	303	-0.71	54.9	0.184
	308	-1.62		
	313	-2.54		
	318	-3.46		
	323	-4.38		
	328	-5.29		
	333	-6.21		

Table 6: Comparison of Biosorption Capacities of Various Biosorbents for the Removal of CR with Different Experimental Conditions

Biosorbent	Adsorption capacity, (q) mgg^{-1}	Temperature, °C	pH	Concentration, C_o, mgL^{-1}	Reference
Magnetic cellulose (Fe_2O_4) activated carbon	66.09	25 – 55	4 – 9.5	70	M. Toor, 2012
Biogas-waste slurry	9.5	25	2.3 – 9.4	15 – 25	G. Gryglewicz, 2007
Kaolin	5.60	25 – 60	3 – 11	150 – 1000	Z. Zhang, 2007
Ag nanoparticles	66.7	10 – 60	4 – 7	15 – 25	B. Jin, 2010
Egg shells	69.45	40	6	50	S. Ray, 2006
Rice husk	14	-	2 – 10	10 – 50	Kadir, 2009
Aspergillus carbonarius	67.2	18 – 36	3 – 4.5	25	Hellel, 2017
Penicillium glabrum	53.4	18 – 36	3.0 – 4.5	25	Yeddou, 2017
Aspergillus niger	14.72	-	2.0 – 9.0	15	Z. Aksu, 2005
Orange peel	22.4	-	2 – 10	25	Mittal, 2006
Phoenix dactylifera seeds	51.245	30 – 60	2 – 12	15	**Present study**

CONCLUSION

Conclusively, the work shows the possibility of using date seeds for the uptake of Congo red dye in aqueous systems. The operating parameters for optimum sorption were determined as follows: adsorbent dosage (700 mg), contact time (120 min), pH of solution (2.0) and temperature (60 °C). The equilibrium adsorption quantity of CR dye onto PDS was appropriately described by the Langmuir isotherm model with a maximum monolayer capacity of 51.245 mg g^{-1}. The rate of sorption was found to obey the pseudo-second order kinetics with good correlation coefficient which suggests that the adsorption mechanism could be chemical in nature. The results of the thermodynamic study inferred that adsorption of CR onto PDS was highly feasible, spontaneous and endothermic. Additionally, the results suggest that PDS, which is a readily-available and eco-friendly biomaterial, may be used as a low-cost, biosorbent for the removal of dyes from aqueous systems.

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