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Removal of inorganic ferric ion from water by using coal of date Palm Seeds (CDPS)

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ABSTRACT

The inorganic ferric ion has been successfully removed from water by adsorption onto *Coal of Date Palm Seeds (CDPS)*. The adsorption experiments are carried out by a batch technique. The influences of adsorption conditions, such as initial concentration of ferric ion (30, 50, 100, 150 and 200 mg L^{-1}), the dosage of CDPS (2, 6, 10., 20, 30, 40 and 100 g L^{-1}), temperature (25, 35 and 45 ºC) and contact time (0 – 180 min.) have been taken in consideration. The results showed that the adsorption percentage increases as the dosage of CDPS and temperature increases; meanwhile, it decreases with increasing the initial concentration of ferric ion in water. The maximum percentage removal achieved is 92 %. Depending on the adsorption thermodynamic model, the adsorption mechanism of aqueous ferric ion onto CDPS follows Freundlich isotherm model ($R^2 = 0.986$). The capacity (K_f) and intensity (n) of Freundlich adsorption are 2.119 and 0.377, respectively. The results reveal that the adsorption mechanism of ferric ion on CDPS solid particles is chemisorptions, heterogeneous multilayer, unfavorable (R_L = 1.609) and spontaneous in nature (ΔG = – 19.927 kJ mol^{-1}). Adsorption of ferric ion onto CDPS solid particles has achieved Lagergren pseudo-second order model (R^2 = 0.999 approx.). The kinetic parameters, rate constant, and sorption capacities have been calculated. The new information in this study suggests that CDPS could be used as a novel filtering materials for removing ferric ions from water.

Keywords: *Ferric ion, Coal, Date Palm Seeds, Adsorption, Freundlich, pseudo-second order.*

1. INTRODUCTION

Several technologies are applied for the removal of pollutants from wastewaters such as precipitation, ion exchange, membrane filtration, reverse osmosis and adsorption [1,2]. Adsorption technique is one of the best techniques used to remove both inorganic and organic pollutants from the aqueous medium [3]. Several adsorbents are used and reported such as, activated alumina, limestone, metal oxides, zeolites, clays, biosorbents, naturally occurring materials and agro-industrial wastes [4].

Recently, the adsorption technique has acquired a great significance in terms of using carbon in the purification of water on an industrial level. Commercial carbon is used widespread as adsorbent for producing pure water [5-6]. The utilization of the commercial activated carbon is restricted due to its high cost and non-renewability. So, it becomes a growing demand for carbon production from renewable sources. This objective is achieved by the conversion of low-cost materials such as agricultural residues and by-products to the carbonaceous material [7].The most common agricultural by-products are date stones [8], rice husks [9], waste apple pulp in cider production [10] and grain sorghum [11]. Wherein, the preparation of their carbon is expected to be low, safe, renewable source and available in a huge quantity [13-14].

Kingdom Saudi Arabia is considered to be the largest producer of dates in the world. There are more than 25 million trees producing various kinds of dates, which represent 15% of total world production [14].

Where the industry of dates produces large quantities of agricultural waste that can be exploited and converted for the production of coal, for example Dates palm seeds (DPS) [15]. Currently, they convert the DPS to the coal; and then they can use this coal in the field of energy [16]. However, some researchers directed towards the use of this coal for the environmental purposes in terms of water purification and wastewater treatment. This is due to several reasons, such as the quantity availability, low cost and economic feasibility, high efficiency and safety.

The adsorption of organic pollutants such as dyes, phenol, pesticides, and miscellaneous pollutants from water and wastewater by activated carbon has been documented [17-21]. In another respect, the activated carbon has also the ability to remove metal ions from aqueous solutions, for example, Cu^{2+}, [3,21], Cd^{2+} [22], Pb^{2+} [23], Cr^{6+} [24], and Zn^{2+} [25]. However, the sorptive capacity of activated carbons of date seeds towards heavy metals is rather low. To our best knowledge, no study has been reported to remove high-level ferric ions from the aquatic systems. In addition, no study has been done concerning the adsorption behavior of ferric ion on the Coal of Date Palm Seeds (CDPS). This knowledge can be supported by the information that have been gotten from the recently published review [26], as well as searching through the databases.

The main objective of this study is to use *Coal of Date Palm Seeds* (CDPS) as a low cost adsorbent to remove high-level ferric ions from a solution model of polluted aquatic system. Sorption process has been applied under different operating conditions, including dosage effect, initial concentration of ferric ion effect, and temperature effect.

Kinetic models are used to understand the sorption mechanism. Sorption isotherms are attained to assess the viability of the adsorption process as well as equilibrium behavior.

2. EXPERIMENTAL SECTION

2.1. Material and methods.

2.1.1. Coal of Date Palm Seeds (CDPS).

The *Date Palm Seeds*(DPS) were obtained locally from the Saudi Arabian region (Hail City). We have used one type of date seeds (Barhy-type) in our experiments.These seeds were washed with distilled water and dried at room condition. They were washed three times by *n*-hexane and then dried at room temperature. After drying, the DPS were burned (450 ºC) in the absence of oxygen for three hours to produce *Coal of Date Palm Seeds*(CDPS). They were crushed and grinding into powdered form. The powder of the CDPS was screened into several size fractions in the range of 150 - 180 μm using standard Tyler screen series.

In the present study physical and chemical treatment was undertaken. However, the chemical compositions are ash content (1.1 ± 0.1 %), lignin (23 ± 3.1 %), holocellulose (75 ± 1.5%), -cellulose (20 ± 1.8%) and hemicelluloses (55 ± 1.5 %) [26].

2.1.2. Reagents.

All chemicals were used as received as analytical grade. Ferric ion salt of $Fe(NO_3)_3.6H_2O$ was purchased by commercial providers from Fluka Chemika. The HNO_3 and HCl were purchased from Merck. Stock solution (1000 mg L^{-1}) of ferric ion was prepared by dissolving exact amount of ferric salt (±0.01 g) in 1000 mL ultrapure deionised water (18 Ω cm). The standard model solutions of 30-200 mg L^{-1} were prepared by appropriate dilution.The initial pH of the solution was adjusted using 1% HNO_3 for all experiment runs.

2.2. Apparatus and instruments.

Atomic Absorption Spectrophotometer, AAS, (Model AA 100, Perkin-Elmer) was used to analyze the concentration of the ferric ion in aqueous solution. The pH of all solutions was recorded by a pH meter (Oiron 520). The temperature was controlled using a temperature controller (Gefellschaft Funn 1003, ±0.1 ºC). Isothermal shaker was also used (Gefellschaft Fur 978). Analytical balance is used with ± 0.0001 mg (Sartorius, CP324-S/ management system certified according to ISO 9001).

2.3. Equilibrium studies.

The uptake of ferric ion was calculated from the mass balance, which was stated as the amount of ferric ion adsorbed onto CDPS. It equals the amount of ferric ionremoved from the aqueous solution. Mathematically, it can be expressed by equations 1-2 [27]:

$$q_e = \frac{(C_i - C_e)}{S} \qquad (1)$$

$$q_t = \frac{(C_i - C_t)}{S} \qquad (2)$$

where, q_e is the ferric ion amount adsorbed on the CDPS surface at equilibrium (mg g^{-1}); q_t is the ferric ion amount adsorbed on the CDPS surface at a specific time (mg g^{-1}); $C_i$is the initial concentration of ferric ion in the aqueous solution (mg L^{-1}); C_e is the equilibrium concentration or final concentration of ferric ion in the aqueous solution (mg L^{-1}); and $C_t$is the final concentration of ferric ion in the aqueous solution (mg L^{-1}) at a specific time, *t*,.

The dosage (slurry), S, concentration of CDPS is expressed by equation 3:

$$S = \frac{m}{v} \qquad (3)$$

where, v is the initial volume of ferric ion solution used (L) and m is the mass of CDPS adsorbent.

The adsorption percentages (%) are calculated by equation 4:

$$\%\ \text{Adsorption} = \frac{C_i - C_e}{C_i} \times 100\% \qquad (4)$$

The simplest and most common method of estimating contaminant retardation is based on the distribution coefficient, K_d. The K_d parameter is a factor related to the partitioning of a contaminant (Fe^{3+} ions) between the solid (CDPS adsorbent) and aqueous phases.

The partition coefficient, K_d, is defined as the ratio of ferric ion quantity that adsorbed per mass of NCF to the amount of ferric ions remaining in the solution at equilibrium.

The distribution ratio (K_d) is calculated by using equation 5:

$$K_d = \frac{\text{amountof Fe(III)in adsorbent}}{\text{amountof Fe(III)in solution}} \times \frac{1}{S} \qquad (5)$$

Furthermore, the adsorption percentages and K_d(L g^{-1}) are correlated by equation 6 [28]:

$$\%\ \text{Adsorption} = \frac{100K_d}{K_d + 1/S} \qquad (6)$$

2.4. Sorption studies and measurements.

2.4.1. Effect of contact time.

Adsorption measurements were made by a batch technique at a temperature of 45 ºC (± 1 ºC). The stopper plastic flasks containing 50 mL of initial concentrations (C_i = 50 mg L^{-1},pH_i = 1.15) of Ferric ion and 10 g L^{-1} of CDPS were shaken vigorously using thermostatic mechanical shaker (300 rpm) for a known period in the interval of 5 to 180 min with increment of 10 min from 10 to 60 min then 30 min from 60 to 120 min and then 60 min from 120 min to 180 min. At the end of the equilibrium, the flasks were removed from the shaker and then the supernatant solution from each flask was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed by AAS. All the reported results were the average of at least triplicate measurements.

2.4.2. Effect of initial concentration

Adsorption measurements were made by a batch technique at a temperature of 45 ºC(± 1 ºC). The stopper plastic flasks containing 50 mL of different initial concentrations (C_i = 30, 50, 100, 150 and 200 mg L^{-1}) of ferric ion and 10 g L^{-1} of

CDPS -adsorbent were shaken vigorously using thermostatic mechanical shaker for 3.0 h. The agitation speed (300 rpm) was kept constant for each run to ensure equal mixing. At the end of the equilibrium time, the flasks were removed from the shaker and then the supernatant solution from each flask was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed by AAS. All the reported results were the average of at least triplicate measurements.

2.4.3. Effect of dosage.

The adsorption experiments were carried out by a batch technique at a temperature of 45 ºC (± 1 ºC). Different doses of CDPS (2, 6, 10, 20, 30, 40 and 50 g L^{-1}) were placed in a 100 mL stopper plastic flask containing 50 mL of aqueous ferric ion (C_i = 50 mg L^{-1}).The solutions were shaken vigorously by using a thermostatic mechanical shaker for 3.0 hours. The agitation speed (300 rpm) was kept constant for each run to ensure equal mixing.

At the end of the equilibrium, the flasks were removed from the shaker, and then the solution was filtered using filter paper (Whatman No. 41). The filtrate supernatant solutions were analyzed by AAS. All the reported results were the average of at least triplicate measurements.

2.4.4. Effect of temperatures.

The adsorption experiments were carried out by shakingvigorously thestopper plastic flasks containing 50 mL of 100 mg L^{-1} of ferric ion and 10 g L^{-1} of CDPS by using thermostatic mechanical shaker at constant contact time (3 hours) and agitation speed (300 rpm) with varying temperatures (25, 35 and 45 ºC). At the end of the equilibrium time, the flasks were removed from the shaker, and then CDPS solid was filtered using filter paper (Whatman No. 41). The filtrate supernatant solutions were analyzed by AAS. All the reported results were the average of at least triplicate measurements.

2.4.5. Equilibrium studies.

The isotherm experiments were conducted by using 50, 100, 150, and 200 mg L^{-1} of ferric ion solutions. The initial pH was adjusted using 1% HNO_3 solution. The mixtures containing 0.5 g CDPS and 50 ml of ferric ion solutions were stirred under the shaking conditions of 300 rpm, 180 minutes and 45 °C. Afterwards, the flasks were removed from the shaker, and then CDPS solid was filtered by filter paper (Whatman No. 41). The filtrate supernatant solutions were analyzed. All the reported results were the average of at least triplicate measurements.

2.4.5. Kinetic studies.

For the kinetic studies, a number of samples containing 0.5 g CDPS and 50 ml of ferric ion solutions (C_i = 50 mg L^{-1}) were placed in the 100 ml flasks. The initial pH was adjusted using 1% HNO_3 solution. These flasks were agitated using a temperature-controlled shaker (T = 45 °C) at 300 rpm for 180 minutes. Afterwards, the flasks were removed from the shaker atevery 10 minutesinthefirst60minutes and then 30 minutesuntil the end of180minutes. The CDPS solid was filtered using filter paper (Whatman No. 41). The filtrate supernatant solutions were analyzed. All the reported results were the average of at least triplicate measurements.

3. RESULTS SECTION

3.1. Sample collections.

The water resources contain varying proportionsof iron (Fe^{2+} and Fe^{3+}) ions, starting fromlowtohigh level. The low level is found in many collected samples starting from 12.2 mg L^{-1}(of industrial wastewater) and 0.80 - 0.075 mg L^{-1} (of tap-water) (see Figure 1). For this we have used 30 – 200 mg L^{-1} to achieve the current and future requirements. The ICP-MS was used to analyze the lower concentration level, while the AAS was used to analyze the higher concentration.

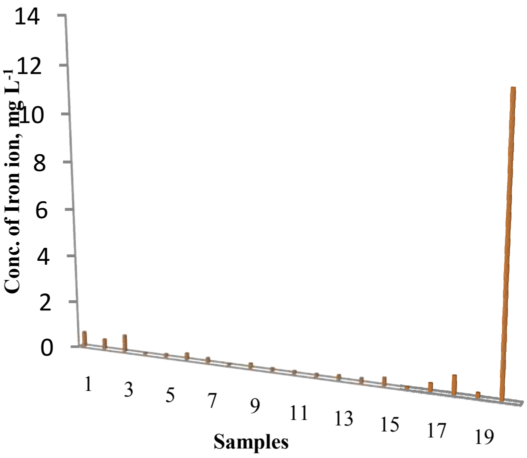

Figure 1. Iron ion concentration in variant collected samples of tap water (Hail City, KSA).

3.2 Preparation and activation of CDPS

The prepared CDPS powders are chemically activated by soaking at ambient temperature in H_3PO_4 (85 wt. %) to an acid concentration 70 % for 16 h. The CDPS powders were then heated in a furnace (105–110 °C) for 24 h. After heating, they were crushed and sieved again for a size distribution of 150 - 180 µm.

The most functional groups that present in the Date seeds are, as shown in the FTIR, O-H stretch functional groups can be seen by the band at 3342.7 cm^{-1} while the C-H stretch (alkane) is indicated by 2928.3 cm^{-1} and the C-H stretch appears at 2845 cm^{-1}. The rest of the functional group ranges between C=O, C=C, C-N, P=O and =C-H bending. The main functional groups are O-H stretching.

(a) (b) (c)

Figure 2. Source of Date Palm Seeds(a & b). Coal Date Palm seeds (c).

Wherein, these functional groups form an active site for sorption on the surface of the material. Our result is found matching with the reported one [29].

3.3. Dosage Effects.

Figure 3 clarifies the removal percentage of the ferric ion from the aqueous solutions using different dosages of CDPS-adsorbent (2, 6, 10, 20, 30, 40 and 100 g L^{-1}). Where,it showsthat the removal percentage increased with increasingdoses ofthe CDPS -adsorbent.

This behavior is expected because of the increase in dose lead to increased surfaces of adsorption, and thus increases the numbers of the ferric ions that attached to adsorbent surfaces. These results in Figure 3 show that the maximum and the minimum removal of ferric ion onto CDPS-adsorbent is 76 % (approx.). This result behavior is found in agreement with the other one reported [30].

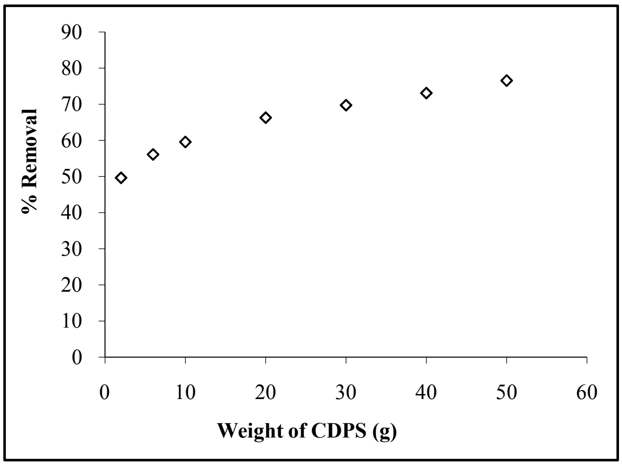

Figure 3. The effect of Dosage of the Coal of Date Palm Seeds (CDPS) (T = 45 °C, C_i = 50 mg L^{-1}, pHi = 1.15, rpm = 300, t = 180 min).

3.4. Effect of initialconcentration.

The effect of ferric ion concentration on the sorption system was investigated between 30 and 200 mg L^{-1}. Figure 4 shows the percentages of removal of variant concentration of ferric ion by using 10 g L^{-1} of CDPS- adsorbent at 45 °C and 180 min of contact time. It shows that the percentage of removal decreases with the increase in the initial concentration of the solutions.

For example, the removal percentage was 89 % using low level concentration (30 mg L^{-1}); while it was 76% using high-level (200 mg L^{-1}). At high-level concentrations, the available sites of adsorption become fewer.

The presence of high amount of ferric ion creates a highly competitive on the pores and cracks of the adsorbent particle surfaces.

This makes the surface of the adsorbent closes faster by large numbers of ferric ion, resulting in leaving many sites in the adsorbent that cannot adsorb any more of iron ion.

3.5. Effect of temperature

Figure 5 shows the percentages of removal of 50 mg L^{-1} of ferric ion solution by using 10 g L^{-1} of CDPS- adsorbent and 180 min of contact time at varying temperatures (25, 35 and 45 °C). The maximum removal percentage was 81% (approx.) and achieved at 45 °C, while the lowest percentage was 55 % (approx.) at a temperature of 25 °C. This is due to the increase in temperature leads to accelerate the speed of ferric ion that can be transferred from a bulk solution to the adsorption sites. Thus, the ferric ion can be activated and then hasten the interaction between ferric ion and adsorbing sites [31-33].

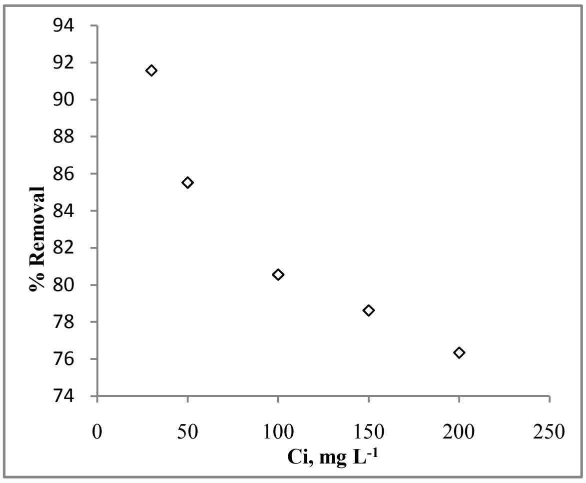

Figure 4. The effect of initial concentration for adsorbing ferric ion onto CDPS -adsorbent (T = 45 °C, C_i = 30, 50, 100, 150 and 200 mg L^{-1}, pHi = 1.15, rpm = 300, adsorbent dosage = 10 g L^{-1}, t = 180 min).

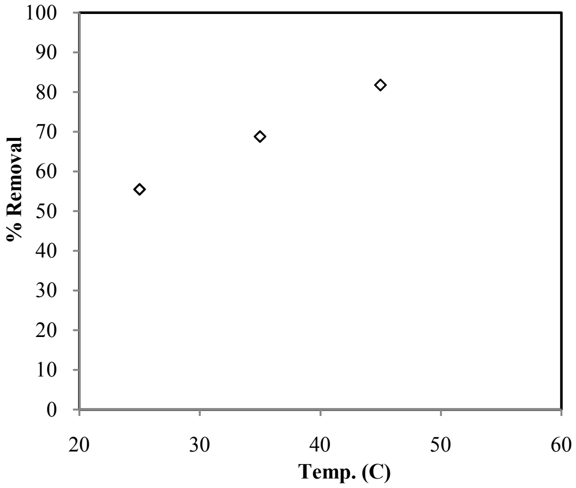

Figure 5. The effect of Temperatures (T = 25, 35, and 45 °C, C_i = 50 mg L^{-1}, pHi = 1.15, rpm = 300, adsorbent dosage = 10 g L^{-1}, t = 180 min).

3.6. Isotherm Modeling.

The experimental data for the adsorption equilibrium are analyzed by well-known isotherms, such as the Langmuir and Freundlich sorption models. The linear form of the Langmuir model [34] is given by Eq. 5:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{1}{q_{\max}} C_e \qquad (5)$$

A plot of C_e/q_e versus C_e, gives a straight line of slope $1/q_{\max}$ and intercept $1/(q_{\max} b)$ as shown in Figure 6. It can be seen that the isotherm data have yielded excellent fits within the Langmuir isotherm based on its correlation coefficient value (R^2 = 0.904). The value of maximum adsorption capacity, q_{max},and adsorption affinity, b, were calculated to be 23.8 mg g^{-1} and 0.03286 L mg^{-1}, respectively. The calculated q_{max} and b in the laboratory scale has a good capacity of adsorbent and stronger adsorption affinity of ferric ion for adsorbing on CDPS.

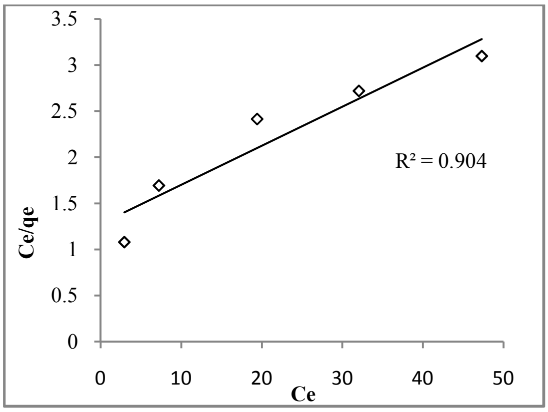

Figure 6. The linearized Langmuir isotherm for the adsorption of Fe^{3+} ions onto CDPS (dosage = 10 g L^{-1}, Temperature = 45 ºC, agitation speed = 300 rpm, and contact time = 180 minutes, C_i = 50 mg L^{-1}, pHi = 1.15).

In other words, the linearized Freundlich isotherm model is expressed as in Eq. 6 [35]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (6)$$

The Freundlich constants K_f and n indicate the adsorption capacity and the adsorption intensity, respectively. They are calculated from the intercept and slope of the $\ln q_e$ vs. $\ln C_e$ plot (see Figure. 7). It can be seen that the Freundlich model fitted the experimental data well, rather than a Langmuir isotherm model based on its correlation coefficient value (R^2 = 0.986). This indicates for the heterogeneous assembly of ferric ions on the CDPS surface. In this case, the Freundlich constants K_f and n were found to be 2.119 and 0.3772, respectively.

The magnitudes of K_f and n show easy separation of the aqueous ferric ion and they indicate favorable adsorption. The intercept K_f value is an indication of the adsorption capacity of the adsorbent; the slope 1/n indicates the effect of concentration on the adsorption capacity and represents adsorption intensity or surface heterogeneity. It becomes more heterogeneous as its value gets closer to zero.A value below unity implies a chemisorptions process [36]. As seen, the value of "*n*" was found high enough for separation.

It was previously reported [37] that the dimensional analysis, separation factor or equilibrium parameter "R_L" was an essential feature of the Langmuir isotherm to predict adsorption system to be "favorable or "unfavorable" by Eq. 7:

$$R_L = 1/(1+bC_i) \qquad (7)$$

where, C_i is the initial ferric ion concentration (50 mg L^{-1}). The calculated R_L was 1.609, indicating for the unfavorable adsorption. The apparent Gibbs free energy of sorption ΔG is the fundamental criterion of spontaneity. If ΔG is negative in value, then the reaction occurs spontaneously at a given temperature. The Gibbs free energy change ΔG can be calculated using thermodynamic Eq. 8:

$$\Delta G = -RT \ln k_L \qquad (8)$$

where, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature in Kelvin and b is the equilibrium constant, related to the Langmuir constant, b (= 0.0328638).

$$k_L = b \times M_A \qquad (9)$$

where, M_A is the molar weight of ferric ion. Equilibrium constant (k_L) is equal 1826.570 L moL^{-1}.

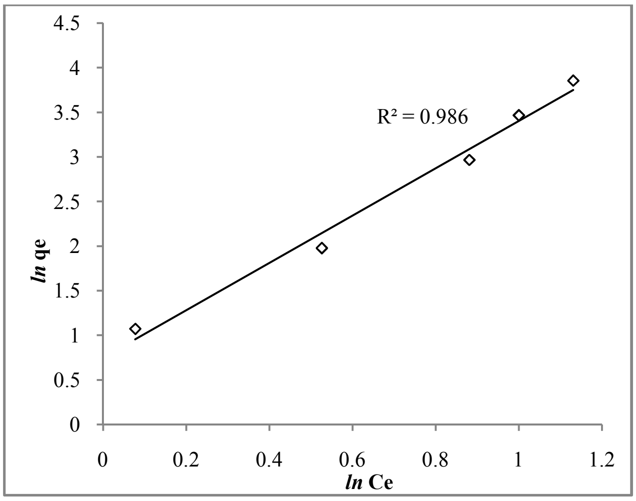

Figure 7. The linearized Freundlich adsorption isotherms for adsorbing Fe^{3+} ion on CDPS (T = 45 ºC; doses = 10 g L^{-1}; C_i= 50 mg L^{-1}; t = 180 min; and rpm = 300, pHi = 1.15).

The value of standard Gibbs free energy change (ΔG) calculated at 45 °C is found to be -19.927 kJ mol^{-1}. This negative sign value shows the spontaneous nature of sorption system.

We can note that, by comparing the values of linear regression coefficients (R^2) of the examined three isotherm models, the Fruendlich model gave much better fitting than the Langmuir model.

3.7. Effect of contact time.

Adsorption of ferric ion was measured at a given contact time using a solution concentration of 50 mg L^{-1}. The plot in Figure 8 reveals that the rate of removal is higher at the beginning. This rapid adsorption of ferric ion is due to the non-reacted adsorption sites of CDPS-adsorbent, which are available in large and high at the beginning of the reaction. It is clear from Figure 8 that the removal rate increased with increasing contact time,so as to reach equilibrium after 180 min of interaction achieving the maximum removal of 77% (approx.).

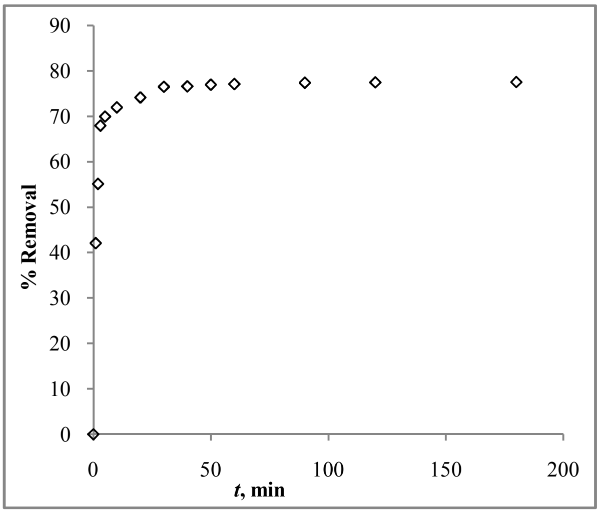

Figure 8. The effect of contact time for adsorbing ferric ion onto CDPS-adsorbent (T= 45 ºC, C_i = 50 mg L^{-1}, pHi = 1.15, rpm = 300, adsorbent dosage = 10 g L^{-1}).

In the first stage, the adsorption is being fast, especially during the first 5 min. But then the adsorption of ferric ion is being quite slow over the remaining period stages of the contact time (i.e., 0 to 180 min). This may indicate that the adsorption occurs mainly at the surface of the solid and some extent in the internal pores. The equilibrium was reached the maximum during the first 20 min.

3.8. Kinetic Modeling.

The obtained results from batch experiments have been analyzed using different kinetics models such as Legergen pseudo first-order [38] and pseudo second-order models [39].

Legergen pseudo first-order model is given by Eq. 11:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (11)$$

where, q_t a ferric ion concentration is adsorbed on CDPS-adsorbent at any time (mg g^{-1}) and k_1 is the adsorption rate constant (min^{-1}).

Pseudo first-order kinetic is plotted at 45 °C as shown in Figure 9. The Lagergren's first-order rate constant (k_1) and q_e are calculated from the intercept and slope of the plot. These constants are found 0.011 min^{-1} and 1.631 mg g^{-1}, respectively, with the corresponding correlation coefficients $R^2 = 0.592$. It was observed that the pseudo first-order model did not fit well. In addition, it was found that the calculated q_e value ($q_{e,\ Cal.}$ = 1.631 mg g^{-1}) do not agree with the experimental q_e value ($q_{e,\ Exp}$ = 3.88 mg g^{-1}). This suggests that the sorption of ferric ion on CDPS does not follow first-order kinetics.

Pseudo second-order model is represented as [39]:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2{}_e} + \frac{1}{q_e} t \qquad (12)$$

where, the equilibrium sorption capacity (q_e) and the adsorption rate constant k_2 (g mg^{-1} min^{-1}) can be determined experimentally from the slop and the intercept of the plot t/q_t versus t (Figure. 10).

The q_e and k_2 are calculated from the model, which are found 3.5335 mg g^{-1} and 0.10242 g mg^{-1} min^{-1} with the corresponding correlation coefficients $R^2 = 0.999$. It was found that the calculated q_e value ($q_{e,\ Cal.}$ = 3.5335 mg g^{-1}) agree with the experimental q_e value ($q_{e,\ Exp}$ = 3.88 mg g^{-1}). This suggests that pseudo second-order better represents the sorption kinetics estimating a chemisorptions process. Apparently, the pseudo-second order model was found to be rate limiting.

The pseudo-firstorder and pseudo-second order kinetic models could not identify the diffusion mechanism. Thus to determine the diffusibility of the ferric ions into the pores of the CDPS-adsorbent, Weber-Moris intraparticle diffusion model [40] can be used in the form Eq. 13:

$$q_t = K_{int} t^{\frac{1}{2}} + C \qquad (13)$$

where, C is constant, q_t the amount of ferric ion adsorbed at a time (mg g^{-1}) and k_{int} is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$).

A plot of q_t vs. $t^{0.5}$ giving straight line confirms an intra-particle diffusion sorption as shown in Figure 11. The plot is not totally linear and the more so do not pass through the origin for all portions. This is indicative of some degree of boundary layer control and this further show that the intra-particle diffusion could not be the only mechanism involved. This plot presents multi-linearity, which it indicates that two or more steps occur. The first, sharper portion (ca. $t^{0.5}$ range from 0 to 1.4142 $min^{0.5}$; i.e., from 0 up to 2 min of adsorption period) is the external surface adsorption or instantaneous adsorption stage. It is a non-controlled and fast adsorption process.

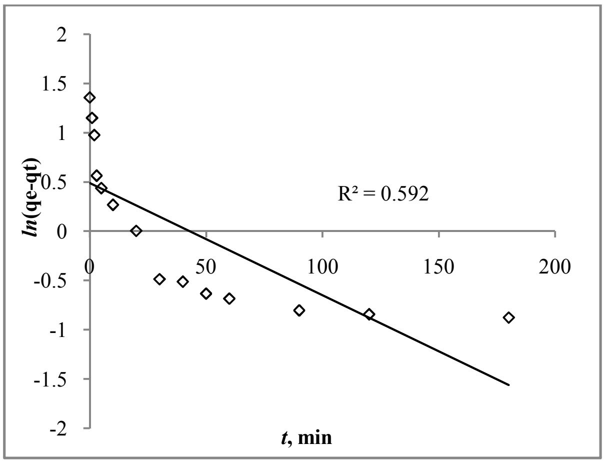

Figure 9. Pseudo-first order model of aqueous Fe^{3+} ion by using 45 °C, dosage = 10 g L^{-1}, pHi = 1.15, 300 rpm, and Ci = 50 mg L^{-1}.

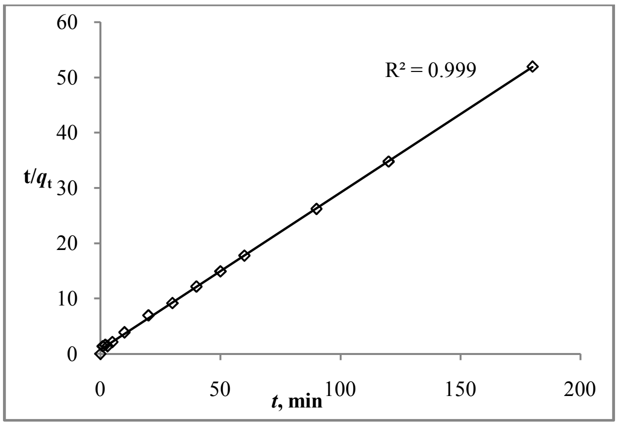

Figure 10. Pseudo-second model of aqueous Fe^{3+} ion by using 45 °C, dosage = 10 g L^{-1}, pHi = 1.15, 300 rpm, and Ci = 50 mg L^{-1}.

The second portion is the gradual adsorption stage (ca. $t^{0.5}$ range from 1.732 to 5.477 $min^{0.5}$; i.e., from 3 up to 30 min of adsorption period), where the intraparticle diffusion is rate-controlled.

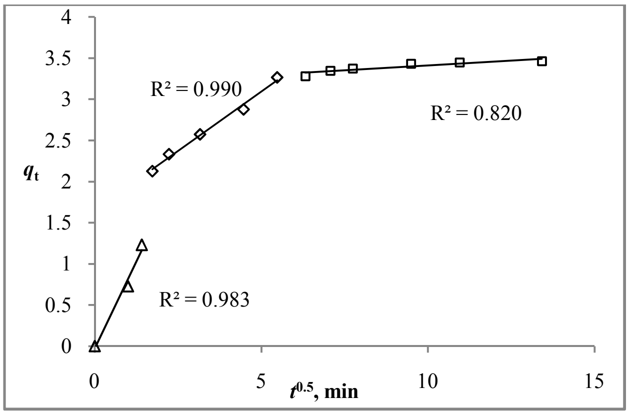

Figure 11. Weber-Moris intra-particular diffusion kinetic model for adsorption of ferric ion on CDPS.

The third portion is the final equilibrium state where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution and chemisorptions stage is taken part on the CDPS surface and pores (which already has been successfully explained by pseudo-second order kinetic model from 40 to 180 min of adsorption period).

Film diffusion mass transfer rate equation is presented by Eq. 14:

$$ln\left\{1-\frac{qt}{qe}\right\} = -kt \qquad (14)$$

where, k (min^{-1}) is the liquid film diffusion constant. A plot of ln[1 - (q_t/q_e)] *vs. t* should be a straight line with a slope -k if the film diffusion is the rate limiting step [41].

Figure 12 shows the film diffusion mass transfer stage from 3 to 30 min of adsorption process. Therefore, this stage could be considered as the rate controlling and limiting step with the value of k = 0.036 min^{-1}.

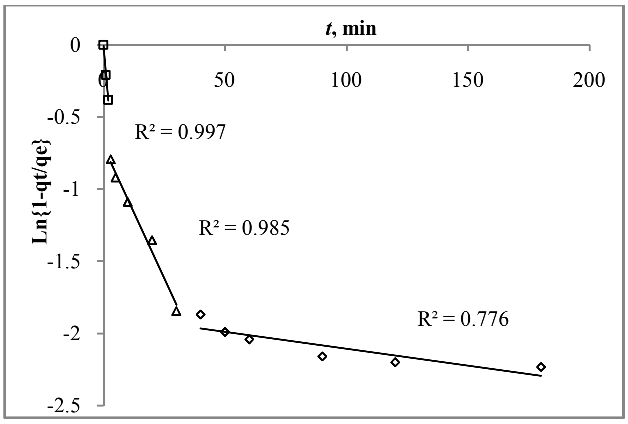

Figure 12. Film diffusion mass transfer kinetic models for the adsorption of ferric ion on CDPS.

4. CONCLUSIONS

Coal of Date Palm Seeds(CDPS)has been successfully used to remove ferricion from water. The maximum removal rate has been found at 92 % by applying the following parameters: lowinitial concentration of ferric ions (30 mg L^{-1}) on 50 g L^{-1}CDPS dosage, pHi = 1.15, Temperature = 45 ºC, contact time = 180 minand 300 rpm. The final equilibrium of sorption starts after 30 min yielded a maximum removal of 76 % (approx.).

The results reveal that the adsorption of ferric ion on CDPS is chemisorptions, spontaneous (ΔG = -19.927 kJ mol^{-1}) and unfavorable in nature (R_L = 1.609). The kinetics of transporting of ferric ion sorption into CDPS surfaces in aqueous-solid phase systems are good modeled by pseudo-second order. The chemisorptionsof ferric ion on CDPS surfaces is considered to be the rate-limiting step (R^2 = 0.999). The kinetic studies show that the adsorption rate is high. The mechanism of adsorption is detected as chemisorptions, which explained by pseudo-second order kinetic model, especially from 30 to 180 min of adsorption period.

The chemisorptions of ferric ion onto CDPS-adsorbent is the rate limiting step (R^2= 0.999). We can describe the adsorption mechanism of ferric ion on CDPS through three steps: (i) the uncontrolled rate of the external surface adsorption or instantaneous adsorption stage within 0 to 3 min of adsorption period. (ii) The intraparticle diffusion stage within 3 up to 30 min of adsorption period. (iii) Chemisorptions stage and final equilibrium state within 40 to 180 min of adsorption period.

This approach can be applied and recommended for purifying ground water resources and industrial wastewater in KSA by using a novel CDPS material as natural membrane.

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