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Kinetics and thermodynamic of Fe(III) adsorption type onto activated carbon from biomass: kinetics and thermodynamics studies

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ABSTRACT

Batch adsorption of Fe (III) from aqueous solution onto activated carbon prepared by chemical activation process from date palm seeds (ADPSC) was studied. The maximum adsorption capacity (98.56%) was obtained at pH 5 and contact time 80 minutes. The adsorption data indicates that the process follows the pseudo-second-order kinetic model. As well as the thermodynamic data indicate that adsorption processes is endothermic. The values of enthalpy (ΔH°) and activation energy (E_a) indicate that the adsorption process is chemisorption.

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KEYWORDS

Adsorption;
Fe (III);
Activated carbon;
Kinetics;
Thermodynamics.

INTRODUCTION

In the Middle East ground water is one of the important sources of drinking water. Iron is common contaminant in groundwater. The World Health Organization (WHO) has set a guideline value of 0.3 mg/L of iron in drinking water^[1]. The presence of high concentrations of iron in water causes harmful effects to human and technological problems. Iron ions precipitate a dark sludge on walls of pipes when contact with air, which lead the corrosion of the pipes^[2]. The presence of iron ions in ground water above a certain limit makes the water un-usable for aesthetic considerations such as metallic taste, odour, staining of laundry and plumping fixtures^[3]. A number of researches have been developed for the removal of iron from water and wastewater. These processes include: chemical precipitation^[4,5], coagu-

lation/ flocculation^[6,7], ion exchange/solvent extraction^[8,9], cementation^[10,11], complexation^[12,13], electrochemical operation^[14], biological operations^[15], evaporation^[16], filtration^[17], membrane processes^[18] and adsorption^[19-21]. Carbon and modified activated carbons obtained from agricultural wastes are low cost and available adsorbent materials. These materials give better performance in the adsorption of heavy metals from water and wastewater. Date palm seeds are agricultural waste which has been widely used for the preparation of activated carbon.

The objective of the present work is the preparation of activated carbon from date palm seeds (ADPSC) by chemical activation process with phosphoric acid. Properties and the chemistry of the surface of the activated carbon prepared were determined. The adsorption of Fe (III) from aqueous solution, at different conditions of contact time, adsor-

bent dose, initial Fe (III) concentration, pH and temperature were studied. Kinetic and thermodynamic of the adsorption process were performed.

MATERIALS AND METHODS

Preparation of adsorbent material

Activated carbon was prepared by chemical activation process from date palm seeds (ADPSC) produced as waste or by-product from many food industries. Date palm seeds (DPS) were washed with distilled water to remove the surface adhered and water-soluble materials. Then it is dried in an oven at 80°C. The dried seeds were ground and sieved to particle size 0.150 mm. DPS were mixed with phosphoric acid (purity 90% Merck, Germany) at 1:1 ratio (weight of DPS /volume of phosphoric acid) for 24 h. The activated carbon was prepared by heating the mixture at temperature 600°C in a muffle furnace for 3 hour. After cooling, the activated carbon was washed several times with distilled water until the pH of the washing solution reached 6.5 -7. The product was dried at 80°C for 10 hours in an oven, ground and sieved through a 0.150 mm sieve. The previous work was carried out with the same sequence with sulfuric acid (purity 99% Merck, Germany) at 1:1 ratio (weight of DPS /volume of sulfuric acid) for 24 h. The final product was kept in tightly closed plastic container for further use.

Preparation of iron stock solution

Stock solution containing 1000 mg/l prepared by dissolving certain amount of FeCl₃ in distilled water and then diluted to appropriate concentrations. All chemicals used were of AR grade (Sigma-Aldrich, Germany). 0.1 N HCl and 0.1 N NaOH were used for pH value adjustment.

Adsorption experiments

Batch technique

Experiments were carried out to determine the optimum parameters of the adsorption process (contact time, pH, initial concentration, adsorbent dose and temperature). 60 mL of 25 mg/L of Fe(III) solutions with a range of pH values from 3 to 10 was transferred in a conical flask with 0.5 g of ADPSC.

The solution was agitated at 150 rpm in a thermostatic shaker water bath for different time (10 to 120 min) at different Temperature (30, 40, 50 and 60 °C). The samples were withdrawn and centrifuged at 5000 rpm for 5 min and the supernatant solutions were analyzed using atomic adsorption spectrophotometer (Perkin Elmer, A 800).

MATHEMATICAL PROCEDURES

Adsorption capacity (q) of Fe (III) was defined as:

$$q = (C_0 - C_e)V/M \quad (1)$$

In addition, the removal efficiency (R_e) is calculated according to the following equation:

$$R_e (\%) = (C_0 - C_e)C_0 \times 100 \quad (2)$$

Adsorption kinetic studies

Kinetics of Fe(III) adsorption ADPSC was analyzed using pseudo first-order and pseudo second-order^[22, 23].

Pseudo-first-order model

The pseudo first order kinetic model^[24], was given by equation:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Values of k₁ and q_e were calculated from the slope and intercept values of the straight line of plotting log (q_e-q_t) versus t.

Pseudo-second-order model

The sorption data were also analyzed in terms of pseudo-second order model^[24,25], given by the equation:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (4)$$

If the initial adsorption rate, h (mg/g. min) is:

$$h = K_2 q_e^2 \quad (5)$$

The plot of t/q_t versus t should give a straight line and the pseudo second order rate constant, K₂ and equilibrium adsorption capacity, q_e, were calculated from the values of intercept and slope, respectively.

Adsorption thermodynamic studies

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Thermodynamic parameters, such as enthalpy variation (ΔH°), entropy variation (ΔS°) and change in Gibbs free energy (ΔG°), were calculated from the curve relating the distribution coefficient (K_D) as a function of temperature using the following equations^[26]:

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

$$K_D = \frac{q}{C_e} \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (8)$$

The values of ΔH° , ΔS° were determined from the slope and intercept values of the straight line of plotting $\ln K_D$ versus $1/T$, respectively

RESULTS AND DISCUSSION

Characteristics of adsorbent

Characteristics of activated carbon produced from date palm seeds are shown in TABLE 1.

The scanning electron microscope images of the ADPSC before and after adsorption are taken to see the change in pores on the surface. Figure 1(a) shows

TABLE 1 : Characteristics of activated carbon produced from date palm seeds

Parameters	Value
Ash content (%)	2.85
Bulk density (g/cm ³)	0.543
Iodine number (mg/g)	1186.43
Fixed carbon(%)	89.0
Surface Area (m ² /g)	954.53

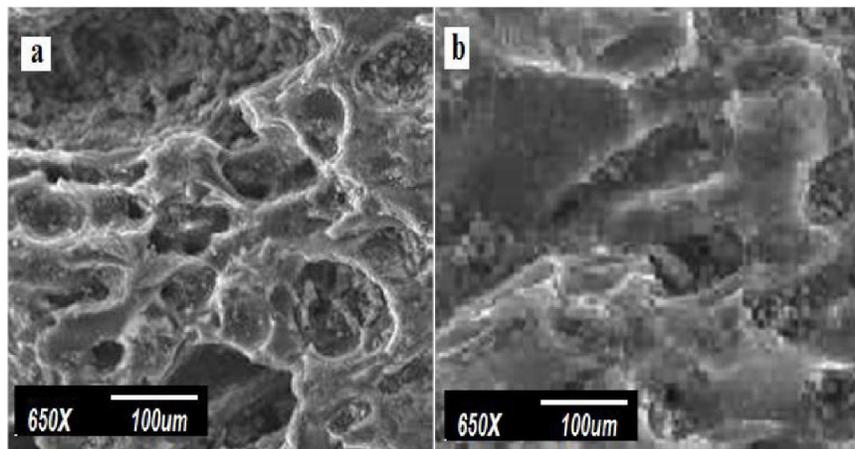


Figure 1 : SEM image of (a) activated carbon and (b) loaded activated carbon

that the adsorbent surface is rough, porous and heterogeneous which lead to increase the binding between Fe (III) ions and ADPSC. After adsorption, the loss of porosity and roughness of the adsorbent surface was observed in Figure 1b.

Adsorption dynamics

Effect of pH

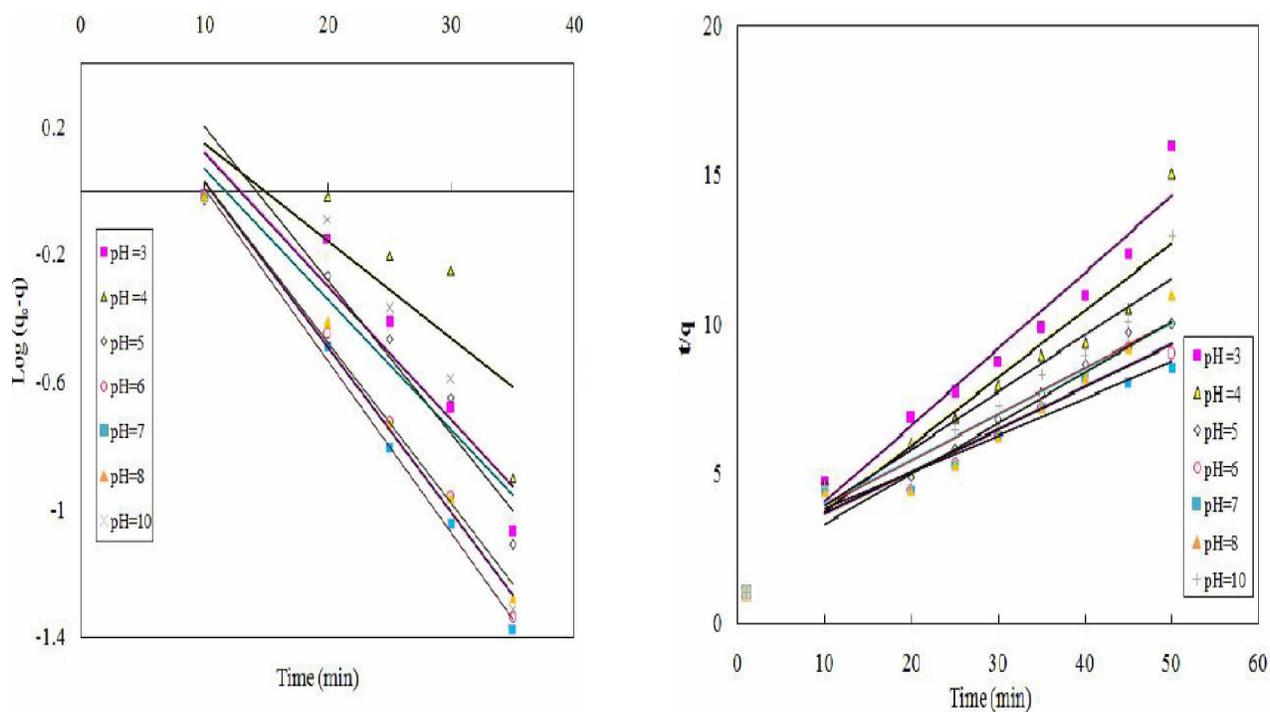
The uptake of Fe (III) onto ADPSC was found to increase with time and attained a maximum value at 80 min. The removal of Fe (III) was studied at different pHs in the range 3-10 by ADPSC at initial Fe (III) concentration of 25 mg/l, and a temperature of 30°C, adsorbent dose 0.5g. It was found that adsorption capacity was highly dependent on pH. The maximum Fe (III) adsorption was obtained at pH 5. The competing of H⁺ with Fe (III) for the adsorption sites on ADPSC, lead to decreasing the removal percent of Fe (III) at low pH. The increase in Fe (III) removal may be due to decrease in competition between H⁺ and Fe (III) and consequently more negatively charged sites were made available and this facilitated greater Fe (III) ions uptake. Above pH 5, the removal efficiency decreases as pH increases, this is due to the hydrolysis effect^[27]. Results indicate that the adsorption reaction can be approximated with the pseudo second-order kinetic model (Figure 2), with higher values of correlation coefficient. The rate constants and values of correlation coefficient represented in TABLE 2.

Effect of initial Fe (III) concentrations

On changing the initial Fe (III) concentration from

TABLE 2 : Kinetics data for adsorption of Fe (III) onto ADPSC

Parameter		Pseudo first-order (Lagergren)			Pseudo second-order	
		K_1	q_e	r^2	h	r^2
pH	3	0.0567	1.575	0.923	0.0335	0.998
	4	0.0678	1.618	0.933	0.2880	0.987
	5	0.1064	1.933	0.904	0.4901	0.990
	6	0.1103	2.022	0.955	0.5421	0.988
	7	0.1202	2.072	0.946	0.5365	0.994
	8	0.1245	2.122	0.876	0.5243	0.987
	10	0.1302	1.989	0.855	0.4198	0.983
Adsorbent dose (mg/l)	0.3	0.1144	2.061	0.858	0.4954	0.999
	0.4	0.1201	1.825	0.913	0.4876	0.987
	0.5	0.1663	1.620	0.822	0.4321	0.996
	0.6	0.1521	1.488	0.911	0.3254	0.995
	0.7	0.1534	1.404	0.911	0.3654	0.988
Temperature (°C)	30	0.1234	1.033	0.913	0.4426	0.995
	40	0.1443	1.165	0.904	0.6101	0.998
	50	0.1607	1.833	0.934	0.6876	0.989
	60	0.1528	2.188	0.922	0.7843	0.978
Adsorbate concentration (mg/l)	25	0.1312	2.128	0.821	0.4870	0.991
	50	0.1395	4.731	0.910	0.8555	0.989
	75	0.1438	7.508	0.831	1.0407	0.988
	100	0.1243	10.30	0.725	1.1207	0.997
	125	0.1576	11.29	0.778	1.3115	0.985

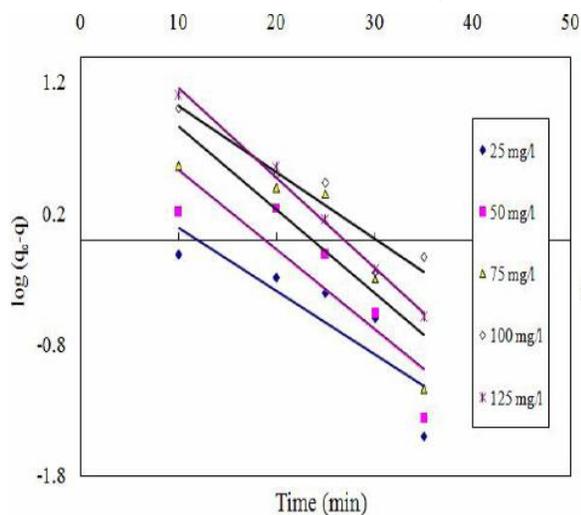


The pseudo first-order model at different pH.

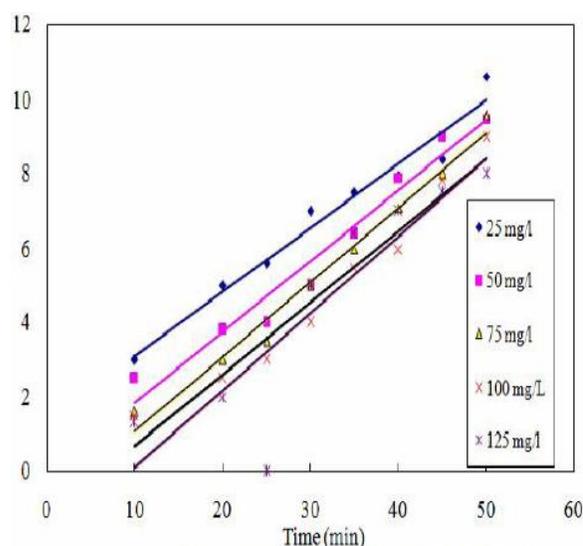
The pseudo second-order model at different pH.

Figure 2 : Kinetic models of adsorption process at different pH

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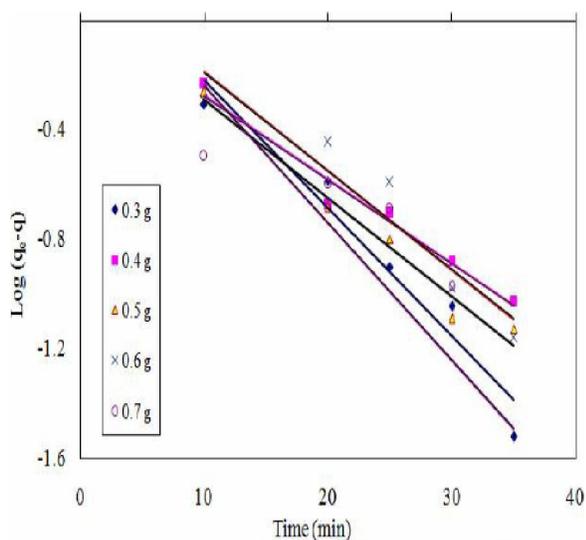


The pseudo Frist-order model at different initial concentrations.

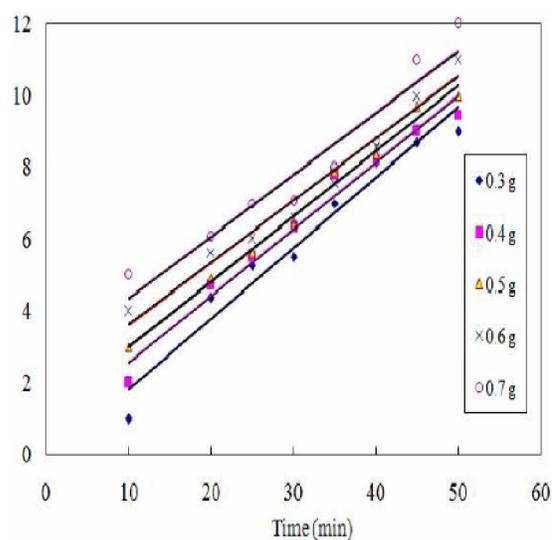


The pseudo second-order model at different initial concentrations.

Figure 3 : Kinetic models of adsorption process at different initial Fe (III) concentrations



The pseudo first-order model at different Adsorbent dose.



The pseudo second-order model at different Adsorbent dose.

Figure 4 : Kinetic models of adsorption process at different adsorbent doses

25 to 125 mg/l, the amount adsorbed increased at 30°C and pH 5. Results obtained show good compliance with the pseudo second-order kinetic model (Figure 3), with values of correlation coefficient, $r^2 \cong 0.98$ (TABLE 2).

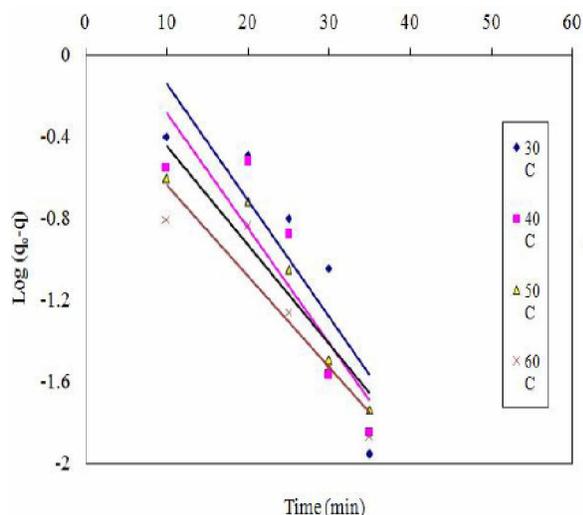
Effect of adsorbent dose

Fe(III) uptake was studied using different doses of ADPSC at pH 5, 30°C, contact time 80 minutes and initial concentration of 25 mg/l. The doses used were 0.3, 0.4, 0.5, 0.6 and 0.7 g adsorbent/ 60ml adsorbate. The results indicated that the percent adsorption increased with the increase in adsorbent

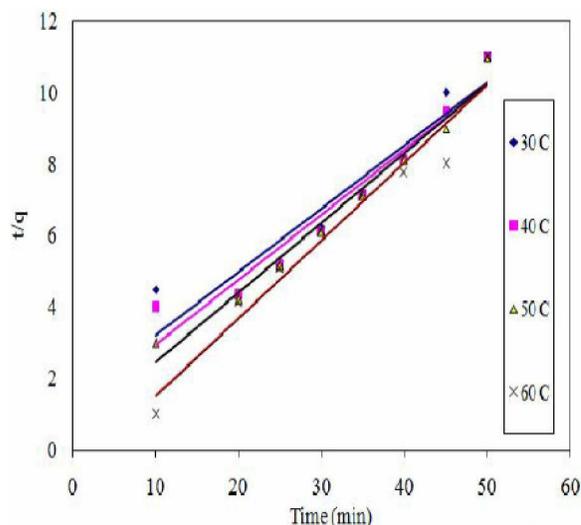
dose. The results (Figure 4 and TABLE 2), showed good compliance with pseudo second-order model with values of correlation coefficient, $r^2 \cong 0.99$.

Effect of temperature

Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle^[26]. The experimental data were obtained at pH 5, dose 0.5g, contact time 80 minutes and initial concentration of 25 mg/l. Increase in temperature from 30°C to 60°C was found to increase the removal efficiency of the adsorbent



The pseudo Frist-order model at different Temperature (°C).



The pseudo second-order model at different Temperature (°C).

Figure 5 : Kinetic models of adsorption process at different temperatures.

TABLE 3 : Thermodynamic parameters of Fe (III) adsorption process at different temperature

ΔH° (kJ/mol)	ΔS° (KJ/mol.K)	ΔG° (kJ/mol)				E_a kJ/ mol
		Temperature(K)				
		303	313	323	333	
91.27	0.295	1.885	-1.065	-4.015	-6.985	89.14

for the metal ions. This is probably due to the effect of temperature on the interaction between the shell surface and the metal ions in solution. The data obtained for each of the kinetic models (Figure 5 and TABLE 2) show a good compliance with the pseudo second-order equation, with values of correlation coefficient, $r^2 \approx 0.99$.

Thermodynamic studies

From Figure 6, the values of ΔH° and ΔS° were determined from the slope and intercept of the curve, respectively as well as the calculated values of ΔG° and are listed in TABLE 3. The obtained values of the thermodynamic parameters show that the adsorption process is endothermic in nature. This is in accordance with increasing adsorption equilibrium with increasing temperature. The value of ΔH° may give an indication about the type of Fe (III) adsorption onto ADPSC as follow^[24, 26]:

$\Delta H^\circ = 2.1-20.9$ kJ/mol (Physical adsorption)

$\Delta H^\circ = 80-200$ kJ/mol (Chemical adsorption)

The value of ΔH° is 91.27 kJ/mol which indicate that the uptake of Fe (III) onto activated carbon could be attributed to a chemical adsorption pro-

cess.

Determination of activation energy

Activation Energy of adsorption (E_a) is the energy change when one mole of adsorbate ions is transferred from solution to the surface of adsorbent material. The increase in the pseudo-second order rate constant with temperature may be described by the Arrhenius equation which is used to calculate the activation energy for the metal ion adsorption^[28,19], as given below:

$$\ln K_2 = \ln A + E_a/RT \tag{9}$$

The value of Activation Energy (TABLE 3), was determined from the slope of the straight line of plotting $\ln K_2$ versus $1/T$. The value of the activation energy may give another indication which confirms the first indication of the value of ΔH° about the type of adsorption of Fe (III) adsorption onto ADPSC. Physical and chemical are the main types of adsorption. In the physical adsorption the equilibrium is usually rapidly attained and easily reversible, because the energy requirement is small ($E_a = 0-40$ kJ. mol⁻¹) and since the forces involved are weak. Chemical adsorption is specific and involves forces

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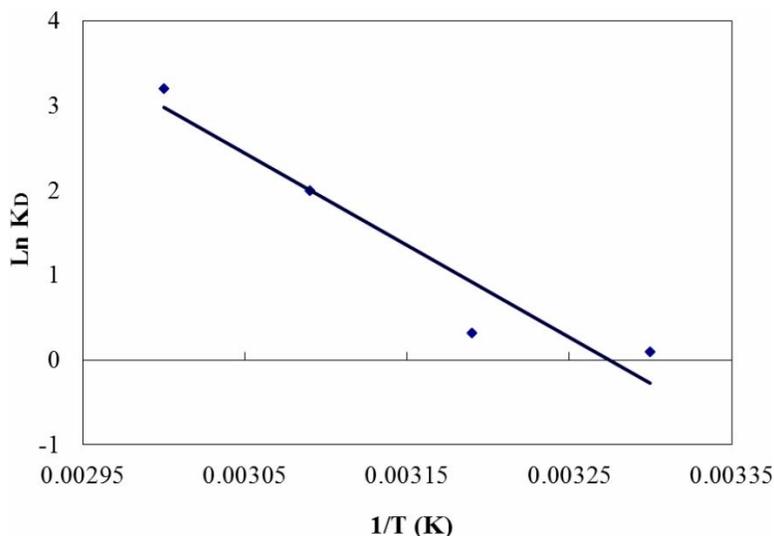


Figure 6 : Van't Hoff plot of Fe (III) adsorption onto ADPSC

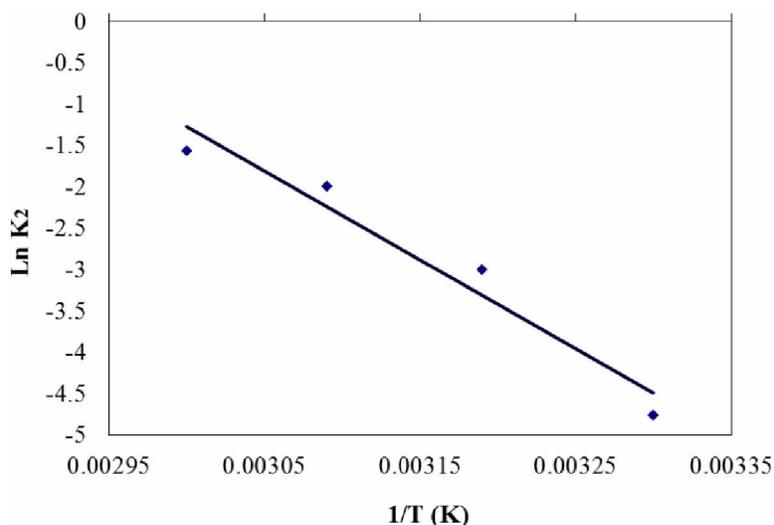


Figure 7 : Plot of $\ln K_2$ versus $1/T$ for activation energy of Fe (III) adsorption onto ADPSC.

much stronger (chemical bonds) than physical adsorption. So the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions which means that the rate varies with temperature according to finite activation energy ($E_a = 40-800 \text{ kJ. mol}^{-1}$) in the Arrhenius equation^[28-34]. The value activation energy for Fe (III) adsorption onto ADPSC, was found as 89.14 kJ/mol obtained from the slope of Figure 7, confirms that the adsorption of Fe (III) adsorption onto ADPSC is chemisorptions.

CONCLUSION

- ADPSC could be used as low cost and avail-

able adsorbent for Fe (III) adsorption from aqueous solution.

- The kinetics of Fe (III) adsorption on ADPSC was found to follow a pseudo second-order rate model.
- The values of thermodynamic parameters indicate that adsorption processes is endothermic in nature, and this is in agreement with the increasing of adsorption capacity with increasing in temperature.
- The values of enthalpy (ΔH°) and Activation Energy (E_a) indicate that, the adsorption of Fe (III) onto ADPSC is chemisorptions where chemical interaction between Fe (III) ions and adsorbent surface occur at different temperature ranges.

Nomenclature

- A_0 : Frequency factor of Arrhenius equation (g/mg.min);
- C_0 : Initial concentration (mg/l);
- C_e : Equilibrium concentration of Fe (III) in solution (mg/l);
- E_a : Activation energy of adsorption (kJ/mol);
- k_1 : Pseudo first-order adsorption rate constant (l/min);
- k_2 : Pseudo second-order adsorption rate constant (g/mg.min);
- K_D : Distribution coefficient (cm³/g);
- M : Weight of adsorbent (mg);
- q : Adsorption capacity, (mg of Fe (III) /g adsorbate);
- q_e : Adsorption capacity at equilibrium, (mg of Fe (III)/g ADPSC);
- q_t : Adsorption capacity at time t, (mg of Fe (III)/g ADPSC);
- R : Gas constant (8.314 J/mol.K);
- R_e : Removal efficiency;
- r^2 : Correlation coefficient;
- T : Temperature (K);
- t : Contact time (min);
- V : Volume of the solution (L);

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