Int. J. Chem. Sci.: 10(2), 2012, 677-690
ISSN 0972-768X
www.sadgurupublications.com

ADSORPTION OF 2, 4-DICHLOROPHENOXYACETIC ACID ONTO DATE SEEDS ACTIVATED CARBON: EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

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ABSTRACT

Adsorption isotherm and kinetics of 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide on activated carbon prepared from Barhi date seeds were determined from batch tests. The effects of contact time, initial herbicide concentration and solution temperature were investigated. The adsorption equilibrium data were processed in accordance with the three most widely used adsorption isotherms: Langmuir, Freundlich and Temkin isotherm models. The equilibrium data were best represented by Langmuir isotherm model, showing maximum monolayer adsorption capacity of 175.4 mg/g. The kinetic data were also examined with the pseudo-first-order and pseudo-second-order models, and was found to follow closely the pseudo-second-order kinetic model. Thermodynamic parameters such as standard enthalpy (ΔH^o), standard entropy (ΔS^o) and standard free energy (ΔG^o) were evaluated. The adsorption interaction was found to be endothermic in nature.

Key words: 2,4-Dichlorophenoxyacetic acid, Adsorption, Kinetic, Thermodynamic, Date seeds, Activated carbon.

INTRODUCTION

A pesticide is any substance used for the destruction or control of pests. They include insecticides used for killing insects, herbicides used for killing weeds and other troublesome plants, fungicides for killing fungi, rodenticides for killing rodents, such as rats and mice, molluscicdes for killing snails and other mollusks and so on. Pesticides may be of the broad spectrum type which kills a wide range of organisms or the selective type which destroys one organism or few specific organisms[1].

Pollution of surface and ground waters causes risk to environment and human health because of the potential health hazards of their contents of inorganic and organic compounds.

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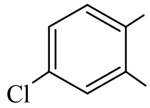
Also, the contamination of these waters by pesticides is an arduous task that the scientists have been battling to resolve over the years. Although much benefit is obtained from the use of pesticides, they have some undesirable side effects, such as their toxicity, carcinogenic and mutagenic nature[2].

2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the oldest herbicides used in the world. It was first developed during World War II and became famous as a component of the controversial Agent Orange used during the Vietnam War. The physiochemical properties of 2,4-D are shown in Table 1. Today, 2,4-D continues to be one of the most commonly used herbicides in the market. Because there is no longer a patent governing the manufacture and sale of 2,4-D, any company is free to produce it[3]. The half-life of 2,4-D in the environment is relatively short, averaging 10 days in soils and less than ten days in water, but can be significantly longer in cold, dry soils, or where the appropriate microbial community is not present to facilitate degradation. In the environment, most formulations are degraded to the anionic form, which is water-soluble and has the potential to be highly mobile[4].

Table 1: Physicochemical properties and molecular structure of 2, 4-D

Chemical formula	$C_8H_6Cl_2O_3$
Formula weight	221.04
Solubility in water (mg/L)	900
UV absorption, max (nm)	284
Chemical structure	

There are several methods that have been used for the removal of pesticides from aqueous solutions, adsorption is one of the most frequently applied methods because of its efficiency, capacity and applicability on a large scale. The most commonly used adsorbent in adsorption process is activated carbon. Data palm seeds (Phoenix dactylifera) are also a low cost, abundantly available and renewable precursor for production of activated carbon as adsorbent for the removal of pesticides from aqueous solutions. The world production of dates is about 16,696.56 million tons yearly[5].

The focus of this research was to evaluate the adsorption potential of the date seeds - based activated carbon in removing 2,4-D from aqueous solution. The equilibrium, kinetic and thermodynamic data of the adsorption process were evaluated to study the adsorption mechanism of 2,4-D molecules onto the prepared activated carbon.

EXPERIMENTAL

Material and methods

Preparation of activated carbon

Barhi date seeds (BDS) were used for preparation barhi date seeds activated carbon (BDSAC). The precursor was first washed with distilled water, dried, cut and sieved to desired mesh size of 1-4 mm. Then, it was carbonized and activated following the same procedure used in our previous study on activated carbon preparation from date seed[6], where the precursor was carbonized in a stainless steel vertical tubular reactor placed in a tube furnace under purified nitrogen (99.995%) flow of 150 cm^3/min at 800^{o}C, with heating rate of 10^{o}C/min and the sample was hold at the carbonization temperature for 2 h. The char produced was soaked in potassium hydroxide (KOH) solution with KOH: char ratio of 3 : 1 (w/w). The mixture was then dehydrated in an oven overnight at 105^{o}C to remove moisture and then activated under the same condition as carbonization, but to a final temperature of 800^{o}C. Once the final temperature was reached, the nitrogen gas flow was switched to carbon dioxide (CO_2) and activation was held for 2 h. The activated product was then cooled under nitrogen gas flow to room temperature and then washed with hot deionized water and 0.1 M hydrochloric acid until the pH of the washing solution reached 6–7.

Characterization of activated carbon

The surface area and porosity properties of BDSAC were determined by nitrogen (N_2) adsorption–desorption isotherms at (77 K) using an automated gas sorption system (Micromeritics, Model ASAP 2020, USA). The specific surface area (SBET) was calculated by the Brunauer–Emmett–Teller (BET) method. The total pore volume was calculated by measuring the amount of N_2 adsorbed at a relative pressure of 0.98. The averaged pore diameter was calculated based on the Barrett-Joyner-Halenda (BJH) method[7]. The surface morphology of the BDSAC, was examined using Scanning Electron Microscope (SEM) – model: Leo Supra 35 VP Field Emission SEM.

Batch equilibrium studies

2,4-D supplied by Sigma–Aldrich was used as an adsorbate. Deionized water was used to prepare all the solutions and reagents. Chemical structure of 2,4-D is shown in Table 1. Adsorption tests were performed in a set of Erlenmeyer flasks (250 mL) where 100 mL of 2,4-D solutions with initial concentrations of 50–500 mg/L were placed in these flasks. Equal mass of 0.30 g of the prepared activated carbon with particle size of 200 μm was added to each flask and kept in an isothermal shaker of 120 rpm at 30°C for 30 h to reach equilibrium. The pH of the solutions was original without any pH adjustment.

Similar procedures were followed for another two sets of Erlenmeyer flask containing the same initial 2,4-D concentrations and same activated carbons dosage, but were kept under 40° and 50°C for thermodynamic studies. Aqueous samples were taken from each of the 2,4-D solutions at preset time intervals using disposable syringes and the concentrations were then analyzed. All samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. The concentrations of 2,4-D in the supernatant solution before and after adsorption were determined using a double beam UV–visible spectrophotometer (UV-1700 Shimadzu, Japan) at 284 nm. The amount of adsorption at equilibrium, q_e (mg/g), was:

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

where C_o and C_e (mg/L) are the liquid phase concentrations of 2,4-D at the initial and equilibrium conditions, respectively. V (L) is the volume of the solution and W (g) is the mass of BDSAC.

Langmuir isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface[8]. The linear form of Langmuir isotherm is given in equation (2):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \qquad \ldots(2)$$

where C_e is the equilibrium concentration (mg/L); q_e is the amount 2,4-D adsorbed at equilibrium (mg/g); q_m is the adsorption for complete monolayer (mg/g) and K_a is the sorption equilibrium constant (L/mg).

Freundlich isotherm

Freundlich isotherm in the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage.[8]

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad \ldots(3)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_F and n are Freundlich constants with n giving an indication of how favorable is the adsorption process. K_F (mg/g $(L/mg)^{1/n}$) is the adsorption capacity of the adsorbent, which can be defined as the adsorption or distribution coefficient and represents the quantity of herbicide adsorbed onto activated carbon for a unit equilibrium concentration. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero[9]. A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption[10].

Temkin isotherm

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions. The Temkin isotherm has been used in the form as follows:

$$q_e = B \ln A + B \ln C_e \qquad \ldots(4)$$

where $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K).

Batch kinetic studies

The procedure of kinetic tests was identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of 2,4-D were similarly measured. The amount of adsorption at time t, qt (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W} \qquad \ldots(5)$$

where C_t (mg/L) is the liquid-phase concentrations of herbicide at time, t. The kinetics of the adsorption of 2,4-D onto BDSAC was investigated using two models, namely, the Lagergren pseudo-first- and the Ho pseudo-second-order models.

Pseudo-first-order kinetic model

The rate constant of adsorption is determined from the pseudo-first-order equation given by Langergren and Svenska[11] as:

$$\log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \qquad \ldots(6)$$

where q_e and q_t are the amounts of 2,4-D adsorbed (mg/g) at equilibrium and at time t (h), respectively, and k_1 is the rate constant adsorption (h^{-1}).

Pseudo-second-order kinetic model

The pseudo-second-order equation[12], based on equilibrium adsorption is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad \ldots(7)$$

where k_2 (g/mg h) is the rate constant of second-order adsorption. The linear plot of $\frac{t}{q_t}$ h, versus t gives $\frac{1}{q_e}$ as the slope and $\frac{1}{K_2 q_e^2}$ as the intercept.

Validity of kinetic model

The validity of each model was determined by the sum of error squares (SSE%) given by equation (8):

$$\mathrm{SSE\%} = \frac{\Sigma(q_{exp} - q_{cal})}{N} \qquad \ldots(8)$$

where N is the number of data points. The lower the value of SSE indicates the better a fit is. The fit is accepted to be good when SSE *is* below 5[13].

Adsorption thermodynamics

The thermodynamic parameters that must be considered to determine the process are: changes in standard enthalpy (ΔH^{o}), standard entropy (ΔS^{o}) and standard free energy (ΔG^{o}) due to transfer of unit mole of solute from solution onto the solid–liquid interface. The value of ΔH^{o} and ΔS^{o} were computed using the following equation:

$$ln\, K_L = \frac{\Delta S^o}{R} \frac{\Delta H^o}{RT} \qquad \ldots(9)$$

The values of ΔH° and ΔS° were calculated respectively from the slope and intercept of the van't Hoff plot of $ln\ K_L$ versus 1/T, where R (8.314 J /mol K) is the universal gas constant, T (K) is the absolute solution temperature, and K_L (L /mg) is the Langmuir isotherm constant. ΔG^{o} was calculated using equation (10):

$$\Delta G^{o} = -RT \ln K_L \qquad \ldots(10)$$

whereas the Arrhenius activation energy of adsorption E_a (J/mol) was obtained from slope of the plot of $ln\ k_2$ versus 1/T according to equation (11):

$$ln\ k_2 = ln\ A - \frac{E_a}{RT} \qquad \ldots(11)$$

where A is the Arrhenius factor and k_2 (g/mg h) is the rate constant obtained from pseudosecond order kinetic model for all initial concentrations at three different solution temperatures of 30°, 40° and 50°C.

RESULTS AND DISCUSSION

Characterization of prepared activated carbon

The BET surface area of the prepared activated carbon was found to be 806 m^2/g. The average pore diameter of the prepared sample was found to be 2.35 nm. This indicated that the activated carbon derived from barhi date seeds was mesoporous, with large surface area. Fig. 1 show the SEM image of the derived activated carbon. Many large pores in a honeycomb shape were clearly found on the surface of the activated carbon. This shows that KOH and CO_2 were effective in creating well-developed pores on the surface of the precursor, hence leading to the activated carbon with large surface area and porous structure.

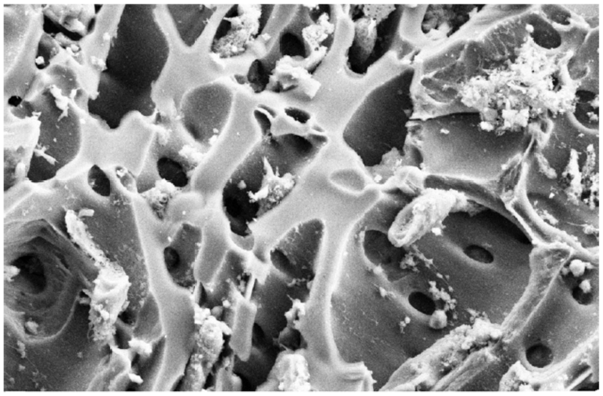


Fig. 1: SEM image of barhi date seeds-based activated carbon (1000X)

It was found that KOH is dehydrated to K_2O, which reacts with CO_2 produced by the water- shift reaction, to give K_2CO_3. Intercalation of metallic potassium appeared to be responsible for the drastic expansion of the carbon and hence, the creation of a large specific surface area[14]. Similar observation was reported by Tseng et al.,[15] where CO_2 gasification was found to promote the formation of mesoporous and enhance the surface area of activated carbon.

Effect of contact time and initial 2,4-D concentration on adsorption equilibrium

It is clear from Fig. 2 that the amount of 2,4-D adsorbed, q_t increased with time. The equilibrium adsorption was achieved in 5-7 h for 2,4-D solution with initial concentrations of 50 -200 mg/L and 11-14 h for 250-300 mg/L to reach equilibrium. This observation could be explained by the theory that in the procees of 2,4-D adsorption, initially the herbicide molecules have to first encounter the boundary layer effect and then diffuse from the boundary layer film onto adsorbent surface and then finally, they have to diffuse into the porous structure of the adsorbent.[16] Therefore, 2,4-D solutions of higher initial concentrations will take relatively longer contact time to attain equilibrium due to higher amount of 2,4-D molecules. The amount of 2,4-D adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. In this study, the adsorption capacity at equilibrium (q_e) increased from 31.66 to 139.7 mg/g with an increase in the initial dye concentrations from 50 to 300 mg/L. When the initial concentration increased, the mass transfer driving force would become larger, hence resulting in higher adsorption of 2,4-D.

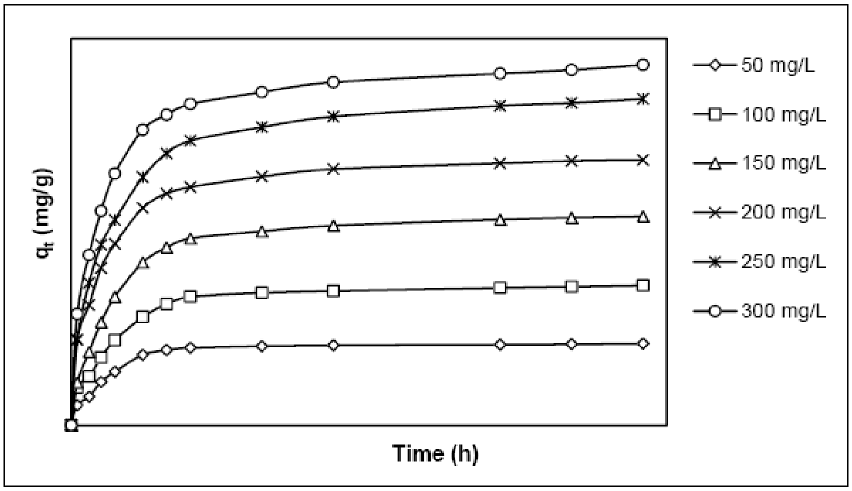


Fig. 2: Adsorption capacity versus adsorption time at various initial 2,4-D concentrations at 30°C

Adsorption isotherms

Adsorption isotherm is a functional expression that correlates the amount of solute sorbed per unit amount of the adsorbent and the concentration of adsorbate in bulk solution at a given temperature under equilibrium conditions. The adsorption data have been subjected to different adsorption isotherms, namely Langmuir, Freundlich, and Temkin models. The applicability of the isotherm models to fit the adsorption data was compared by judging the correlation coefficients, R^2 values. The closer the R^2 value to unity, the better the fit. The analysis of the isotherm data was done by fitting them to these isotherm models to find the suitable model that can be used for design purposes.

The adsorption isotherm parameters values obtained for adsorption of 2,4-D on the activated carbon prepared (BDSAC) at 30°, 40° and 50°C are listed in Table 2. Based on the correlation coefficient, R^2 listed in Table 2, it can be concluded that the adsorption of 2,4-D on BDSAC at 30°, 40° and 50°C was demonstrated well by both of Langmuir and Freundlich isotherm models. The correlation coefficient, R^2 for both models was $0.80 \leq R^2 \leq 0.96$. The adsorption process was favorable as Langmuir separation factor, R_L was $0 < R_L < 1$ and supported by 1/n values of Freundlich which were less than one. A value for 1/n below one indicates a Langmuir-type isotherm because it becomes more and more difficult to adsorb additional adsorbate molecules at higher and higher adsorbate concentrations[17].

Table 2: Langmuir, Freundlich and Temkin isotherm model parameters and correlation coefficients for adsorption of 2,4-D onto BDSAC

Isotherm models	Parameters	Solution temperature		
		30°C	40°C	50°C
Langmuir	q_m (mg/g)	175.4	196.1	200
	b(L/mg)	0.036	0.041	0.04
	R^2	0.898	0.860	0.800
Freundlich	K_F (mg/g(L/mg)$^{1/n}$)	19.32	20.16	22.11
	1/n	0.433	0.467	0.446
	R^2	0.952	0.961	0.944
Temkin	A (L/g)	5.05	1.36	1.11
	B	29.28	34.63	33.14
	R^2	0.975	0.847	0.810

Adsorption kinetics

The batch kinetic data were fitted to pseudo-first (PFO)- and pseudo-second-order models (PSO) and the derived kinetic models parameters obtained are summarized in Table 3. The linear plot of t/q_t versus t, for (PSO) as shown in Fig. 3, shows a good agreement between the experimental and the calculated q_e values. The highest values of the adjusted coefficient of determination (R^2) and good agreement between the experimental and the calculated q_e values as well as lowest values of the relatively large validity of the sum of error squares (SSE%) obtained for PSO kinetic model, as shown in Table 3 and Fig. 3, indicate that the PSO kinetic model fits the experimental data more accurately than the PFO model. This, therefore, suggests that adsorption of 2,4-D onto BDSAC follows the PSO rate law and implies that the adsorption depends on the availability of sites on BDSAC rather than 2,4-D concentration in solution[18].

Table 3: Pseudo-first- and pseudo-second-order rate constants for adsorption of 2,4-D onto BDSAC at 30°C

C_o (mg/L)	q_{exp} (mg/g)	Pseudo-first-order				Pseudo-second-order			
		$q_{cal.}$ (mg/g)	k_1 (1/h)	R^2	% SSE	$q_{cal.}$ (mg/g)	k_2 (g/mg h)	R^2	% SSE
50	31.7	30.2	0.606	0.993	0.5	32.7	0.041	0.998	00.32
100	54.2	48.9	0.476	0.996	1.7	56.2	0.019	0.998	0.62
150	81.0	70.6	0.436	0.996	3.3	84.0	0.014	0.998	0.96
200	102.8	72.3	0.413	0.985	9.7	105.3	0.013	0.999	0.77
250	126.5	95.1	0.394	0.978	10.0	129.9	0.01	0.998	0.10
300	139.7	94.1	0.365	0.993	14.4	142.8	0.009	0.999	0.99

Effect of temperature on adsorption capacity of activated carbon

The effect of temperature on adsorption of herbicide (2,4-D) solution onto BDSAC was studied at 30°, 40° and 50°C. The adsorption uptake increases with an increase in temperature if the adsorption process is endothermic and decreases with the increase in temperature if the adsorption process is exothermic. The adsorption of 2,4-D onto BDSAC at different temperatures (Figure not shown), which include increase in adsorption uptake with increasing solution temperature (30°, 40° and 50°C), indicates the endothermic nature of the adsorption reaction. The endothermic reaction detected due to the presence of functional groups such as hydroxyl, carbonyl which dissociate and hence the electrostatic attraction between the activated carbon surface and herbicide.

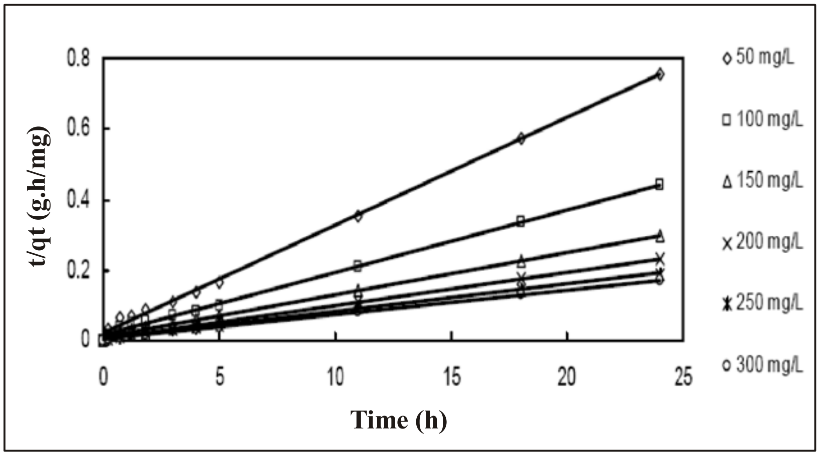


Fig. 3: Linearized plots of pseudo-second-order kinetic model for 2,4-D adsorption on BDSAC at 30°C

Adsorption thermodynamics

Based on Equation (9), the values of ΔH^{o} and ΔS^{o} were calculated respectively from the slope and intercept of the plot of *ln* K_L versus $1/T$, where K_L (L/mg) was the Langmuir isotherm constant obtained at three different solution temperatures of 30°, 40° and 50°C. ΔG^{o} was then determined from Equation (10), whereas the Arrhenius activation energy of adsorption, *Ea* (KJ/mol) was obtained from the slope of the plot of *ln* k_2 versus $1/T$ (equation 11), where k_2 (g/mg h) was the average rate contained from the pseudo-second-order kinetic model for all initial concentration at three different solution temperatures of 30°, 40° and 50°C. The values of ΔH° and ΔS° were calculated from the slope and intercept of plot between *ln* k_2 versus $1/T$ for initial 2,4-D concentration of 300 mg/L (Figure not shown). The calculated values of ΔH^{o}, ΔS^{o} and ΔG^{o} are listed in Table 4. The positive value of ΔH^{o} indicated the endothermic nature of the adsorption interaction.

Table 4: Thermodynamic parameters for adsorption of 2,4-D on BDSAC

ΔH° **(KJ/mol)**	**ΔS°** **(KJ/mol K)**	**Ea** **(KJ/mol)**	**ΔG°** **(KJ/mol)**		
			303 K	313 K	323 K
4.638	- 0.0122	27.88	8.374	8.357	8.624

All the calculated values of ΔH^{o}, ΔS^{o}, ΔG^{o} and Ea for adsorption of 2,4-D on BDSAC are listed in Tables 4. The results presented in the table referred to positive value of ΔH^{o} (endothermic nature) for adsorption of 2,4-D on BDSAC. The negative value of ΔS^{o}, which indicate that there is a decrease in state of disorderness in the molecules during process, which in turn is due to the binding of molecules with adsorbent surface[19].

As can be seen from Table 4, the value obtained for Ea is positive, indicating the feasibility of the adsorption processes. For the activated state, $Ea > 0$, it showed that energy barrier exist in the system for the adsorption of pesticide 2,4-D by bituminous shale as adsorbent[20].

The values of ΔG^{o} obtained for adsorption of 2,4-D on the activated carbons prepared gave positive value, which indicated the non-spontaneous nature of the adsorption process. The positive value of ΔG^{o} also shows that there is an energy barrier. When the ions enter from the solution into the particle surface, some of the water molecules forming hydration shell of ions are stripped off and simultaneously the degree of freedom of ions declines[20].

CONCLUSION

The results showed that BDSAC is a promising adsorbent for the adsorption of the herbicide, 2,4-D, from aqueous solution over a wide range of concentrations. The surface area of the prepared activated carbon was relatively high and was found to be mesoporous. Equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherms and the equilibrium data were best described by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 175.4 mg/g at 30°C. The maximum monolayer adsorption capacity increased with increasing temperature. The pseudo-second-order model described the kinetics of the adsorption of 2,4-D onto BDSAC better than the pseudo-first-order model, which implies that the adsorption depended on the availability of sites on BDSAC rather than the concentration of 2,4-D in solution. The thermodynamic calculations indicated that the adsorption was endothermic in nature.

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Accepted : 24.01.2012