Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.791764

51 (2013) 6049–6057
September

Taylor & Francis
Taylor & Francis Group

Kinetic and thermodynamic study of removal of o-chlorophenol from potable water using activated carbon prepared by Date Pits

K. Akhrib*, F. Kaouah, T. Berrama, Z. Bendjama

Faculté de Génie Mécanique et de Génie des Procédés - Laboratoire de Génie des Procédés et Environnement,
USTHB, BP 32, El-Alia 16111, Bab-Ezzouar, Algeria
Email: a_kenze@yahoo.fr

Received 6 December 2011; Accepted 10 January 2013

ABSTRACT

The adsorption of o-chlorophenol (o-CP) on date carbon was investigated to assess its possible use as an adsorbent for the processing of phenolic waste water. The influences of initial concentration, the temperature, and speed agitation on the adsorption capacity have been studied. The percentage removal of 2-CP was observed to increase with increase an initial concentration of o-CP. The adsorption of o-CP decreases with an increase in temperature indicated the exothermic nature of the reaction. The Langmuir and Freundlich equation interprets adsorption isothermal data. Process parameters, including the rate of agitation, initial concentration and temperature, were examined, and the obtained data were modeled using four kinetic models, including a pseudo-first order, pseudo-second order, the pore diffusion model, and the Elovich equation to understand the reaction mechanism. Thermodynamic parameters, such as enthalpy, entropy, and Gibb's free energy changes, were also calculated.

Keywords: Date cores; o-Chlorophenol; Adsorption; Isotherm; Water pollution; Kinetic model; Thermodynamic parameters

1. Introduction

Carbon adsorbents prepared from different precursors are widely used for concentration, pre treatment and separation of organic substances present in air, soil, and water [1]. Fruit stones are appropriate raw material for the production of activated carbons [2–5]. In the recent years, many other agricultural by-products have been used as sources for activated carbons production, such as cherry stones [6,7], olive stones [8,9], oil palm stones [10,11], apricot stones [12,13], almond shells [14], sugar cane bagasse [15,16], walnut shells [8], pecan shells [17,18], cotton stalks [19], and date stones [20,21]. World production of dates was approximately 6.7 million tonnes in 2004. The major producers in the world are the following: Egypt, Iran, Saudi Arabia, United Arab Emirates, Pakistan, Algeria, and other Mediterranean countries. Algeria produces 450,000 t/year of dates [22].

The use of these materials as adsorbents of inorganic and organic pollutants from water is due to their unique versatility resulting from their high surface area, porous structure, high adsorption capacity, and surface chemical nature, which can be appropriately modified by physical and chemical treatments to enhance the extent of a given adsorption process [23]. Many studies have been carried out for

---

*Corresponding author.

Table 1
Textural characteristic of the activated carbon

Sample	SN_2 ($m^2 g^{-1}$)	V_{Poreux} ($cm^3 g^{-1}$)	pH	Bulk density	Humidity (%)
AC	425	0.17	5.45	0.578	9.82

the production of activated carbon from this agricultural waste by using the chemical process. Haimour and Emeish [20] have prepared activated carbon from date pits by chemical activation with phosphoric acid. In addition, Kannan et al. [24] have obtained activated carbon from date pits under chemical activation using sulfuric acid.

Phenolic compounds and their derivatives are classified as priority pollutants. They enter into environment through industries such as coal conversion, petroleum refining, textile and pharmaceutical, as well as large-scale use of herbicides, insecticides and pesticides in agriculture [25]. Phenols are also released as intermediate products during microbial degradation of pesticides or some other xenobiotics [26].

Extensive characterization studies have been performed as per the standard methods to assess the quality of activated carbon. The adsorptive property of the activated carbon was tested by the adsorption of o-chlorophenol (o-CP) from aqueous solution. A thorough study of adsorption kinetics and equilibrium sorption isotherm revealed the potential use of this carbon as an adsorbent. Efficiency of carbon mainly depends on surface area and binding forces present within the particles of adsorbent, as well as chemical characteristics of adsorbate. This work reports the results obtained on the preparation of activated carbon from date cores and their ability to remove o-CP from aqueous solution in batch study.

The objective of this paper was to use date stones for the production of activated carbon by chemical activation with H_3PO_4 and their ability to remove o-CP from wastewater. The influence of several operating parameters for the adsorption of CP, such as initial concentration, temperature, and speed .Were investigated in batch mode. The kinetic data was fitted to different models, and the thermodynamic parameters such as ΔG, ΔH, and ΔS, for the adsorption process were calculated.

2. Experimental

2.1. Preparation of activated carbons

Activated carbons used in this study were prepared from date pits. The precursor is impregnated with chemical reagent (H_3PO_4) in a liquid form. The impregnated precursor was carbonized in a muffle furnace at 800°C for 2 h. After carbonization, the carbons were washed with distilled water and heated in an oven at 383 K overnight. The sample so obtained will be referred in the text as activated date (AC).

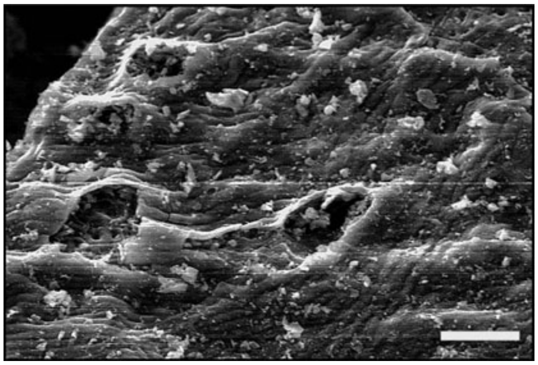

Fig. 1. Carbonized date pits (CD).

2.2. Characterization of activated carbon

2.2.1. Textural characterization

Some of the texture characterizations of activated carbon are compiled in Table 1, which shows values for SN_2, the nitrogen surface area, obtained by applying the BET method to the N_2 adsorption isotherms at 77 K, V_{Poreux} the pore volume.

2.2.2. Scanning electron microscopy

Scanning electron micrographs realized on raw (NDS), carbonized date pits at 800°C for 2 h (CD) AC pits are shown in Figs. 1 and 2. The examination of the carbonization creates gradual porosity (Fig. 1). After activation, the porosity is more developed. Macropores and more elliptical macropores are obtained after activation for 2 h (Fig. 2). The comparison of Fig. 2 indicates clearly that a regular macroporosity and a rather homogeneous surface are obtained by activation at 800°C for 2 h.

2.2.3. Chemical characterization

To measure the pH values of the aqueous suspensions of the carbon sample, 1-g portions of carbon

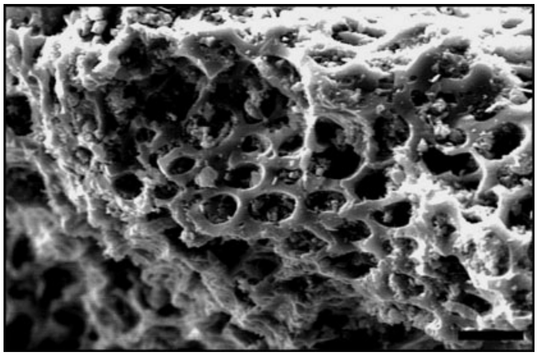

Fig. 2. Activated date pits (AC).

were mixed with 100 cm^3 of distilled water, the suspensions were shaken mechanically for 48 h at 298 K, and then, their pH value was determined using a glass electrode.

2.2.4. FTIR analysis

The assignments of IR absorption bands of carbonized and activated date stones are collected in Table 2. The IR spectrum of carbonized date stones is in good agreement with the results of El-Hendawy [27] who studied the carbonization and oxidation of date pits by FTIR. The assignment of absorption bands shows that the functional groups alkene, ester, aromatic, ketone, alcohol, hydroxyl, ether, and carboxyl are present in the material [28]. This is in accordance with the composition of date pits, which are essentially composed of cellulose, hemicellulose and lignin. IR spectra obtained for carbonized date stones exhibit a similar shape, which shows that the same functional groups are present in the material. After activation, the IR absorption bands between 400 and 1,400 cm^{-1} exhibit a lower intensity than after carbonization this change in intensity is the result of the activating action at high temperature. Oxygen and hydrogen groups are decomposed and extracted from the surface [29]. In addition, the disappearance of bands and the emergence of others suggest that the aromaticity of the material increases during activation. Basically, FTIR results show that the heating up to 800°C is sufficient to perform a complete carbonization and activation of date pits.

2.3. Adsorption of o-CP under static conditions

The adsorption processes from aqueous solutions of o-CP on the activated carbons were carried out at different operating parameters. After which the equilibrium concentrations were determined spectrophotometrically at the maximum absorbance wavelength (λ) using a UV-SOFAS-MONACO, spectrophotometer.

The sorption capacity at time t, q_t (mg/g) was obtained as follows:

$$q_t = (C_0 - C_t).\frac{v}{m} \quad (1)$$

where C_0 and C_t (mg/l) were the liquid-phase concentrations of solutes at initial and a given time t, v (l) was the solution volume and m *is* the mass carbon (g).

The amount of adsorption at equilibrium, q_e, was given by the following equation:

$$q_e = (C_0 - C_e).\frac{v}{m} \quad (2)$$

where C_e (mg/l) was the o-CP concentration at equilibrium. (Table 3 also shows some physical characteristics of the o-CP used).

Table 2
Assignments of IR absorption bands for carbonized dates (CD) and activated (AC) dates stones

	Comments	AC σ (cm^{-1})	CD σ (cm^{-1})
C=O	Stretching in aldehydes, ketones groups and esters	1,739.86	
C–H	Stretching in alkyl groups	2,851.76 et 2,918.76	2,930
O–H	Stretching in hydroxyl groups	3,434.17	3,435.65
–C–O–C–	Stretching vibration in pyranose ring skeletal or stretching aromatic ring	1,118.81	
P=O		1,227.97	
P–O–C		1,029.37	
N–H		1,633.56	1,630.76
–CH$_2$–		1,454.54	
P=S	Amides	699.3	
NH$_2$–CR=O		497.9	

Note: σ is the wave number.

Table 3
Physical characteristic of o-CP

Compound	λ (nm)	p*K*a at 298 K	Solubility at 298 K, g/100 g H_2O
o-CP	273	8.8	2.6

2.4. Equilibrium isotherms

Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH. An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Equations often used to describe the experimental isotherm data are those developed by Freundlich and by Langmuir. The Freundlich and Langmuir isotherms are the most commonly used to describe the adsorption characteristics of adsorbent used in water and wastewater.

For the determination of adsorption isotherms, accurately weighted amount of AC (1 g) were continuously stirred at 300 rpm with 100 mL of 100 mg L^{-1} pollutant aqueous solution in bath. The temperature was controlled at 20˚C. The solution pH was 5.45. At this pH all the o-CP is in their protonated forms. Agitation was provided for 2 h, which is more than sufficient time to reach equilibrium. At the end of the equilibrium period, the contents of the flasks were analyzed for residual concentration of adsorbate using spectrophotometer.

3. Modeling of adsorption isotherms

3.1. Langmuir model

The Langmuir model [30] assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir equation may be written as follows:

$$q_e = \frac{q_m\ b\ C_e}{1 + b\ C_e} \tag{3}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of the solute in the bulk solution (mg L^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), and b is the constant related to the free energy of adsorption (L mg^{-1}). Eq. (1) can be linearized.

3.2. Freundlich model

The Freundlich [31] equation can be written as follows:

$$q_e = K_F C^{1/n} \tag{4}$$

where K_F is a constant indicative of the relative adsorption capacity of the adsorbent, and n is a constant indicative of the intensity of the adsorption. The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases.

3.3. Discussion of Equilibrium isotherms

Freundlich and Langmuir adsorption isotherm plots of adsorption of o-CP on activated carbon are shown in Figs. 3 and 4, respectively. It is seen from the linearity of plots in Figs. 3 and 4, that adsorption of o-CP on date carbon follows both Freundlich and Langmuir isotherm models with a regression constant greater than 0.97. The values of Freundlich and Langmuir constants are listed in Table 4. The adsorption capacity K_F and the intensity of adsorption n are calculated from intercept and the slope of Freundlich isotherm plot. The value of q_m is significantly higher for date carbon for o-CP. The prepared activated car-

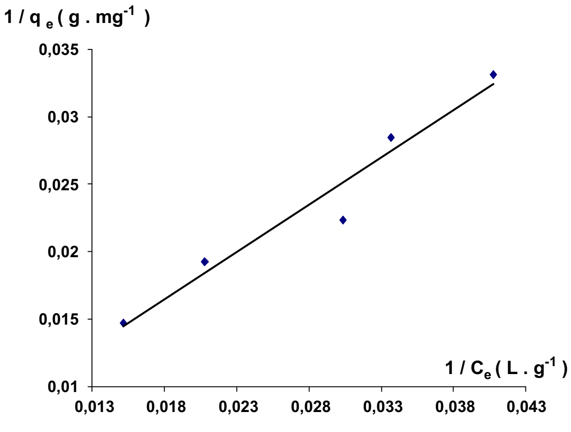

Fig. 3. Freundlich plot for adsorption of o-CP on AC.

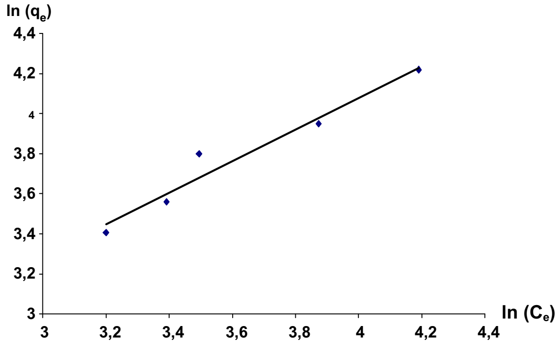

Fig. 4. Langmuir plot for adsorption of o-CP on AC.

bon showed an adsorption capacity better than that of many activated carbons in current use such as jute fiber, wood charcoal, and biologically activated carbons [32–34].

4. Kinetics of the adsorption process

The process efficiency is controlled by the kinetics of adsorption, and hence, several kinetic models are available in order to predict the mechanism involved in the sorption process. Among these models, Lagergren's rate equation appears to be one of the most widely used for the sorption of a solute from a liquid solution [35].

Pseudo-first order:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}.t \tag{5}$$

Pseudo-second order:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2.q_e^2} \tag{6}$$

The intraparticle diffusion model has been applied to various adsorption systems and was found to account for adsorption mechanism in many well-stirred adsorption systems [36]:

$$q_t = K_p.t^{1/2} \tag{7}$$

Elovich equation:

$$q_t = \left(\frac{1}{\beta}\right).\ln(\alpha.\beta) + \left(\frac{1}{\beta}\right)\ln(t) \tag{8}$$

In this work, the activated carbon was used as the adsorbent and o-CP as the adsorbate.

4.1. Adsorption kinetics

The process efficiency is controlled by the kinetics of adsorption, and hence, several kinetic models are available in order to predict the mechanism involved in the sorption process. Among these models, models including pseudo-first order of Lagergren, pseudo-second order, Elovich, and pore diffusion models were tested for simulation of the experimental data. The linear plots $\log(q_t - q_e)$ versus t, t/q_t vs. t, ln q_t versus ln t and q_t versus $t^{0.5}$ allowed checking the validity of the different models. The kinetic parameters calculated from Eqs. (3)–(6) for the adsorption of the pollutant at different temperatures, different agitation rates, and different concentration of o-CP on activated carbon are given in Tables 5–7. Pseudo-second order and pore diffusion models successfully fit the adsorption kinetic. From Tables 5–7, the pseudo-second order seems to be the most appropriate, owing to the highest correlation coefficients recorded (always above 0.99).

4.1.1. Effect of agitation rate

As can be seen from Fig. 5, there is a small effect of shaking rate on uptake capacity but a great effect on the adsorption rate. At a strong agitation rate, the resistance of the boundary layer surrounding the adsorbent weakens. The rate constants of pseudo-second order and pore diffusion were calculated in Table 5. As can be shown by the k_2 constant, o-chloroprenee are adsorbed faster at higher shaking rate, but k_p did not change with agitation rate. The highest sorption was at 300 rpm.

Table 4
Freundlich isotherm and Langmuir isotherm constants of adsorption of o-CP on AC

Freundlich constants			Langmuir constants		
K_F	N	R^2	q_m (mg g^{-1})	b (L mg^{-1})	R^2
2.52	1.26	0.97	263.15	0.0054	0.97

Table 5
Kinetic model parameters for the adsorption of 2-CP at different agitation rates on activated carbon

Kinetic model parameters	Speed agitation (rpm)					
		60	80	100	200	300
Pseudo-first-order	k_1	5.08	6.8	6.53	7.88	5.61
	r^2	0.79	0.95	0.95	0.98	0.96
Pseudo-second-order	k_2 (10^3)	7.89	5.35	4.92	3.33	3.09
	r^2	0.99	0.99	0.99	0.99	0.99
Pore diffusion	k_p (10^2)	7.93	8.44	9.71	9.81	10.52
	r^2	0.98	0.95	0.98	0.98	0.97
Elovich	α	294.14	179.95	50.60	46.236	30.22
	β	0.23	0.20	0.11	0.11	0.09
	r^2	0.96	0.96	0.97	0.96	0.98

Table 6
Kinetic model parameters for the adsorption of 2-CP at different temperature on activated carbon

Kinetic model parameters	Temperature (°C)					
		15	18	20	25	30
Pseudo-first-order	k_1 (10^2)	7.43	8.69	7.90	6.21	8.90
	r^2	0.9	0.96	0.96	0.89	0.89
Pseudo-second order	k_2 (10^3)	3.29	3.16	3.09	2.71	2.53
	r^2	0.99	0.99	0.99	0.99	0.99
Pore diffusion	K_p (10^2)	12.29	10.77	10.52	9.18	8.67
	r^2	0.93	0.95	0.98	0.95	0.93
Elovich	α	60.760	43.320	28.280	17.79	15.74
	β	0.1	0.10	0.09	0.08	0.08
	r^2	0.97	0.97	0.98	0.97	0.97

Table 7
Kinetic model parameters for the adsorption of 2-CP at different concentration on activated carbon

Kinetic model parameters	Concentration of o-CP (mg/l)					
		75	100	150	200	250
Pseudo-first-order	k_1 (10^2)	8.02	8.69	6.64	5.82	5.33
	r^2	0.93	0.96	0.94	0.84	0.87
Pseudo-second-order	k_2 (10^3)	3.92	3.09	1.73	1.19	1.11
	r^2	0.99	0.99	0.99	0.99	0.99
Pore diffusion	K_p (10^2)	11.66	10.52	8.12	7.16	5.95
	r^2	0.99	0.98	0.97	0.98	0.98
Elovich	α	20.33	30.21	27.9	31.1	31.24
	β	0.11	0.09	0.07	0.061	0.05
	r^2	0.96	0.98	0.98	0.94	0.95

4.1.2. *Effect of temperature*

Temperature dependence of the adsorption process is associated with several thermodynamic parameters. Fig. 6 and Table 6 show a decreasing trend of o-CP removal with the rise in temperature from 15 to 35°C. In the rate law, the temperature dependence appears

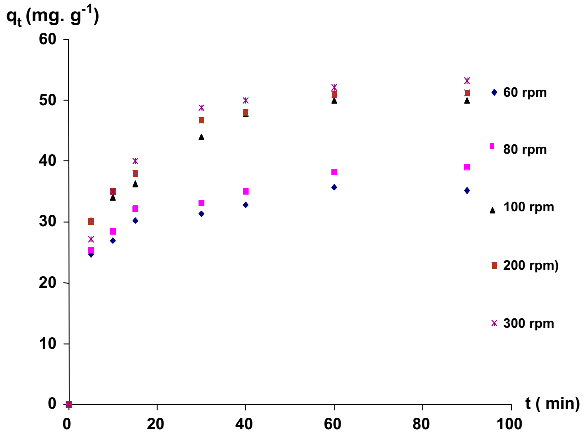

Fig. 5. Effect of agitation rate on adsorption ($T = 20$°C, pH = 5.45, concentration of o-CP = 100 mg/L, and carbon dose = 1 g/L).

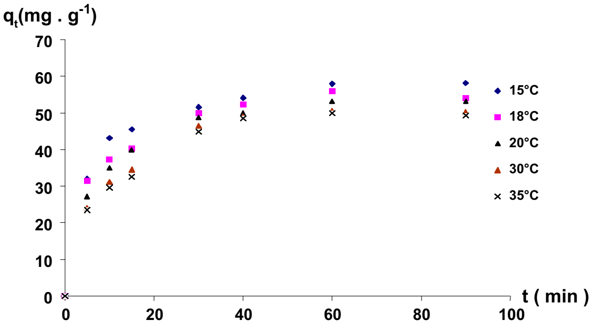

Fig. 6. Effect of temperature on the adsorption(concentration of o-CP = 100 mg/L, pH = 5.45, speed = 300 rpm, and carbon dose = 1 g/L).

in the rate constant. Quite remarkably, the temperature dependence of virtually all reactions can be fit successfully to the Arrhenius equation [37]:

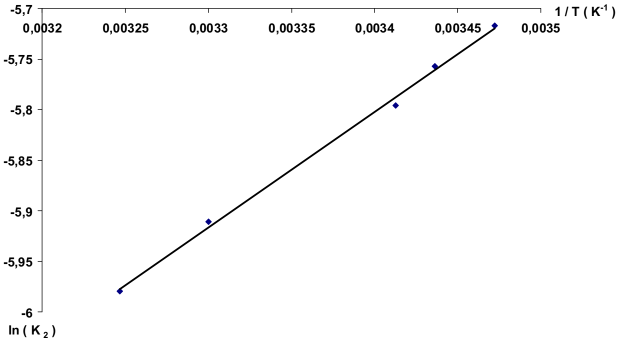

Fig. 7. Arrhenius plot for adsorption of o-CP.

$$k_2 = k_0 . \exp\left(\frac{E}{RT}\right) \tag{9}$$

where k_0 is the temperature-independent factor (gmg^{-1} min^{-1}), E is the activation energy of sorption (kJ mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the solution temperature (K). From this equation, the rate constant of sorption, k_0, is 6.17.10^{-5} g mg^{-1} min^{-1}, and the activation energy of sorption, E, is −9.51 kJ mol^{-1}. These results show that adsorption process by activated carbon is exothermic the low value of the energy of activation that there is physical adsorption Fig. 7.

4.1.3. Effect of initial concentration

The effect of the initial concentration on the sorption by carbon was investigated at concentrations in the range 75–250 mg/l. Fig. 8 shows the effect of the initial concentration of o-CP on the process kinetics. It was found that with the increase in the initial concentration q_t increased. The increase in q_t with the increase in C_i was expected was expected (it was confirmed by the equilibrium studies — isotherms) due to the increase in the sorption surface area.

The pseudo-second order rate constant k_2 and the corresponding linear regression correlation coefficient value r^2 are given in Table 7, it can be noticed that at all initial concentrations the linear regression correlation coefficients r^2 values were found to be higher ranging from 0.996 to 0.999.

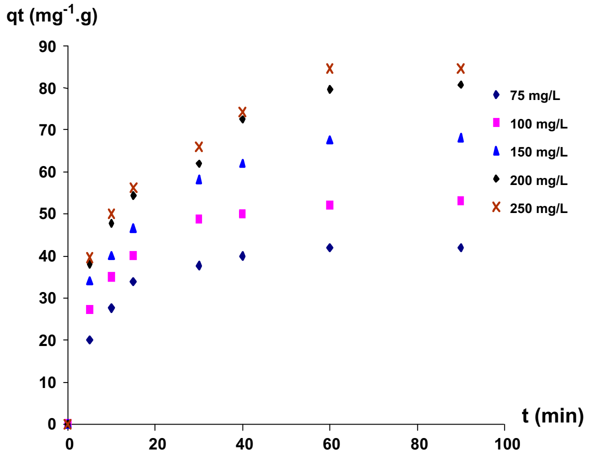

Fig. 8. Effect of initial concentration on the adsorption (concentration of adsorbent = 1 g/L, pH = 5.45, speed = 300 rpm, and $T = 20$°C).

Table 8
Thermodynamic parameters

T (˚K)	ΔH^0 (kJ mol^{-1})	ΔS^0 10^{-3} (J mol^{-1} K^{-1})	ΔG^0 (kJ mol^{-1})
288	−15.9	−47.41	−6.59
291			−5.92
293			−5.11
303			−4.55
308			−4.49

5. Thermodynamic parameters

Thermodynamic parameters such as free energy, enthalpy and entropy changes can be estimated using equilibrium constants changing with temperature. The free energy change of the sorption reaction is given by using the following equation [38]:

$$\Delta G^0 = -RT\ln(k_\mathrm{d}) \tag{10}$$

where R is universal gas constant, k_d coefficient of distribution, T temperature (K), and ΔG^0 *is* the free energy change (J mole^{-1}). The free energy change indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption [39]. The free energy change may be expressed in terms of enthalpy change of adsorption as a function of temperature as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{11}$$

Combining Eqs. (10) and (11) and rearranging:

$$\ln(k_\mathrm{d}) = \frac{-\Delta H^0}{R.T} + \frac{\Delta S^0}{R} \tag{12}$$

$-\Delta H^0$ and ΔS^0 values for iron sorption can be evaluated from the slope and intercept of the linear plot Ln k_d versus $1/T$, Where ΔS^0 and ΔH^0 are changes in entropy and enthalpy of adsorption, respectively.

5.1. Determination of thermodynamic parameters

For the sorption of 2-CP the free energy change $-\Delta G^0$ values at different temperatures were calculated from Eq. (10), while the enthalpy $-\Delta H^0$ and entropy changes $-\Delta S^0$ were calculated from the slope and intercept of the line plotted according to Eq. (10) and they are presented in Table 8. The adsorption enthalpy (ΔH^0 obtained is -15.9 kJ mol^{-1}. Negative ($-\Delta G^0$) value indicates that a high equilibrium constant was obtained.

6. Conclusion

The use of activated carbon prepared by date cores for the adsorption of o-CP was examined. The following conclusions can be deduced from experimental data.

- Initially, the rate of adsorption of o-CP onto activated carbon was very high, followed by decreasing rates, until an almost constant value.
- The adsorption isotherms of o-CP were better with Langmuir and Freundlich models.

Among the five tested models, the pseudo-second order appears to be the most convenient to describe the adsorption kinetic of o-CP in activated carbon.

- The activation energy value was found to be -9.51 kJ mol^{-1}. The determination of thermodynamic parameters, such as enthalpy, entropy, and Gibb's free energy changes showed the spontaneous and exothermic adsorption of o-CP by activated carbon.

References

[1] E. Matisova, S. Skrabakova, E. Benick, I. Novak, D. Berek, Use of a novel carbon sorbent for the adsorption of organic compounds from water, J. Chromatogr. 665 (1994) 27–32.

[2] R. Leboda, J. Skubiszewska-Zieba, W. Grzegorczyk, Effect of calcium catalyst loading procedure on the porous structure of active carbon from plum stones modified in the steam gasification process, Carbon 36 (1998) 417–425.

[3] C. Moreno-Castilla, J. Rivera-Utrilla, M.V. Lopez-Ramon, F. Carrasco-Marin, Adsorption of some substituted phenols on activated carbons from a bituminous coal, Carbon 33 (1995) 845–851.

[4] H. Marsh, M. Iley, J. Berger, T. Siemieniewska, The adsorptive properties of activated plum stone chars, Carbon 13 (1975) 103–109.

[5] J.D. Lopez-Gonzalez, F. Martinez-Vilchez, F. Rodriguez-Reinoso, Preparation and characterization of active carbons from olive stones, Carbon 18 (1980) 413–418.

[6] L.M. Nieto, S. Ben Driss Alami, G. Hodaifa, C. Faur, S. Rodríguez, J.A. Giménez, J. Ochando, Adsorption of iron on crude olive stones, Ind. Crops Prod. 32 (2010) 467–471.

[7] K. Rouibah, A.-H. Meniai, M.T. Rouibah, L. Deffous, M. Bencheikh Lehocine, Chromium VI and cadmium II removal from aqueous solutions by olive stones, Desalin. Water Treat. 16 (2010) 393–401.

[8] J.M. Ramos, R. Arana, R.R. Mazzoco, Adsorption studies of methylene blue and phenol onto black stone cherries prepared by chemical activation, J. Hazard. Mater. 180 (2010) 656–661.

[9] M. Olivares-Marín, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, Preparation of activated carbon from cherry stones by physical activation in air. Influence of the chemical carbonisation with H_2SO_4, J. Anal. Appl. Pyrolysis 94 (2012) 131–137.

[10] J. Guo, A.C. Lua, Activated carbon prepared from oil palm stone by one-step CO_2 activation for gaseous pollutant removal, Carbon 38 (2000) 1985–1993.

[11] A.C. Lua, F.Y. Lua, J. Guo, Influence of pyrolysis conditions on pore development of oil-palm-shell activated carbons, J. Anal. Appl. Pyrolysis 76 (2006) 96–102.

[12] C. Sentorun-Shalaby, M.G. Ucak-Astarlıoglu, L. Artok, C. Sarici, Preparation and characterization of activated carbons by one-step steam pyrolysis/activation from apricot stones, Microporous Mesoporous Mater. 88 (2006) 126–134.

[13] K. Gergova, Effects of activation method on the pore structure of activated carbons from apricot stones, S. Eser, Carbon 34 (1996) 879–888.

[14] C.A. Toles, W.E. Marshall, M.M. Johns, L.H. Wartelle, A. McAloon, Acid-activated carbons from almond shells: Physical, chemical and adsorptive properties and estimated cost of production, Bioresour. Technol. 71 (2000) 87–92.

[15] C. Erlich, E. Bjornbom, D. Bolado, M. Giner, T.H. Fransson, Pyrolysis and gasification of pellets from sugar cane bagasse and wood, Fuel 85 (2006) 1535–1540.

[16] A. Arenillas, T.C. Drage, K. Smith, C.E. Snape, CO_2 removal potential of carbons prepared by co-pyrolysis of sugar and nitrogen containing compounds, J. Anal. Appl. Pyrolysis 74 (2005) 298–306.

[17] R.R. Bansode, J.N. Losso, W.E. Marshall, R.M. Rao, R.J. Portier, Bioresour, Adsorption of volatile organic compounds by pecan shell- and almond shell-based granular activated carbons, Technol. 90 (2003) 175–184.

[18] S.A. Dastgheib, D.A. Rockstraw, Pecan shell activated carbon: Synthesis, characterization, and application for the removal of copper from aqueous solution, Carbon 39 (2001) 1849–1855.

[19] E. Putun, B.B. Uzun, A.E. Putun, Fixed-bed catalytic pyrolysis of cotton-seed cake: Effects of pyrolysis temperature, natural zeolite content and sweeping gas flow rate, Bioresour. Technol. 97 (2006) 701–710.

[20] N.M. Haimour, S. Emeish, Utilization of date stones for production of activated carbon using phosphoric acid, Waste Manage 26 (2006) 651–660.

[21] M.A. Abdulkarim, N.A. Darwish, Y.M. Magdy, A. Dwaidar, Adsorption of Phenolic Compounds and Methylene Blue onto Activated Carbon Prepared from Date Fruit Pits, Eng. Life Sci. 2 (2002) 161–165.

[22] W.H. Barreveld, Date Palm Products, FAO Agricultural Services, Bulletin no. 101, Food and Agriculture Organization of the United Nations, Rome, Italy, 1993.

[23] I. Bautista-Toledo, J. Rivera-Utilla, M.A. Ferro-Garcia, C. Moreno-Castilla, Influence of the oxygen surface complexes of activated carbons on the adsorption of chromium ions from aqueous solutions: Effect of sodium chloride and humic acid, Carbon 32 (1994) 93–100.

[24] N. Kannan, S. Murugavel, R.K. Seenivasan, G. Rengasamy, Preparation and characterization of activated carbons obtained from agricultural wastes, Indian J. Environ. Prot. 23 (12) (2003) 1367–1376.

[25] Toxicological profile for chlorophenols. Agency for Toxic Substances and Disease Registry, Atlanta, GA; US Department of Health and Human Services, July, 1999.

[26] C.S. Hottenstein, S.W. Jourdan, M.C. Hayes, F.M. Rubio, D.P. Herzog, T.S. Lawruk, Determination of pentachlorophenol in water and soil by a magnetic particle based enzyme immunoassay, Environ. Sci. Technol. 29(11) (1995) 2754–2758.

[27] A.A. El-Hendawy, Variation in the FTIR spectra of a biomass under impregnation, carbonization and oxidation conditions, J. Anal. Appl. Pyrolysis 75 (2006) 159–166.

[28] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, Fuel 86 (2007) 1781–1788.

[29] H. Jankowska, A. Swiatkowski, J. Choma, Active Carbon, Ellis Horwood, New York, NY, 1991.

[30] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[31] H.M.F. Freundlich, Über die adsorption in Lösungen, Z. Phys. Chem 57 (1906) 385–470.

[32] S.S. Rayalu, A. Srivastava, Adsorption of phenol on new adsorbent activated carbon cloth, Indian J. Environ. Prot. 13 (1993) 407–411.

[33] M.S. Palanichamy, B. Joseph, S. Chandran, Adsorption kinetics of phenol controlled burnt wood charcoal system, Indian J. Environ. Prot. 14 (1994) 591–596.

[34] S.R. Ha, S. Vinithantharat, Competitive Removal of Phenol and 2,4-Dichlorophenol in Biological Activated Carbon System, Environ. Technol. 21 (2000) 387–394.

[35] M. Ahmaruzzaman, D.K. Sharma, Adsorption of phenols from wastewater, J. Colloid Interface Sci. 287 (2005) 14–24.

[36] X. Yang, B. Al-Duri, Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon, J. Colloid Interface Sci. 287 (2005) 25–34.

[37] M. Dogan, M. Alkan, Adsorption kinetics of methyl violet onto perlite, Chemosphere 50 (2003) 517–528.

[38] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes Pigm. 54 (2002) 47–58.

[39] Y.S. Choi, J.H. Cho, Color removal from dye wastewater using Vermiculite, Environ. Technol. 17 (1996) 1169–1180.