Desalination and Water Treatment
www.deswater.com

1944-3994 / 1944-3986 © 2009 Desalination Publications. All rights reserved.

7 (2009) 182–190

Adsorption of phenol and dye from aqueous solution using chemically modified date pits activated carbons

Meriem Belhachemi[a*], Zohra Belala[a], Driss Lahcene[a], Fatima Addoun[b]

[a]*Université de Béchar, 08000, Bechar, Algeria*
Tel. +213 49815591; Fax +213 49815244; email: bel_meriem@yahoo.fr
[b]*Laboratoire d'étude physico-chimique des matériaux et application à l'environnement, Faculté de Chimie, USTHB, B.P. 32, El Alia 16111 Bab Ezzouar Alger, Algeria*

Received 22 August 2008; accepted in revised form 28 May 2009

ABSTRACT

The adsorption of phenol and methylene blue (MB) on modified activated carbons has been investigated. The activated carbon was prepared from date pits by physical activation (CO_2 as activating agent). Oxidation in the liquid phase with nitric acid and thermal treatment under flowing nitrogen were carried out in order to produce samples with different surface chemical properties but with no major differences in their textural properties. The surface area and porosity were characterized by N_2 adsorption at 77 K and CO_2 adsorption at 273 K. The changes in surface chemistry were studied by temperature programmed decomposition. Kinetic and equilibrium adsorption data of phenol and dye were carried out. Adsorption kinetic data were tested using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Equilibrium data were analyzed by Langmuir and Freundlich isotherm models. The maximum adsorption capacities calculated from the Langmuir isotherm model were 161.8 and 216.4 $mg.g^{-1}$ for phenol and MB, respectively. The different uptakes obtained are discussed in relation to the chemical properties of the adsorbents. The results show that surface chemistry of the activated carbon plays a key role in phenol and dye adsorption. Finally, activated carbon from date pits with appropriate preparations can rich a high adsorption capacity.

Keywords: Date pits; Activated carbon; Acid treatment; Thermal treatment; Adsorption

1. Introduction

Water has been found to contain small amounts of a large number of synthetic organic compounds such as phenols, pesticides, herbicides, dyes, ethers, amines, nitro compounds, etc. More than 1500 different organic compounds are suspected to be present in drinking waters. These organic compounds are derived from industrial and municipal wastewater, rural and urban run off, natural decomposition of animal and vegetable matter, and from agricultural practices [1]. Such waters are an increasing concern and represent a serious potential hazard for human health and aquatic life.

Adsorption of organic solutes from the aqueous phase is a very important application of powdered and granular activated carbons. This covers a wide spectrum of systems such as drinking water and wastewater treatments, and applications in food, beverage, pharmaceutical and chemical industries [1,2].

This could be related to the extended surface area, high adsorption capacity, microporous structure and special surface reactivity of activated carbons [3,4]. However, the adsorption capacity of activated carbons depends

---

* Corresponding author.

Presented at EuroMed 2008, Desalination for Clean Water and Energy Cooperation among Mediterranean Countries of Europe and the MENA Region, 9–13 November 2008, King Hussein Bin Talal Convention Center, Dead Sea, Jordan.

mainly on the precursor nature, the operating conditions of adsorption and the adsorbate characteristics. Activated carbons have been studied with varying success for the removal of colour and organic matters [5]. The main benefits of using activated carbons are the possibility of tailoring their physical and chemical properties for a specific application [6]. This approach has been applied successfully in catalysis [7].

The nature of the surface functional groups can be modified through physical and chemical treatments, by liquid phase oxidation treatments, using acidic solutions (HNO_3, H_2O_2, etc.) at different concentrations, temperatures, and contact times, by gas phase oxidation with O_2 or N_2O at different temperatures, pressures, and contact times, and by thermal treatments at different temperatures and in different gaseous environments (N_2, H_2), to selectively remove some of the oxygen surface compounds [8].

Date pits are among the most common agricultural by-products available commercially in the palm growing countries such as Algeria. Date pits constitute roughly 10% in weight of the fruit [9]. They are suitable for preparing activated carbon due to their excellent natural structure and low ash content [10]. So, the development of activated carbon with high surface area, micropore volume and different surface properties from date pits that can be used in practical applications is a very interesting subject.

In the present work, the activated carbon was prepared from date pits by thermal activation, then, the sample was modified by appropriate treatments in order to obtain two additional activated carbons with different surface chemical properties but with no important differences in their textural properties. The adsorbents prepared were subsequently tested in the removal of phenol and methylene blue from aqueous solution. The aim of the present paper is to study the interactions between the adsorbates (phenol and dye) and the functional groups of modified activated carbons produced from date pits in order to develop optimised adsorbent materials for water treatment.

2. Experimental

2.1. Preparation of activated carbons

The starting date pits were washed several times with water and then dried at 150°C. The dried pits were crushed and sieved, the fraction of particle size 0.5–1.0 mm being used for the preparation of activated carbon. The char was obtained by carbonization in a horizontal furnace under a flow of nitrogen (150 $ml.min^{-1}$) at 825°C with a heating rate of 5°C min^{-1}, for 2 h. Activation of the char was carried out in the same furnace, by heating the char in flowing nitrogen up to 800°C. At this temperature, N_2 was replaced by CO_2 (150 ml min^{-1}) and activation was carried out during different activation times to cover different burn-off. Then, the activating agent was replaced with nitrogen to cool down to room temperature. In this application, we choose the activated carbon with 37% burn-off; it exhibits uniform microporosity ($V_0(N_2) \approx V_0(CO_2)$) [11], the contribution from mesoporosity being relatively small. The sample was named C37.

The sample C37 was treated with concentrated HNO_3 (14 M) at boiling temperature (105°C) during 10 min. Then it was washed with distilled water to neutral pH and dried at 110°C. This carbon was referred as C37N.

The thermal treatment was performed on a fraction of sample C37N under an N_2 flow with a heating rate of 10°C/min until final temperature of 700°C and kept at this temperature for 1 h. The sample obtained was referred as C37NT.

2.2. Characterization of activated carbons

2.2.1. Texture

The textural characterization of activated carbons was carried out by nitrogen and dioxide carbon adsorption at 77 K and at 273 K respectively, using a static manometric apparatus. The N_2 apparent surface area (S_{BET}) was calculated by using the B.E.T equation [12].

The Dubinin–Radushkevich equation was used to calculate the micropore volume (V_0) from both nitrogen and carbon dioxide adsorption isotherms [13]. The mesopore volume was deduced from the N_2 adsorption isotherm, by subtracting the value of V_0 (N_2) from the amount adsorbed at $P/P_0 = 0.95$ [14].

2.2.2. Surface chemistry

There is a variety of techniques for the surface chemistry characterisation of activated carbons. However, temperature-programmed decomposition (TPD) is the most suitable one for characterizing oxygen containing surface groups in carbons [15]. The TPD profiles were obtained by using a vertical quartz reactor inside an electric furnace, connected to a quadrupole mass spectrometer. About 100 mg of the sample were introduced into it and thermally treated at 10°C min^{-1} from room temperature up to 1050°C under a flow of helium, and the evolved gases were analyzed. The amounts of CO and CO_2 evolved during the thermal treatment were calculated by integration of the desorption profiles. Both $CaC_2O_4 \cdot H_2O$ and known mixtures of both gases were used as references for the calibration of the spectrometer.

2.3. Adsorption experiments

Phenol and methylene blue were used to evaluate the adsorption capacity of the prepared materials. Kinetic tests were carried out in order to determine the equilibrium time, which was found to depend on the adsorbate. Phenol or dye solutions were put in contact with the activated carbons for different times, at a constant temperature of 25°C. For that purpose, a number of samples were prepared by mixing 10 mg of activated carbon with 10 mL of a solution of phenol or dye at concentration 100 mg/L. After equilibrium time was reached, the solutions were centrifuged at 2000 rpm for 2 min. The solutions were carefully decanted to be analyzed using a UV/VIS spectrophotometer (Unicam helios δ), at 269 nm and 665 nm, which were the maximum wave lengths for phenol and methylene blue respectively. Dilution was undertaken when absorbance exceeded 1.0 for dye; the phenol's solutions were in the range of calibration. The final concentration of the solution was then determined from the calibration curve.

The amount of adsorption at equilibrium was calculated based on the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of phenol or dye solutions, respectively, *m is* the amount of adsorbent and *V* is the volume of solution.

The equilibrium adsorption isotherms at 25°C were obtained by introducing 10 mL of phenol or dye solutions of different concentrations with 10 mg of the activated carbons and measuring the adsorbate concentration after 24 h, following the procedure mentioned above. The solution pH was used without adjustment for all experiments.

3. Results and discussion

3.1. Textural characterization

The N2 adsorption–desorption isotherms for activated carbons (C37, C37N and C37NT) are shown in Fig. 1. Additionally, Table 1 reports the texture parameters obtained for the three activated carbons. The isotherms are of type I, which corresponds to microporous materials, all isotherms present a hysteresis (the desorption is not coexistent with the adsorption isotherm), indicating the presence of mesopores. As it can be observed C37N (oxidized activated carbon) presents the lowest adsorption capacity. After oxidation with HNO_3 the sample C37N exhibits the lower surface area and the lower total pore volume, this is a consequence of the fixation of oxygen groups essentially at the entrance of the pores, which increased their constriction. Indeed, the micropore volume $V_0(N_2)$ has decreased more than the narrow micropore $V_0(CO_2)$, probably because the limit accessibility of nitrogen to the porous structure. When C37N was treated under an inert flow of nitrogen at the temperature of 700°C, it lost the oxygenated groups, together with carbon atoms. This led to an activation process that increased the surface area and the pore volume of carbon C37NT with regard to the respective values of the original sample C37.

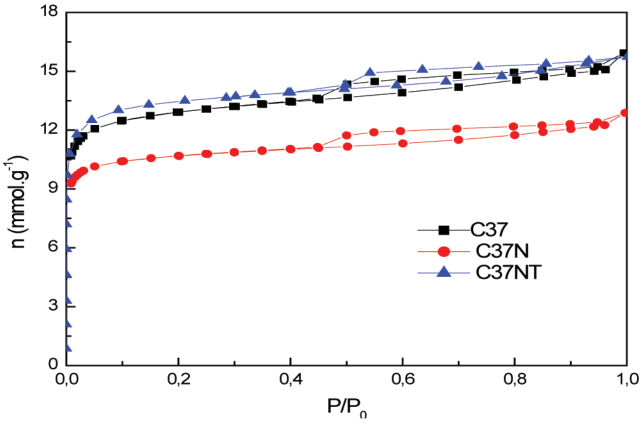

Fig. 1. Adsorption-desorption isotherms of N_2 at 77K for C37, C37N and C37NT activated carbons.

Table 1
Surface area, micropore volume and mesopore volume of activated carbon samples

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	$V_0(N_2)$ ($cm^3 \cdot g^{-1}$)	V_{meso} ($cm^3 \cdot g^{-1}$)	$V_T(N_2)$ ($cm^3 \cdot g^{-1}$)	$V_0(CO_2)$ ($cm^3 \cdot g^{-1}$)
C37	1069	0.44	0.08	0.52	0.36
C37N	950	0.37	0.05	0.42	0.35
C37NT	1160	0.46	0.07	0.53	0.39

3.2. Surface chemistry characterization

The amount and the nature of the oxygen surface groups on the parent, oxygenated and thermally treated carbons were analyzed by temperature programmed desorption experiments. Fig. 2 shows the CO_2 and CO profiles of the activated carbon before and after treatment. Additionally, Table 2 reports the total amount of oxygen surface groups evolved both as CO_2 and CO. An increase in the amount of surface oxygen groups was evidenced by the increase of the CO_2 and CO peaks for the sample after oxidation (C37N). It presented higher peaks of both CO_2 and CO; nitric acid treatment increased the CO_2 evolution at low temperature (from 200 to 500°C). It may be undoubtedly attributed to carboxylic acid functions, while the higher temperature CO_2 peak was at about 625°C, which may result from carboxylic anhydrides and lactones [15]. The CO evolution profile presents a large shoulder with two peaks at high temperature from 400°C to 980°C which is attributed to carbonyl, ether and quinone [15,16]. This behaviour has been observed in others activated carbons after oxidation with nitric acid [17]. On the other hand, C37 and C37NT exhibited a CO peak at high temperature from 800 to 1000°C. After thermal treatment, the sample retained only a small amount of CO-releasing groups at higher temperatures. These groups can be assigned to carbonyl, quinine, etc. type of structure which has basic properties. Previous studies on activated carbon showed that thermal treatment with N_2 and H_2 produces carbons

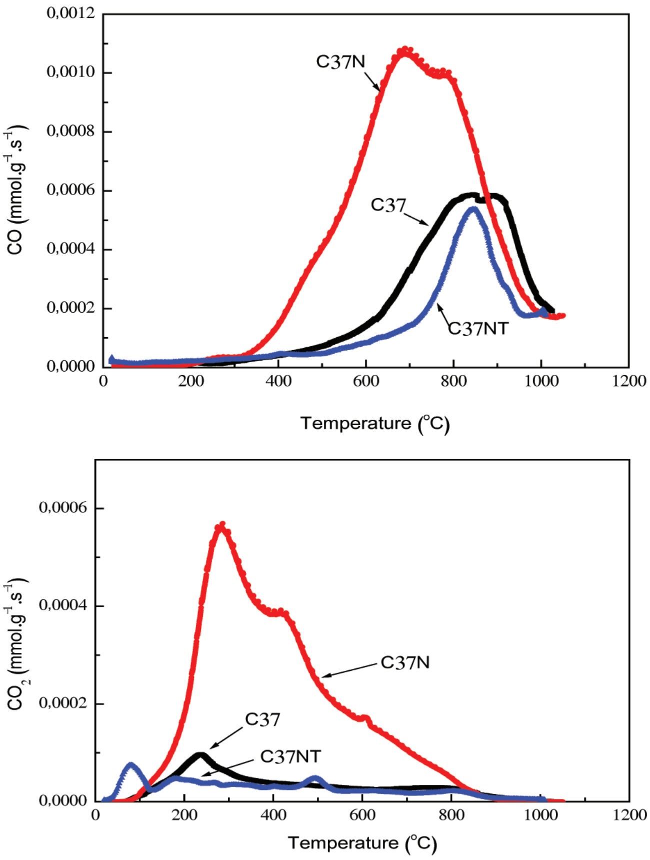

Fig. 2. TPD spectra of C37, C37N and C37NT activated carbons: CO and CO_2 evolutions.

Table 2
Amount of CO_2 and CO evolved during TPD experiments of the activated carbon samples

Activated carbons	CO_2 (mmol.g^{-1})	CO (mmol.g^{-1})
C37	0.43	1.17
C37N	1.04	2.55
C37NT	0.15	0.92

with basic characterizations [18]. However the amount of CO_2 evolved is almost nil for C37NT and presents a low peak at low temperature for sample C37.

3.3. Adsorption kinetics

Fig. 3 shows the kinetics of phenol and methylene blue removal for the three activated carbons. It can be observed that phenol shows faster removal kinetics than methylene blue for the three samples. The kinetics adsorption was studied by applying three different models. One is the pseudo-first-order model which is also known as Lagergren equation [19]. This equation has the form as follows:

$$q_t = q_e(1-\exp^{-k_1 t}) \tag{2}$$

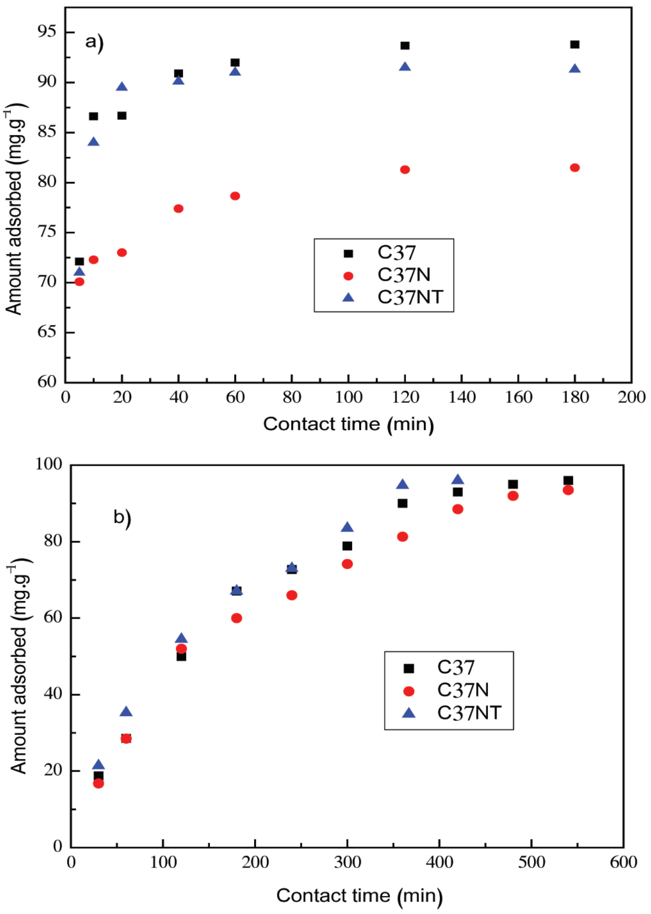

Fig. 3. Kinetic curves for the adsorption of: a) phenol and b) methylene blue on activated carbons.

where q_e and q_t are the amount of adsorption (mg.g^{-1}) at equilibrium and at time t (min), respectively, and k_1 is the rate constant adsorption (min^{-1}). Eq. (2) may be written in linear form:

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

Values of k_1 and q_e were obtained from the slope and the intercept of the linear plots of log $(q_e - q_t)$ vs. t. On the other hand, the pseudo-second-order equation [20] based on equilibrium adsorption is expressed as:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

where k_2 (g.mg^{-1}.min^{-1}) is the rate constant of second-order adsorption model. Eq. (4) can be linearized to:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

If the second-order kinetics is applicable, the plot of

t/q_t vs. t should show a linear relationship. Values of q_e and k_2 can then be determined from the slope and the intercept of the plot. The experimental kinetics data for phenol and MB onto activated carbons were fitted to the linear and non-linear forms of pseudo-first-order kinetic and pseudo-second-order kinetic models. For non-linear fitting procedure, Origin software was used.

Intraparticle diffusion model based on the theory proposed by Weber and Morris [21] was tested to identify the diffusion mechanism. According to this theory:

$$q_t = k_p t^{1/2} \qquad (6)$$

where k_p (mg/g min$^{1/2}$), the intraparticle diffusion rate constant, is obtained from the slope of the straight line of q_t vs. $t^{1/2}$. Such plots may present multi-linearity indicating that two or more steps take place [22]. The first, sharper portion is the instantaneous adsorption stage or external surface adsorption. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-limiting. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in the solution.

Table 3 summarizes the kinetic constants and correlation coefficients, R^2 of the three kinetic models for activated carbons at 25°C. From Table 3, the best fit of pseudo-first-order kinetics in the experimental kinetics data of phenol and MB suggests that it is not appropriate to use the linear regression method. The q_e values calculated by the non-linear method agreed with the experimental $q_{e,\exp}$ ones suggesting the applicability of this model. The correlation coefficient values ($R^2 > 0.99$ for MB) indicate that this model is more suitable for describing MB adsorption. Non-linear method of the pseudo-first-order model was found to be a better method than the linear method for predicting the kinetic parameters [23].

The $q_{e,\exp}$ and q_e values from pseudo second order kinetic model (linear and non-linear method) of phenol are similar to each other, which indicates that the phenol adsorption obeys the pseudo-second-order kinetics model. On the other hand, the higher R^2 values of methylene blue suggest that the pseudo-second-order kinetic model can be used to represent the kinetic uptake. While comparing

Table 3
Kinetic parameters of the pseudo-first-order, pseudo-second-order and intraparticle diffusion models for phenol and methylene blue adsorption

		1st order model					
		Linear method			Non-linear method		
Activated carbon	$q_{e,\exp}$ (mg.g^{-1})	q_e (mg.g^{-1})	k_1 (min^{-1})	R^2 (mg.g^{-1})	q_e (min^{-1})	k_1	R^2
Phenol							
C37	93.80	16.34	$7.4\ 10^{-3}$	0.93	90.50	$2.9\ 10^{-1}$	0.97
C37N	81.48	12.64	$4.9\ 10^{-3}$	0.98	77.67	$4.4\ 10^{-1}$	0.42
C37NT	91.30	17.75	$12.9\ 10^{-3}$	0.91	91.42	$3.0\ 10^{-1}$	0.90
MB							
C37	96.10	122.73	$8.2\ 10^{-3}$	0.96	99.10	$5.7\ 10^{-3}$	0.99
C37N	95.00	142.87	$5.8\ 10^{-3}$	0.96	97.45	$5.3\ 10^{-3}$	0.99
C37NT	97.22	123.32	$8.9\ 10^{-3}$	0.92	100.66	$6.3\ 10^{-3}$	0.99

	2nd order model						Intraparticle model	
	Linear method			Non-linear method				
Activated carbon	q_e (mg.g^{-1})	k_2 (g.mg^{-1}.min^{-1})	R^2 (mg.g^{-1})	q_e (g.mg^{-1}.min^{-1})	k_2	R^2 (mg.g^{-1}.min$^{-1/2}$)	k_p	R^2
Phenol								
C37	94.78	$7.1\ 10^{-3}$	1.00	94.51	$7.1\ 10^{-1}$	0.94	1.42	0.77
C37N	82.10	$6.7\ 10^{-3}$	1.00	79.87	$9.7\ 10^{-1}$	0.78	1.05	0.95
C37NT	92.50	$9.5\ 10^{-3}$	1.00	93.34	$7.1\ 10^{-1}$	0.95	1.25	0.69
MB								
C37	143.00	$0.4\ 10^{-4}$	0.99	130.28	$5.4\ 10^{-3}$	0.99	4.84	0.98
C37N	123.90	$0.4\ 10^{-4}$	0.99	125.29	$5.1\ 10^{-3}$	0.99	4.34	0.99
C37NT	116.82	$0.6\ 10^{-4}$	0.99	130.02	$6.6\ 10^{-3}$	0.99	5.22	0.99

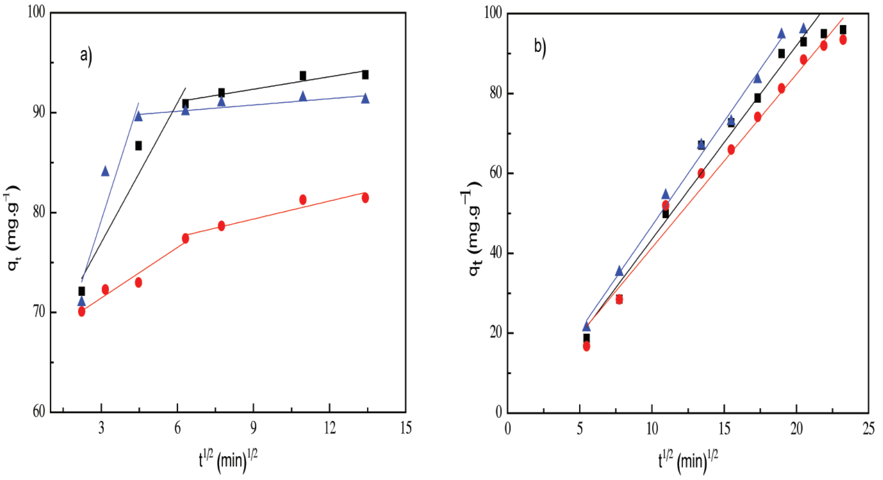

Fig. 4. Weber and Morris intraparticle diffusion plots for removal of (a) phenol and (b) methylene blue.

the $q_{e,\exp}$ and q_e values, it can be observed (Table 3) that the second-order model (linear and non-linear regression method) fails to well represent the kinetics of MB onto activated carbons.

Fig. 4 shows the plots of phenol and methylene blue uptake vs. $t^{1/2}$ for the three activated carbons. The phenol data points are related by two straight lines (Fig. 4a), indicating that two steps are considered, the first one is assumed to mass transfer and the second to the intraparticle diffusion according to Fierro et al. [24]. On the other hand, Fig. 4b presents a linear portion of the plot for a wide range of contact time between adsorbent and dye. The correlation coefficient is greater than 0.98. Further, it may be seen from Fig. 4b that there are two distinct regions — the initial pore diffusion due to external mass transfer effects followed by the intraparticle diffusion which occurred after 360 min for C37NT, 420 min for C37 and 480 min for C37N.

3.4. Adsorption isotherms

Fig. 5 shows the adsorption isotherms of phenol and methylene blue on the three activated carbon samples at 25°C. Correlation of isotherms using an empirical and theoretical equation is desired for practical operation. According to the data, the Freundlich and Langmuir equations seemed applicable:

The Freundlich adsorption isotherm assumes that adsorption occurs on heterogenous surface through a multilayer adsorption mechanism, and that the adsorbed amount increases with the concentration according to the following equation:

$$q_e = k_f \cdot C_e^{1/n} \tag{7}$$

where q_e is the amount of the adsorbate per unit mass of carbon (mg.g^{-1}), k_f is the Freundlich constant related to the adsorption capacity (mg.g^{-1}.(mg.L^{-1})$^{1/n}$, C_e is the

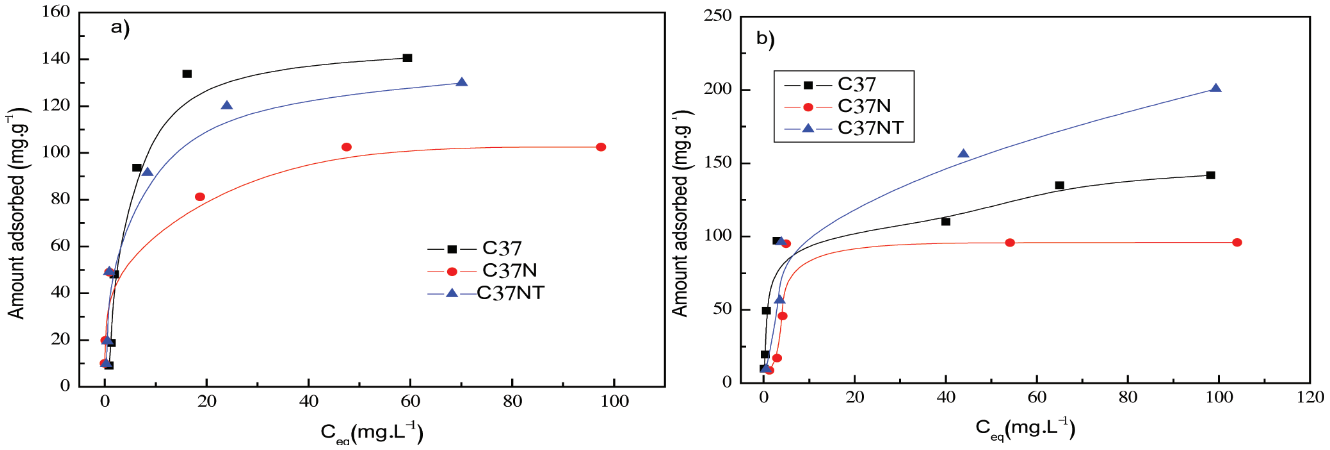

Fig. 5. Adsorption equilibrum isotherms of (a) phenol and (b) methylene blue on activated carbons.

concentration of adsorbate in the solution at equilibrium (mg/L) and *n* is the empirical parameter representing the energetic heterogeneity of adsorption sites.

The Langmuir adsorption model is based on the assumption that a maximum limiting uptake exists, corresponding to a saturated monolayer of adsorbate molecules at the adsorbent surface. In this model, all the adsorption sites have the same sorption activation energy. The Langmuir equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot \beta} + \frac{C_e}{Q_0} \tag{8}$$

where C_e and qe have the same meaning as in the Freundlich isotherm. Q_0 is the maximum uptake per unit mass of carbon (mg.g^{-1}), and b is the Langmuir constant related to the adsorption energy (L.g^{-1}).

The Langmuir models consider several assumptions: the adsorption is localized, all the active sites on the surface have similar energies, none interaction between adsorbed molecules exists, and the limiting reaction step is the surface reaction as heterogeneous catalytic reaction.

Table 4 summarizes all the constants obtained for the two isotherm models, for phenol and methylene blue on the activated carbons. The Langmuir adsorption isotherm yielded the best fit, as the R^2 values were relatively high (close to unity). From Freundlich isotherm model, the $1/n$ values obtained for all activated carbons were below one. This indicated that the adsorption process followed a normal Langmuir isotherm [25]. So, this model was used, particularly Q_0, for the discussion of the results.

Since no important changes were made in the textural properties of the adsorbents, the disparity in adsorbate uptakes for different activated carbons may be explained almost entirely by the differences in the chemical nature of the prepared samples. It may be observed in Table 4 that the maximum adsorption capacity Q_0 varies in the order C37N< C37NT< C37 for phenol and C37N< C37< C37NT for methylene blue.

Three mechanisms are necessary to understand and discuss the adsorption of organic solutes on activated carbons with different chemicals properties. Acidic groups were reported to be unfavourably for the adsorption of aromatics compounds since (i) they extract electronic density from the basal of carbon, this reducing the π-π interactions; and (ii) they increase the affinity of carbon for water molecules that can form surface complexes and then block part of micropores entrance [4,26]. In addition to the π-π interactions between the aromatic rings of solute and those of carbon substrate, another adsorption mechanisms exists, (iii) which is based on the formation of donor-acceptor complexes between the surface carbonyl groups (electron donors) and the aromatic rings of solute acting as acceptors [4,27].

The low capacity of adsorption of phenol was found for C37N, which presented higher surface oxygen groups. The adsorption increased when the carbon C37N was thermally treated at 700°C. The sample C37NT (thermally treated) had less adsorption capacity than the parent sample (C37). The extent of increase depended on the amount of acidic groups removed. The amount adsorbed was at maximum when the activated carbon surface had lost most of its acidic surface groups and when carbonyl groups were the dominating surface groups favours the adsorption of phenol.

The oxidized sample (C37N) presents the lowest adsorption capacity for the methylene blue too. The acidic treatment can remove the hydroxide groups and produce acidic surface groups on the carbon surface, which extract electrons from the π band of the carbon, reducing the interactions between the methylene blue molecule and carbon. This is due to the weakening of dispersion forces between the π electron system of the aromatic ring of MB and the π band of the graphitic planes of the carbon, which are responsible for the adsorption [28]. However, the thermally treated sample C37NT provides higher adsorption uptakes than the parent activated carbon C37. These samples are characterised by high content of elec-

Table 4
Parameters of the Freundlich and Langmuir models for phenol and methylene bue adsorption isotherms.

Activated carbon	Freundlich model			Langmuir model		
	k_f (mg.g^{-1})(mg.L^{-1})$^{1/n}$	$1/n$	R2	Q_0 (mg.g^{-1})	b (L.g^{-1})	R^2
Phenol						
C37	6.5	0.57	0.96	161.8	0.13	0.98
C37N	36.0	0.26	0.98	103.7	0.69	0.99
C37NT	28.1	0.43	0.92	135.5	0.32	1.00
BM						
C37	35.8	0.34	0.92	140.8	0.36	0.99
C37N	15.7	0.46	0.78	105.4	0.11	0.99
C37NT	22.8	0.53	0.91	216.4	0.09	0.99

Table 5
Phenol and methylene blue adsorption capacities of various adsorbents

Adsorbent	Adsorption capacity (mg/g)		Reference
	Phenol	MB	
Commercial activated carbon	137.3		[29]
Bentonite	1.7		[30]
CCM200 (carbon cryogel)	140		[31]
Clay (quartz, kalinite, etc.) 50 mm	30.3		[32]
Olive seed activated carbon		263	[33]
Oil palm shell based activated carbon		243.9	[25]
Oil palm wood activated carbon		90.9	[34]
Commercial activated carbon		160.4	[35]
Date pits activated carbon	161.8	216.4	This work

tron rich sites on the basal planes and a low concentration of electron withdrawing in this order C37<C37NT, since this latter contains less amount of oxygen surface groups.

The phenol and MB adsorption capacities of various potential adsorbents are shown in Table 5. Although the adsorption capacity of date pits activated carbon for phenol was higher than the other adsorbents; for methylene blue it was lower than that of olive seed activated carbon and oil palm shell based activated carbon; it was higher than that of other potential adsorbents. According to the results obtained, activated carbon prepared from date pits could be employed as effective adsorbents and could be considered as an alternative to adsorbents for the removal of phenol and dye.

4. Conclusions

Date pits can be used as precursors to produce activated carbons with a well developed porosity and tailored oxygen surface groups.

Oxidation with nitric acid produces a slight decrease of the porosity and the surface area of activated carbon, although drastic changes in the chemical nature of the surface take place. Thermal treatment at 700°C of the acid-treated carbon produces elimination of the oxygen surface complexes, only a fraction of CO groups with high thermal stability remain. However, the surface area and microporosity increase up to that of the original carbon.

The adsorption kinetics of the phenol on the three activated carbons is well described by the pseudo-second order model. However, the pseudo-first-order model by non-linear method is more suitable for describing MB adsorption. The adsorption isotherms could be very well fitted by the Langmuir equation and the highest phenol and methylene blue were obtained with C37 and C37NT respectively.

The surface chemistry of activated carbons plays a key role in the performance of the phenol and dye adsorption process. The presence of acid oxygenated groups on the activated carbon surface is detrimental to the adsorption of both adsorbates, whereas the thermal treatment increases the adsorption capacity for phenol and methylene blue. The elimination of oxygen surface complexes, increase the electronic density in the basal planes. The π-π interactions are favoured in thermally treated carbon.

References

[1] H. March and F. Rodríguez-Reinoso, Activated Carbon, Elsevier, Amsterdam, 2006.

[2] R.C. Bansal, J.B. Donnet and H.F. Stoeckli, Active Carbon, Marcel Dekker, New York. 1988.

[3] Md. Ahmaruzzaman, Adv. Colloid Interf. Sci. J., 143 (2008) 48–67.

[4] C. Morino-Castilla, Carbon, 42 (2004) 83–94.

[5] R.C. Bansal and M. Goyal, eds., Activated Carbon Adsorption, Taylor and Francis Group, 2005.

[6] L.R. Radovic and F. Rodriguez-Reinoso, in P.A Thrower, ed., Chemistry and Physics of Carbon, vol.25, Dekker, New York, 1997, pp.243–358.]

[7] N. Bouchenafa-Saib, P. Grange, P. Verhasselt, F. Addoun and V. Dubois, Appl. Catal. A: General, 286 (2005) 167.

[8] Z. Merzougui and F.Addoun, Desalination, 222 (2008) 394–403.

[9] N.M. Haimour and S. Emeish, Waste Manage., 26 (2006) 701–710.

[10] C. Bouchelta, M.S. Medjram, O. Bertrand and J.P. Bellat, J. Anal. Appl. Pyrolysis, 82 (2008) 70–77.

[11] D. Lozano-Castelló, D. Cazorla-Amorós and A. Linares-Solano, Fuel Process. Technol., 77–78 (2002) 325–330.

[12] S. Brunauer, P.H. Emmett and E.J. Teller, J. Am. Chem. Soc., 60 (1938) 309.

[13] M.M. Dubinin, J. Colloid Interf. Sci., 23 (1967) 487.

[14] S.J. Gregg and K.S.W. Sing, Adsorption, Surface and Porosity, Academic Press, London,1982.

[15] J.L. Figuiredo, M.F.R. Pereira, M.M.A. Freitas and J.J.M. Orfao, Carbon, 37 (1999) 1379–1389.

[16] Y. Otake and R.G. Jenkins, Carbon, 31 (1993) 109.

[17] C.O. Ania, J.B. Parra and J.J. Pis, Fuel Process. Technol., 79 (2002) 265–271.

[18] P.C.C. Faria, J.J.M. Orfao and M.F.R. Pareira, Water Res., 38 (2004) 2043–2052.

[19] S. Langergren and B.K. Svenka, Veterskapsakad Handl, 24 (1898)1–39.

[20] Y.S. Ho and G. McKay, Chem. Eng. J., 70 (1998) 115–124.

[21] W.J. Weber and J.C. Morris, Proc. Int. Conf. Water Pollution, Pergamon, Oxford, 2 (1962) 231.

[22] G. McKay, J. Chem. Technol. Biotechnol., 33A (1983) 196–204.

[23] K.V. Kumar, J. Hazard. Mater., B137 (2006) 1538–1544.

[24] V. Fierro, V. Torné-Fernández, D. Montané and A. Celzard, Micropor. Mesopor. Mater., 111 (2008) 276–284.

[25] I.A. Tan, A.L. Ahmad and B.H. Hameed, Colloid Surface A: Physicochem. Eng., 318 (2008) 88–96.

[26] R.W. Coughlin and F.S. Ezra, Environ. Sci. Technol., 2 (1968)291.

[27] J.S. Mattson and H.B. Mark, Surface Chemistry and Adsorption from Solution, Marcel Dekker, New York, 1971.

[28] S. Wang, Z.H.Zhu, A. Coomes, F. Haghseresht and G.Q. Lu, Colloid Interf. Sci., 284 (2005) 440–446.

[29] V. Fierro, V. Torné-Fernández, D. Montané and A. Celzard, Micropor. Mesopor. Mater., 111 (2008) 276–284.

[30] F. Banat, B. Al-Bashir, S. Al-Asheh and O. Hayajneh, Environ. Pollut., 107 (2000) 391.

[31] S.I. Kim, T. Yamamoto, A. Endo, T. Ohmori and M. Nakaiwa, Micropor. Mesopor. Mater., 96 (2006) 191–196.

[32] P.S. Kayak and B.K. Singh, Desalination, 207 (2007) 71–79.

[33] W.K. Lafi, Biomass Bioenerg., 20 (2001) 57.

[34] A.L. Ahmad, M.M. Loh and J.A. Aziz, Dyes Pigments, 75 (2007) 263.

[35] S. Karaca, A. Gürses, M. Açikyıldız and M. Ejder, Micropor. Mesopor. Mater., 115 (2008) 376–382.