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Adsorption Of Phenol And P-Nitro Phenol Onto Date Stones: Equilibrium Isotherms, Kineticsand Thermodynamics Studies

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Abstract

Adsorption capacity of a waste biomass, date stones, for phenolic compounds such as phenol (Ph) and p-nitro phenol (PNPh) was investigated. The characteristics of such waste biomass were determined and found to have a surface area and iodine number of 495.71 m^2/g and 475.88 mg/g, respectively. The effects of temperature, initial sorbate concentration, and contact time on the adsorption process were studied. Experimental equilibrium data for adsorption of Ph and PNPh on date stones were analyzed by the Langmuir, Freundlich and Sips isotherm models. The results show that the best fit was achieved with the Sips isotherm equation with maximum adsorption capacities of 147.09 and 179.62 mg/g for Ph and PNPh, respectively. The kinetic data were fitted to pseudo-first order, pseudo-second order and intraparticle diffusion models, and was found to follow closely the pseudo-second order model for both Ph and PNPh. The calculated thermodynamic parameters, namely ΔG, ΔH, and ΔS showed that adsorption of Ph and PNPh onto date stones was spontaneous and endothermic under examined conditions.

الخلاصة

يهدف البحث إلى دراسه اشتخدام نوى التمر لازاله الملوثات الفينوليه مثل الفينول والبارا نايتروفينول من مخلفات المياه. تم تحديد المساحه السحطحيه والرقم الايوديني لنوى التمر وهي 495.71 م^2 /غرام و 475.88 ملي غرام / غرام على التوالي. تم دراسة تأثير درجه الحراره ، التركيز الاولي للماده الملوثه ، وزمن الامنزاز على سعه امتزاز نوى التمر. تم تمثيل نتائج امتزاز الفينول والبارانايتروفينول على نوى التمر يشكل جيد جدا بواسطه معادله سيس، حيث تم الحصول على اعلى سعه امتزاز للفينول(147.09 ملي غرام/غرام) والبارانايتروفينول (179.62 ملي غرام/ غرام). ايضا تم دراسه حركيه عمليه الامتزاز وبينت النتائج ان معادله الدرجه الثانيه مثلت النتائج التجريبيه لعمليه الامتزاز بشكل جيد لكل من الفينول والبارانايتروفينول. بينت نتائج دراسه ثرموديناميكيه العمليه ان الامتزاز من النوع الماص للحراره لكل من الفينول والبارانايتروفينول .

Keywords: Date stones, phenol, p-nitro phenol, adsorption isotherms, kinetics.

Introduction

Wastewaters from paint, pesticide, coal conversion, polymeric resin, gasoline, rubber proofing, steel, petroleum, and petrochemical industries contain considerable amounts of phenols. These pollutants are known to be toxic, carcinogenic, and posing serious hazards to aquatic living organisms. Phenol (Ph) and p-nitro phenol (PNPh) are the most hazardous polluting phenols to the environment. The presence of Ph even at low concentrations can cause unpleasant taste and odor of drinking water. PNPh can enter the human body through all routes and reacts easily in the blood to convert hemoglobin to methamoglobin, thereby preventing oxygen uptake. Indeed, it is necessary to remove these pollutants from wastewaters before discharge into the environment (Zhu et al., 2000).

Various processes have been employed for the removal of phenols from aqueous media including chemical oxidation (He et al., 2009), membrane filtration (Kujawski et al., 2004), biodegradation (El-Naas et al., 2009), electro coagulation (Ugurlu et al., 2008), photo degradation (Gomez et al., 2011), solvent extraction (Xu et al., 2006), and adsorption (Yang et al., 2008). Among these methods adsorption is still the most popular and widely used technique for phenols removal, because of its simple design, easy operation, and relatively simple regeneration (Nevskaia et al., 2004).

In the design and optimization of adsorption processes the adsorption isotherms and kinetics are of utmost importance to study. Adsorption isotherms are important for the description of how adsorbate will interact with adsorbent and are critical in optimizing the use of adsorbent. Thus, the correlation of experimental equilibrium data using either a theoretical or empirical equation is essential for adsorption data prediction. Adsorption kinetics involves the study of the rate at which pollutants are removed from aqueous solution onto adsorbent surface, which in turn controls the residence time of the adsorbate uptake at the solid-solution interface (Altenor et al., 2009).

Currently adsorption on activated carbon is widely used for removal of phenols, but it is still considered expensive material (Sulaymon and Ahmed, 2008). Recently agricultural waste biomass, have been investigated intensively as adsorbents for removal of pollutants from aqueous solutions. Because these materials are cheaper, renewable and abundantly available; also constitute an environmental problem (Adiuata et al., 2007). Date stones can be considered as one of the best candidate among the agricultural wastes because it is cheap and quite abundant, especially in Mediterranean countries. Carbohydrates are the major components of date stones; they are composed of 42% cellulose, 18% hemi cellulose, 25% sugar and other compounds, 11% lignin and 4% ash. This lignocellulosic composition promotes the use of date stones as adsorbents for removal of pollutants. Date stones as a waste stream have been a problem to the palm oil and palm syrup factories. Therefore, its recycling or reutilization is useful (Hameed et al., 2009).

Many studies have been done on adsorption isotherms and kinetics of phenols on various agricultural wastes and natural materials such as red mud (Gupta et al., 2004), soil (Subramanyam and Das, 2009), chitin (Dursun and Kalayci, 2005), clinoptilolite rock (Sprynskyy et al., 2009), lignite (Polat et al., 2006), olive pomace (Stasinakis et al., 2008), deolied soya (Mittal et al., 2009), wood fly ash (Daifullah and Gad, 1998), mauritonian clay (Ely et al., 2011), mansonia wood sawdust (Ofomaja, 2011), rice husk (Ahmaruzzaman and Sharma, 2005), chitosan (Li et al., 2009), and alignate (Peretz and Cinteza, 2008). Though date stones-based activated carbon has been widely used to remove phenols from wastewaters (Alhamed, 2009; El-Naas et al., 2010; Alhamed, 2008), literature is scant where raw date stones were employed directly for phenols adsorption.

Therefore, the main objective of the present work is to study experimentally and theoretically the equilibrium isotherms, kinetics, and thermodynamics of Ph and PNPh adsorption onto raw date stones.

Materails And Methods

Materials

Date stones were used as adsorbent. Stones as received were first washed with water to get rid of impurities, dried at 110 ˚C for 24 h, crushed using disk mill, and sieved. Fraction of average particle size of 250 µm was selected for the study. The properties of chemicals used are listed in Table 1.

Adsorbent characteristics

Date stones were characterized by selected physical properties including bulk density and surface area, chemical properties including ash and moisture contents, and adsorption properties including iodine number. The details of characterization methods are illustrated as follows.

Bulk density

Bulk or apparent density was determined according to procedure followed by Ahmedna et al. (1997). 10 ml cylinder was filled to a specified volume with date stones that had been dried in an oven at 80 ˚C for 24 h (Ahmedna et al., 1997). The bulk density was then calculated as follows:

$$\text{bulk density} = \frac{W_C}{V_C} \tag{1}$$

Where W_C is the weight of dried adsorbent (g) and V_C is cylinder volume packed with dried adsorbent (ml).

Ash content

The ash content of date stones was determined by standard methods (ASTM standard, 2000). 0.5 g of date stones with average particle size of 0.250 mm was dried at 80 ˚C for 24 h and placed into weighted ceramic crucibles. The samples were heated in an electrical furnace at 650 ˚C for 3 h. Then the crucibles were cooled to ambient temperature and weighed. The percent of ash was calculated as follows:

$$\text{ash}\,(\%) = \frac{W_{S3} - W_{S2}}{W_{S1}} \text{ x } 100 \tag{2}$$

Where W_{S3} is the weight of crucible containing ash (g), W_{S2} is the weight of crucible (g), and W_{S1} is the weight of original adsorbent used (g).

Moisture content

The moisture content of date stones was determined using oven drying method (Adekola and Adegoke, 2005). 0.5 g of adsorbent with average particle size of 250 mm was placed into weighed ceramic crucible. The samples were dried at 110 ˚C to constant weight. Then the samples were cooled to ambient temperature and weighed. The moisture content was calculated by the following equation:

$$\text{mositure}\,(\%) = \frac{W_{m3} - W_{m2}}{W_{m1}} \text{ x } 100 \tag{3}$$

Where W_{m3} is the weight of crucible containing original sample (g), W_{m2} is the weight of crucible containing dried sample (g), and W_{m1} is the weight of original sample used (g).

Iodine number

Iodine number which is a measure of the micropore content of structure (0 to 20 Å) was determined as follows: 10 ml of 0.1 N iodine solution in a conical flask is titrate with 0.1 N sodium thiosulfate solution in the presence of 2 drops of 1 wt% starch solution as an indicator, till it becomes colourless. The burette reading is corresponding to V_b. Then weigh very accurately 0.05 g of date stones and add it to conical flask containing 15 ml of 0.1 N iodine solution, shake the flask for 4 min and filter it, then titrate 10 ml of filtrate with standard sodium thiosulfate solution using 2 drops of starch solution as indicator, now the burette reading is corresponding to Vs. The iodine number was then calculated by using the following equation (Lubrizol, 2007):

$$IN = \frac{(V_b - Vs) . N . (126.9) . (15/10)}{M} \qquad (4)$$

Where IN is iodine number (mg/g), V_b and Vs are volumes of sodium thiosulfate solution required for blank and sample titrations (ml), respectively, N is the normality of sodium thiosulfate solution (mole/l), 126.9 is atomic weight of iodine, and M is the mass of adsorbent used (g).

Surface area

The surface area of the date stones was estimated through a calibration curve which has a correlation coefficient of 0.997 between the iodine numbers and BET surface area from the literature (Fadhil and Deyab, 2008) as shown in Fig. 1.

Adsorption isotherms

The equilibrium isotherms of Ph and PNPh adsorption on date stones were determined by performing adsorption tests in 100 ml Erlenmeyer flasks where 40 ml of Ph or PNPh solutions with different initial concentrations (50-250 mg/l) was placed in each flask. The pH of the solutions was gradually adjusted to 7 by adding small amounts of 0.1 M HCl or NaOH solution. 0.02 g of date stones, with particle size of 250 μm, was added to each flask and kept in a shaker of 120 rpm at different temperatures (303-323 K) for 90 min to reach equilibrium. Then the samples were filtered and the residual concentrations of Ph or PNPh in the filtrate were analyzed by a UV-Visible Spectrophotometer (Shimadzu UV-160A) at maximum wave lengths of 269 and 400 nm for Ph and PNPh, respectively. The uptake of Ph or PNPh at equilibrium, q_e (mg/g) was calculated by the following expression:

$$q_e = \frac{(C_o - C_e) V}{W} \qquad (5)$$

Where C_o and C_e (mg/L) are the initial and equilibrium concentrations of Ph or PNPh solution, respectively, V (L) is the volume of solution, and W (g) is the weight of date stones.

Three famous isotherm equations, namely the Langmuir (1916), Freundlich (1906), and Sips (1948) were applied to fit the experimental isotherm data of Ph and PNPh adsorption on date stones. These equations can be written as:

Langmuir isotherm

$$q_e = \frac{q_L K_L C_e}{1 + K_L C_e} \qquad (6)$$

Freundlich isotherm

$$q_e = K_F C_e^{1/n} \qquad (7)$$

Sips isotherm

$$q_e = \frac{q_S K_S C_e^{1/m}}{1 + K_S C_e^{1/m}} \qquad (8)$$

Where q_L (mg/g) is the Langmuir maximum uptake of Ph or PNPh per unit mass of date stones, K_L (L/mg) is the Langmuir constant related to rate of adsorption, K_F ((mg/g).(L/mg)$^{1/n}$) and n are Freundlich constants which give a measure of adsorption capacity and adsorption intensity, respectively, q_S (mg/g) is the Sips maximum uptake of Ph or PNPh per unit mass of date stoned, K_S (L/mg)$^{1/m}$ is Sips constant related to energy of adsorption, and parameter m could be regarded as the Sips parameter characterizing the system heterogeneity. Least-squares regression program based on Hooke-Jeeves and Gauss-Newton method was used to analyze experimental data. This program gave the parameters of each equation and the agreement between experimental and calculated data in terms of correlation coefficient R^2.

Adsorption kinetics

The procedure used for kinetic tests was identical to that used for equilibrium experiments. The aqueous samples were taken at present time intervals, and the concentrations of Ph or PNPh were similarly measured. The uptake of Ph or PNPh at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)\,V}{W} \qquad (9)$$

Where, C_t (mg/L) is the liquid-phase concentration of Ph or PNPh solution at time t (min). Pseudo-first order model (Langergen and Svenska, 1898), pseudo-second order model (Ho and Mckay, 1999), and intraparticle diffusion model (Weber and Morris, 1963) were used to analyze the kinetic data. These models can be expressed as:

Pseudo-first order model

$$\ln(q_t - q_e) = \ln(q_e) - K_1\, t \qquad (10)$$

Pseudo-second order model

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \qquad (11)$$

Intraparticle diffusion model

$$q_t = K_3\, t^{1/2} + C \qquad (12)$$

Where q_e and q_t (mg/g) are the uptake of Ph or PNPh at equilibrium and at time t (min), respectively, K_1 (1/min) is the adsorption rate constant, K_2 (g/mg.min) is the rate constant of second-order equation, K_3 (mg/g.min$^{1/2}$) is the intraparticle diffusion rate constant, and C (mg/g) is a constant that gives an idea about the thickness of the boundary layer..

Adsorption thermodynamics

Thermodynamic behavior of the adsorption of Ph and PNPh on date stones was evaluated by the thermodynamic parameters including the change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). These parameters are calculated from the following equations:

$$\text{In}\,(K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (13)$$

$$\Delta G = -RT\,\text{In}\,(K_d) \qquad (14)$$

$$K_d = \frac{q_e \cdot (W/V)}{C_e} \qquad (15)$$

Where, R is the universal gas constant (8.314 J/mole.K), T is temperature (K), and K_d is the distribution coefficient for the adsorption.

RESULTS AND DISCUSSION

Adsorbent characteristics

The characteristics of date stones were determine and summarized in Table 2. The most important characteristics are surface area and iodine number, and the results showed that their values are 495.71 m^2/g and 475.88 mg/g, respectively. This high surface area for an agricultural waste biomass enables date stones to be used successively for removal of dyes from aqueous solutions, as explained by Belala et al. (2011) and Banat et al. (2003). Also this high iodine number which is a measure of micropore content (0 to 20 Å), can be a good indication for the capability of date stones to remove most of phenols which have molecular sizes in the range of micropores content (Lu and Sorial, 2007).

Effect of contact time

The effect of contact time on uptakes of Ph and PNPh onto date stones is shown in Fig. 2. This figure shows that the uptake of both adsorbate increases with the increase of contact time, and the adsorption reached equilibrium in about 90 min. Maximum uptakes of 59.77 and 65.79 mg/g for Ph and PNPh, respectively, are reported at 90 min contact time, 50 mg/L initial concentration, 7 pH, and 0.5 g/L adsorbent dose. Fig. 2 also shows that rapid increase in uptakes of Ph and PNPh is observed during the first 15 min. The fast adsorption at the initial stage may be due to the higher driving force making fast transfer of Ph and PNPh ions to the surface of date stone particles and the availability of the uncovered surface area and the remaining active sites on the adsorbent (Aroua et al., 2008).

Adsorption isotherms

The experimental equilibrium data for Ph and PNPh adsorption on date stones, calculated from Eq. (5), are fitted with Langmuir, Freundlich and Sips isotherms, Eqs.(6)-(8). The calculated constants of the three isotherm equations along with R^2 values are presented in Table 3. This table shows that the Sips isotherm correlates experimental data with highest R^2 values for both Ph and PNPh at three different temperatures. Also this table shows that the Sips isotherm gave maximum adsorption capacities of 147.09 and 179.62 mg/g for Ph and PNPh, respectively. The equilibrium data for Ph and PNPh correlated with Sips isotherm are shown in Figs. 3 and 4, respectively. It can be seen from these figures that the uptake of PNPh is higher than that of Ph; this may be due the smaller molecular size of Ph as compared with that of PNPh. This implies that only a small part of the micropores is filled in Ph adsorption, and the micropore phenomenon is more evident for PNPh, as explained by Liu et al. (2010). Also these figures show that the adsorption capacities of Ph and PNPh increases with increasing temperature, which indicate the endothermic nature of adsorption on date stones. Table 4 lists a comparison of Ph and PNPh adsorption capacities for the date stones with those for different agricultural and natural adsorbents. It can be seen that date stones can be classified as one of the effective adsorbents for this purpose.

Effect of temperature

Fig. 5 shows the maximum adsorption capacities of date stones for Ph and PNPh, calculated from sips isotherm, versus temperature. It can be seen that the increase in temperature from 303 to 323 K leads to an increase in adsorption capacity from 125.26 to 147.09 mg/g for Ph and from 152.66 to 179 .62 mg/g for PNPh. This is an indication for endothermic nature of the adsorption of Ph and PNPh on date stones. Similar trend was reported by Al-Mutairi (2010) for adsorption of 2, 4-dinitrophenol on date stones. It was explained that as temperature increased, the surface activity and kinetic energy of 2, 4-dinirphenol also increased which caused the interaction forces between the solute and adsorbent to become stronger than solute and solvent.

Adsorption kinetics

The experimental kinetic data for Ph and PNPh adsorption on date stones, calculated from Eq. (9), are fitted with pseudo-first order, pseudo-second order and intraparticle diffusion models, Eqs. (10)- (12), and presented in Figs. 6, 7 and 8, respectively. The calculated constants of the three isotherm equations along with R^2 values at 50 mg/L initial adsorbate concentration are presented in Table 5. The linear plot of $\ln(q_e\text{-}q_t)$ versus t (Fig. 6) for pseudo-first order equation is of low R^2 values for both Ph and PNPh, as shown in Table 5. Also, there is a large difference between the experimental and calculated adsorption capacity for both adsorbates, indicating a poor pseudo-first order fit to the experimental data. High R^2 values are obtained for the linear plot of t/q_t versus t (Fig. 7) for pseudo-second order equation, as shown in Table 5. It can be seen that the pseudo-second order kinetic model better represented the adsorption kinetics and the calculated q_e values agree well with the experimental q_e values for both Ph and PNPh (Table 5). This suggests that the adsorption of Ph and PNPh on date stones follows second-order kinetics. A similar result was reported by Ofomaja (2011) for the adsorption of PNPh on mansonia wood sawdust. From Table 5, the value of rate constant K_2 for PNPh is lower than that for Ph, this probably due to the low adsorption capacity of Ph as compared to that of PNPh. On the other hand, for the intraparticle diffusion model, the low values of R^2 (Table 5) for the linear plot of q_t versus $t^{½}$ (Fig. 8) indicate that this model could not fit properly the experimental kinetic data.

Adsorption thermodynamics

According to Eqs.(13)-(15), the ΔH and ΔS parameters for Ph and PNPh can be calculated from the slope and intercepts of the plot of $\ln(K_d)$ versus 1/T (Fig. 9). The calculated values of ΔH, ΔS, and ΔG are listed in Table 6.

The obtained values for Gibbs free energy change (ΔG) are -1090.79, -1347.98, and -1860.99 J/mole for Ph and -1770.96, -2443.52, and -3227.88 J/mole for PNPh adsorption on date stones at 303, 313, and 323 K, respectively. The negative ΔG values indicate thermodynamically spontaneous nature of the adsorption. The increase in ΔG values with increasing temperature shows an increase in feasibility of adsorption at higher temperatures. The ΔH parameters are 10535.30 and 20277.34 J/mole for Ph and PNPh adsorption on date stones, respectively. The positive ΔH is an indicator of endothermic nature of the adsorption and also its magnitude gives information on the type of adsorption, which can be either physical or chemical. The enthalpy of adsorption, ranging from 2.1 to 20.9 kJ/mole corresponds to a physical sorption. The adsorption heat of Ph and PNPh is in range of physisorption. Therefore, the ΔH values show that the adsorption of Ph and PNPh on adsorbent was taken place via physisorption.

The ΔS values are 38.24 and 72.71 J/mole for Ph and PNPh, respectively. The positive ΔS value suggests an increase in the randomness at sorbate-solution interface during the adsorption process.

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NOMENCLATURE

C	: Intraparticle diffusion kinetic model constant (mg/g)
C_e	: Equilibrium concentrations of Ph or PNPh solution (mg/L)
C_o	: Initial concentrations of Ph or PNPh solution (mg/L)
C_t	: Concentration of Ph or PNPh at time t (mg/L)
IN	: Iodine number (mg/g)
K_1	: First order kinetic model constant (1/min)
K_2	: Second order kinetic model constant (g/mg.min)
K_3	: Intraparticle diffusion rate constant (mg/g.min$^{1/2}$)
K_d	: Adsorption distribution Coefficient
K_F	: Freundlich isotherm equation constant ((mg/g).(L/mg)$^{1/n}$)
K_L	: Langmuir isotherm equation

constant (L/mg)
K_S : Sips isotherm equation constant $(L/mg)^{1/m}$
m : Sips isotherm equation parameter
M : Mass of adsorbent used (g).
n : Freundlich isotherm equation constant
N : Normality of sodium thiosulfate solution (mole/l)
Ph : Phenol
PNPh : P-nitro phenol
q_e : Uptake of Ph or PNPh at equilibrium (mg/g)
q_L : Langmuir maximum uptake of Ph or PNPh per unit mass of date stones (mg/g)
q_S : Sips maximum uptake of Ph or PNPh per unit mass of date Stone (mg/g)
q_t : Uptake of Ph or PNPh at time t (mg/g)
R : Universal gas constant (8.314 J/mole.K)
R^2 : Correlation coefficient
T : Temperature (K)

V : Volume of solution (L)
V_b : Volume of sodium thiosulfate solution required for blank titration (ml)
V_C : Cylinder volume packed with dried adsorbent (ml).
Vs : Volume of sodium thiosulfate solution required for sample titration (ml)
W : Weight of date stones (g)
W_C : Weight of dried adsorbent (g)
W_{m1} : Weight of original sample used (g).
W_{m2} : Weight of crucible containing dried sample (g).
W_{m3} : Weight of crucible containing original sample (g).
W_{S1} : Weight of original adsorbent used (g).
W_{S2} : Weight of crucible (g)
W_{S3} : Weight of crucible containing ash (g)
ΔH : Change in enthalpy (J/mole)
ΔG : Change in free energy (J/mole)
ΔS : Change in entropy (J/mole.K)

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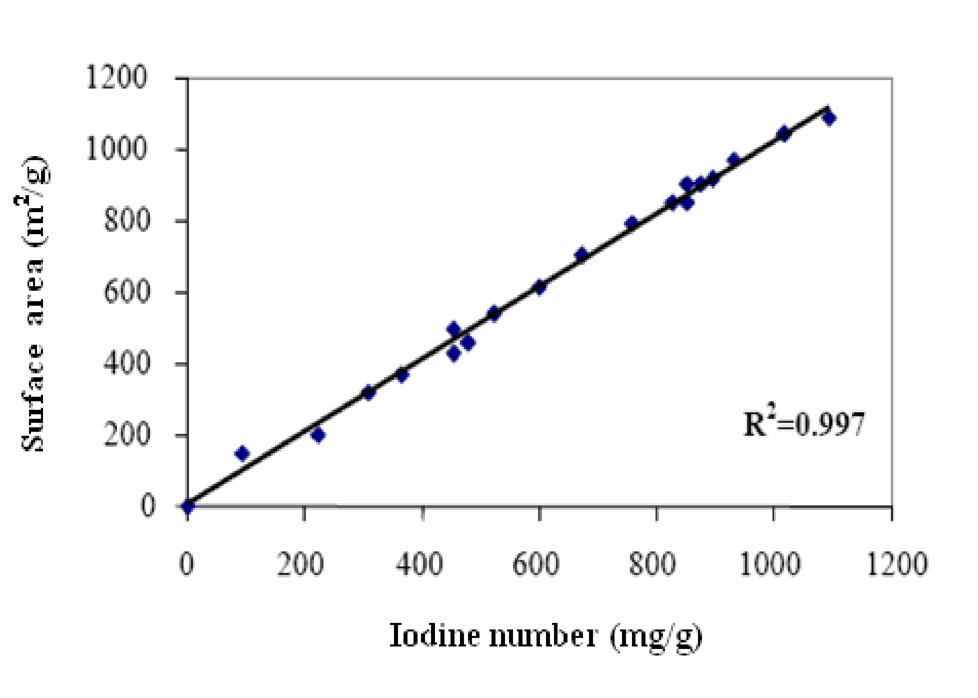

Fig. 1 Estimated surface area calibration curve

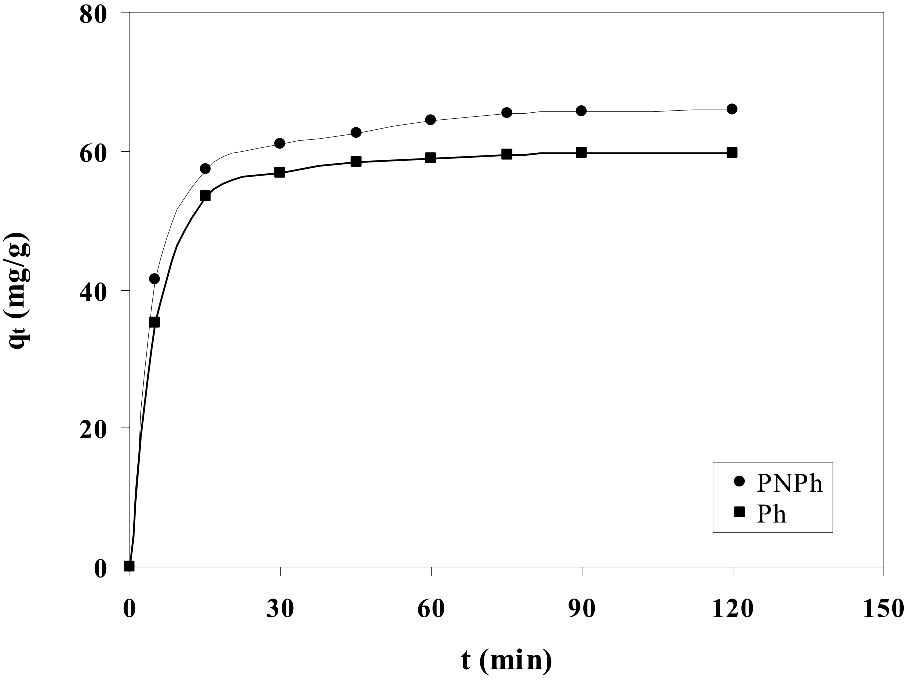

Fig. 2 Effect of contact time on adsorbed amounts of Ph and PNPh on date stones at 303 K

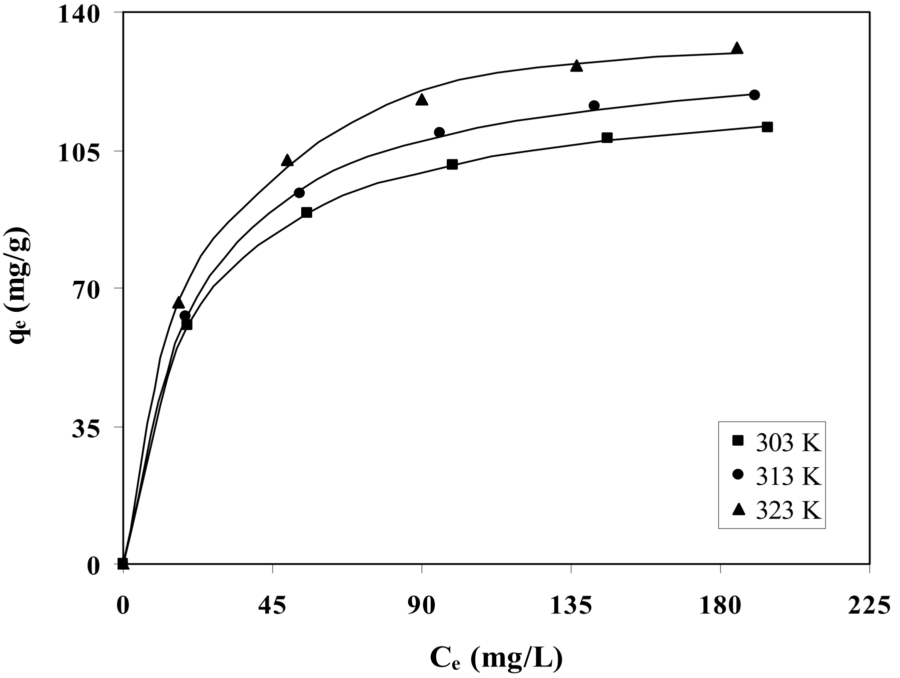

Fig. 3 Adsorption isotherm of Ph on date stones correlated

by Sips isotherm equation

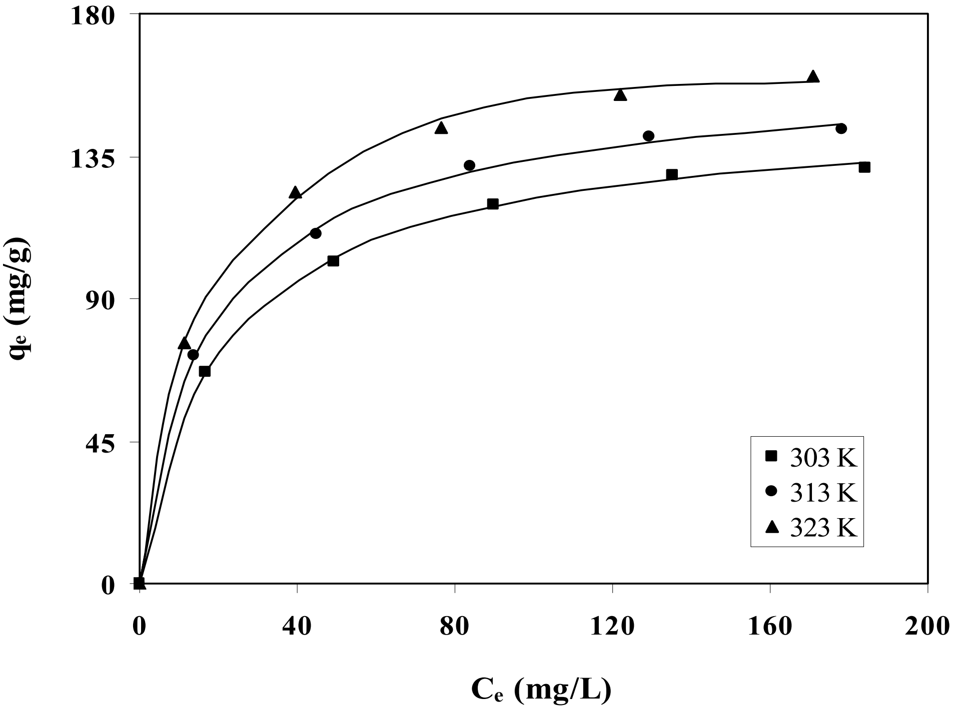

Fig. 4 Adsorption isotherm of PNPh on date stones correlated by Sips isotherm equation

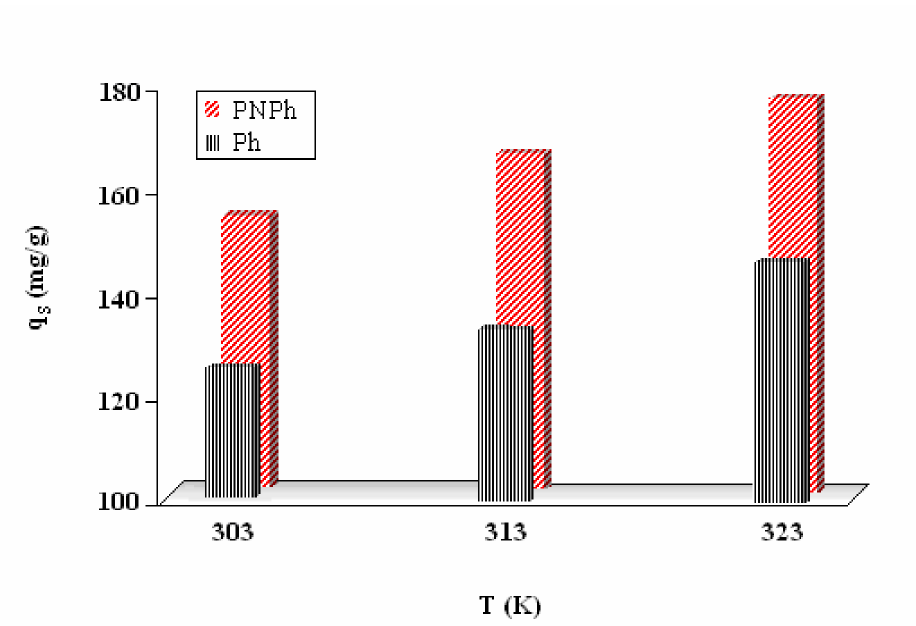

Fig. 5 Effect of temperature on maximum adsorbed amounts of Ph and PNPh on date stones calculated from Sips isotherm

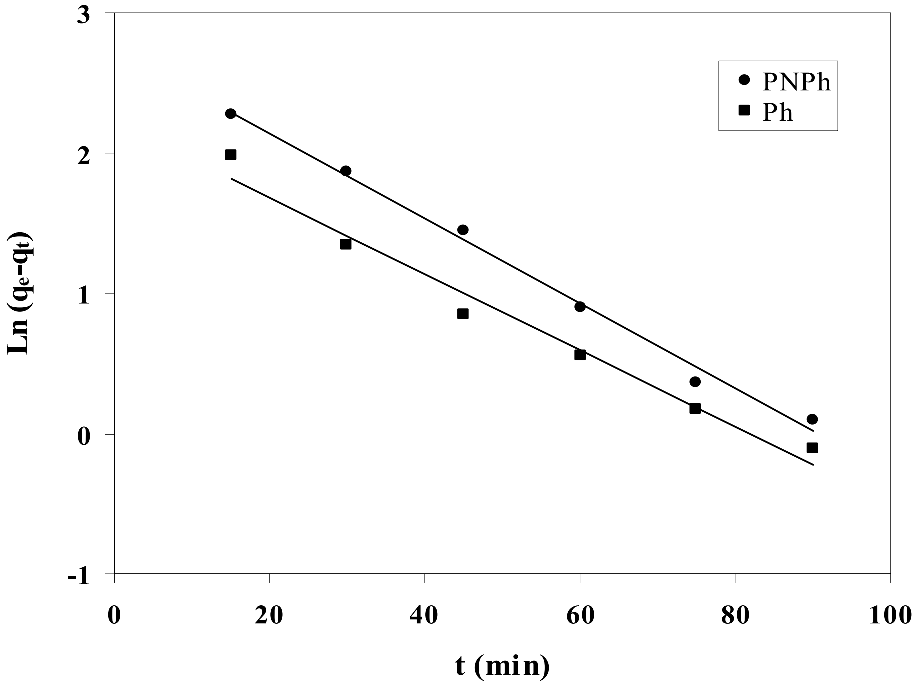

Fig. 6 Pseudo-first order kinetic for adsorption of Ph and PNPh on date stones at 303 K

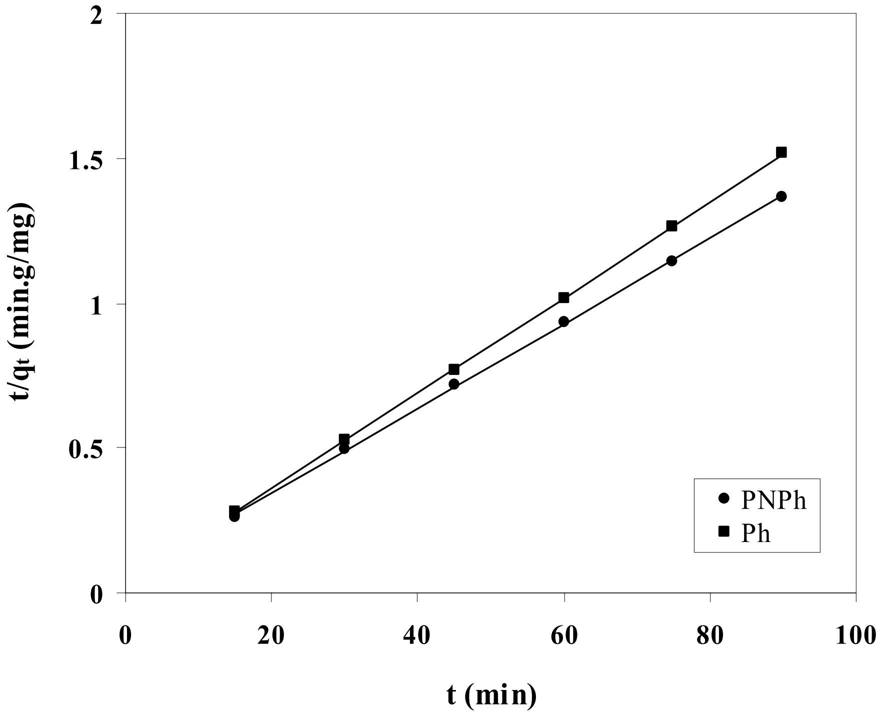

Fig. 7 Pseudo-second order kinetic for adsorption of Ph and PNPh on date stones at 303 K

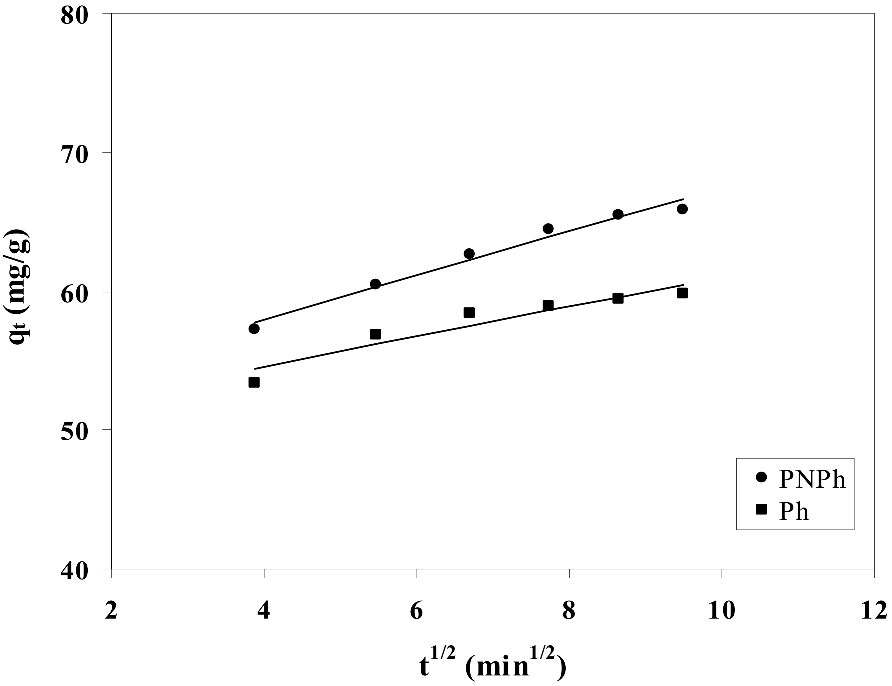

Fig. 8 Intraparticle diffusion plot for adsorption of Ph and PNPh on date stones at 303 K

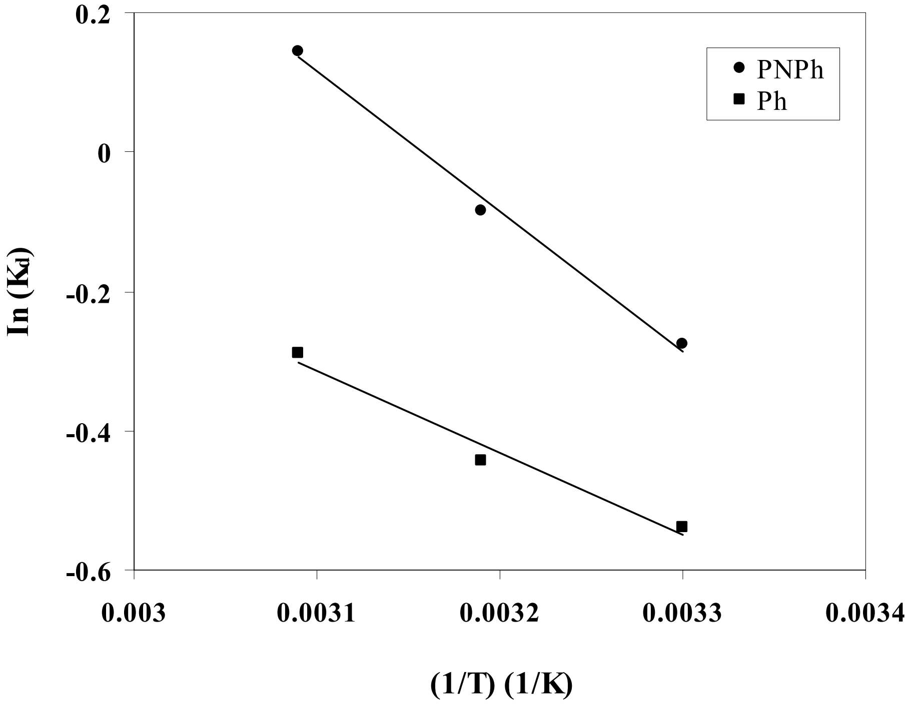

Fig. 9 Plot of In Kd versus 1/T for 50 mg/L initial Ph and PNPh Concentration

Table 1, Properties of chemicals

Compound	Molecular formula	Purity (%)	Source
Phenol	C_6H_5OH	>99	BDH chemicals Ltd company
P-nitro phenol	$C_6H_5NO_3$	>99	BDH chemicals Ltd company
Hydrochloric Acid	HCl	35-38	Poch S.A. Company
Sodium Thiosulfate	$Na_2O_3S_2.5H_2O$	>99	Fluka Chemie AG Company
Iodine	I_2	99.9	Sigma Aldrich Company

Table 2, Characteristics of date stones

Characteristic	Value
Bulk density (g/ml)	0.393
Surface area (m^2/g)	495.71
Ash content (%)	1.66
Moisture content (%)	7.80
Iodine number (mg/g)	475.88

Table 3, Adsorption isotherm parameters of Ph and PNPh on date stones

adsorbate	Temperature (K)	Langmuir isotherm			
		q_m (mg/g)	K_L(L/mg)		R^2
PNPh	303	146.64	0.0489		0.9993
	313	158.36	0.0567		0.9989
	323	173.60	0.0660		0.9987
Ph	303	122.17	0.0494		0.9998
	313	132.37	0.0476		0.9997
	323	144.65	0.0501		0.9991
		Freundlich isotherm			
		K_F ((mg/g)(L/mg)$^{1/n}$)	n		
PNPh	303	34.865	3.7975		0.9899
	313	40.290	3.9285		0.9884
	323	46.773	4.0331		0.9852
Ph	303	31.539	4.0764		0.9916
	313	32.402	3.9134		0.9893
	323	35.422	3.8804		0.9878
		Sips isotherm			
		q_m (mg/g)	K_S ((L/mg)$^{1/m}$)	m	
PNPh	303	152.66	0.0626	1.1167	0.9995
	313	165.50	0.0739	1.1347	0.9993
	323	179.62	0.0812	1.1087	0.9990
Ph	303	125.26	0.0595	1.0805	0.9999
	313	133.43	0.0506	1.0249	0.9997
	323	147.09	0.0564	1.0515	0.9991

Table 4, Comparison of Ph and PNPh maximum capacity onto various adsorbents

adsorbate	adsorbent	maximum capacity (mg/g)	Ref.
Ph	date stones	147.09	This study
	red mud	59.20	(Gupta et al., 2004)
	soil	34.27-51.83	(Subramanyam and Das, 2009)
	chitin	25.06	(Dursun and Kalayci, 2005)
	clinoptilolite rock	11.70	(Sprynskyy et al., 2009)
	lignite	10.00	(Polat et al., 2006)
	olive pomace	4-5	(Stasinakis et al., 2008)
	deoiled soya	1.59	(Mittal et al., 2009)
PNPh	date stones	179.62	This study
	wood fly ash	134.90	(Daifullah and Gad, 1998)
	mauritanian clay	43.7 ± 9.8	(Ely et al., 2011)
	mansonia sawdust	21.28	(Ofomaja, 2011)
	Rice husk	15.3	(Ahmaruzzaman and Shama, 2005)
	chitosan	1.98	(Li et al., 2009)
	alignate	0.69	(Peretz and Cinteza, 2008)

Table 5, Kinetic adsorption parameters of Ph and PNPh at 50 mg/L and 303 K

adsorbate	Pseudo-first order model			
	$q_{e, exp}$ (mg/g)	$q_{e, cal}$ (mg/g)	K_1(1/min)	R^2
PNPh	66.89	3.292	0.0303	0.9935
Ph	60.67	2.624	0.0271	0.9749
	Pseudo-second order model			
	$q_{e, exp}$ (mg/g)	$q_{e, cal}$ (mg/g)	K_2 (g/mg.min)	
PNPh	66.89	68.27	0.0042	0.9998
Ph	60.67	60.89	0.0080	0.9999
	Intraparticle diffusion model			
	$q_{e, exp}$ (mg/g)	C (mg/g)	K_3 (mg/g.min$^{1/2}$)	
PNPh	66.89	51.68	1.572	0.9722
Ph	60.67	50.18	1.089	0.8969

Table 6, Thermodynamics adsorption parameters of Ph and PNPh at 50 mg/L

adsorbate	ΔH (J/mole)	ΔS (J/mole)	-ΔG (J/mole)		
			303 K	313 K	323 K
Ph	10535.30	38.24	1090.79	1347.98	1860.99
PNPh	20277.34	72.71	1770.96	2443.52	3227.88