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Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon

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ABSTRACT

Experiments were carried out to evaluate the batch adsorption of phenol from petroleum refinery wastewater on a locally prepared date-pit activated carbon (DP-AC). Adsorption equilibrium and kinetics data were determined for the uptake of phenol from real refinery wastewater and from synthetically prepared aqueous phenol solution. The data were fitted to several adsorption isotherm and kinetics models. Sips as well as Langmuir models gave the best fit for equilibrium isotherms, whereas the kinetics data were best fitted by the pseudo-second order model. The enthalpy of adsorption showed an exothermic nature of the adsorption process. Several chemical and thermal techniques were tested for the regeneration of saturated activated carbon; using ethanol was found to be the most effective with more than 86% regeneration efficiency after four regeneration cycles.

1. Introduction

Phenols are generally considered among the most hazardous organic pollutants in refinery wastewater and they are highly toxic even at low concentrations. In addition, the presence of phenol in natural waters can lead to the formation of other toxic substituted compounds during disinfection and oxidation processes [1]. Phenol is a combustible compound that is very soluble in water, oils, carbon disulfide and numerous organic solvents [2]. It is characterized by a typical pungent sweet, medicinal, or tar-like odor [3]. Phenol has been registered as priority pollutants by the US Environmental Protection Agency (USEPA) with a permissible limit of 0.1 mg/l in wastewater [4].

Several methods have been developed to remove phenol from wastewater, including microbial degradation [5–7], chemical oxidation [8,9], photocatalytic degradation [10], ultrasonic degradation [11], enzymatic polymerization [12], membrane separation [1], solvent extraction [13] and adsorption [14–22]. Yet, still the adsorption technique using activated carbon is the most favorable method due to its efficiency, high adsorption capacity and low operational cost.

Another important advantage of AC is that it can be regenerated and reused for several cycles. During the adsorption process, phenol is not degraded but rather removed from the wastewater and passed into another phase, which results in the formation of hazardous by-products (secondary pollution). Therefore, regeneration is not only needed for economical reasons in terms of reusing the AC, but also essential for the collecting and reusing the phenol in different applications. The largest single use of phenol is as an intermediate in the production of phenolic resins. Nevertheless, it may also be used in the production of caprolactam and bisphenol A, which are used in the manufacture of aqueous fibers and resins, respectively [2].

Many researchers have successfully regenerated activated carbon using different methods. These methods include water under sub-critical conditions [23], steam [24], pyrolysis [25], direct ozonation [26], ultrasound [27], wet peroxide oxidation [28], surfactants [29], bio-regeneration [30], microwave [31,32] and electrochemical methods [33,34]. Although the effectiveness of any method depends on the application and the type of wastewater treated, the activated carbon was reported to be fully regenerated in most of these cases and reused for many cycles. In the present study, the batch regeneration of activated carbon loaded with phenol was evaluated using several chemical and thermal techniques.

The high cost associated with commercial activated carbon as an effective adsorbent has lead to the search for a less expensive activated carbon of properties comparable to those of the commercially available. Recently, date-pits (DP) have received considerable attention as a lignin-origin material for preparing low-cost activated carbon. DP constitutes approximately 10% of the total weight of dates [35], making them the largest agricultural by-product in palm growing countries, including the UAE [36].

Several studies have examined different DP activation processes including physical [37,38] and chemical means [39,40]. El-Naas

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Nomenclature

a_F	Freundlich isotherm constant ($mg^{(1-1/n)}\ l^{(1/n)}/g$)
a_{LF}	Sips isotherm constant (l/mg)
ARE	Average relative error
b	Langmuir isotherm constant (l/mg)
B_D	Dubinin–Radushkevich isotherm constant (mol^2/kJ^2)
C_b	the thickness of the boundary layer (mg/g)
C_e	equilibrium concentration of solute in solution (mg/l)
C_f	final phenol concentration (mg/l)
C_i	initial phenol concentration (mg/l)
E	mean free energy of sorption (kJ/mol)
k_L	external mass transfer coefficient (cm/min)
K	intraparticle diffusion rate ($mg/g\ min^{0.5}$)
K_{LF}	Sips isotherm constant (1/g)
m	adsorbent dosage (g)
n	Freundlich isotherm constant
n_{LF}	Sips isotherm constant
q_D	Dubinin–Radushkevich isotherm constant (mg/g)
q_e	equilibrium amount of solute adsorbed in mg per gram of solid (mg/g)
q_m	maximum amount of solute adsorbed in mg per gram of solid (mg/g)
q_r	adsorption capacity of regenerated carbon after the re-adsorption equilibrium (mg/g)
R	the gas constant (8.314 J/mol K)
RE%	parameter represent percent regeneration efficiency
T	temperature (K)
V	solution volume (l)
ΔG	Gibbs free energy (kJ/mol)
ΔH	change in enthalpy (kJ/mol)
ΔS	entropy (J/mol K)

et al. [36,37] have reported that physically activated date-pit has properties and adsorption capacities comparable to those of commercial activated carbon. Physically activated DP was evaluated for the adsorption of phenol from aqueous solutions and proved to have adsorption capacity of 16 times higher than that of non-activated date-pits [41]. However, the study did not report any information on the particle pore size, surface area or the functional groups on the activated date-pit. There were also no indications of the effectiveness of DP-AC in removing phenol from real wastewater.

To the best of the authors' knowledge, there are no reports in the open literature on the characteristics of DP-AC or its uptake of phenol from industrial or refinery wastewater. The objective of the present study, therefore, is to explore the effectiveness of physically activated DP, as a low-cost adsorbent, for the removal of phenol from aqueous and real petroleum refinery wastewater and to assess the regeneration of the spent activated DP.

2. Experimental methods

2.1. Preparation of DP-AC

DP-AC was prepared from raw DP granules, obtained from Al-Saad Date Processing Factory, Al-Ain, UAE. Details of the preparation of AC by physical activation method were reported earlier [36]. The particle size ranged from 125 to 212 μm, whereas the BET surface area and the average pore diameter were 490.1 m^2/g and 18.8 A, respectively. The pore size distribution for the DP-AC is shown in Fig. 1.

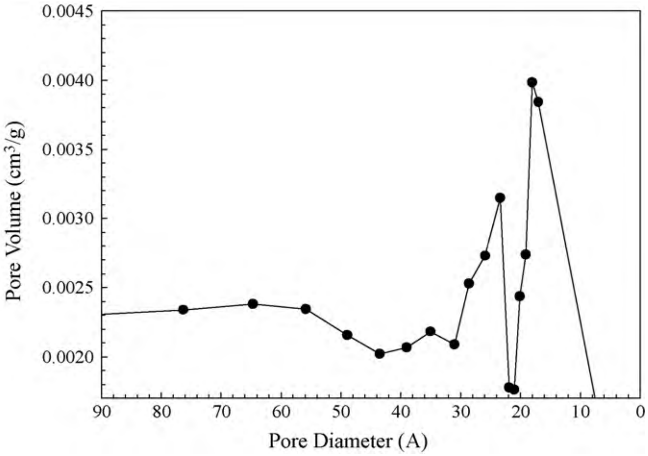

Fig. 1. Pore size distribution for DP-AC (125–212 μm).

Table 1
Surface functional groups for date-pits activated carbon.

Functional group	mmol/g
Carboxyl	0.05
Lactones and lactols	0.19
Phenols	0.72
Total basic sites	0.22
Total acid sites	0.96

2.2. Functional groups on DP-AC

The functional groups on DP activated carbons were determined using the Boehm titration method [42]. Hydrochloric acid (HCl), sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) solutions were used for the determining the total and specific acid sites, while sodium hydroxide solution was used for specifying the total basic sites [42]. A weighed amount of 2 ± 0.1 g of DP activated carbon was placed in 100 ml of the prepared 0.1N solution and shaken for about 72 h at 298 K. After filtration, the excess base and acid were titrated with 0.1N HCl and 0.1N NaOH, respectively. The concentration of acidic sites was calculated using the assumption that NaOH neutralizes carboxylic, phenolic and lactonic groups; Na_2CO_3 neutralizes carboxylic and lactonic; and $NaHCO_3$ neutralizes only carboxylic groups. Table 1 lists the different functional groups available on DP activated carbon.

2.3. Batch adsorption

Refinery wastewater samples were collected from a local petroleum refinery and preserved in dark color plastic containers at room temperature. The main characteristics of the refinery wastewater are given in Table 2. Batch adsorption equilibrium experiments were carried out by contacting a specified amount of DP-AC with 50 ml wastewater sample, of a known initial phenol

Table 2
Characterization of used refinery wastewater.

Characteristic	Value
pH	8.2
COD (mg/l)	3504
Phenols (mg/l)	88
TSS (g/l)	0.08
TDS (g/l)	10

concentration, in a sealed glass bottle. Real refinery wastewater samples with two different initial phenol concentrations, namely 88 and 46 (±0.5) mg/l were tested. In addition, a series of different initial concentrations of phenol solution ranging from 100 to 300 mg/l was prepared from phenol stock solution for the aqueous wastewater. The bottles were kept on a shaker (WSB-30, Korea) at a specified temperature for 24 h to reach equilibrium. For the kinetics study, samples were withdrawn at regular intervals and filtered. The phenol concentration was then measured using UV spectrophotometer (DR-5000, Germany). All experiments were carried out in duplicates and the average values were reported.

The uptake, q, was calculated from the difference between the initial and the final phenol concentrations as follows:

$$q = \frac{(C_i - C_f)V}{m} \tag{1}$$

where, q (mg/g) is the uptake (mg/g), C_i and C_f (mg/l) are the initial and final phenol concentrations, respectively, m is the adsorbent dosage (g) and V is the solution volume (l).

2.4. Theory

2.4.1. Adsorption isotherms

Many theoretical and empirical models have been developed to represent the various types of adsorption isotherms. At present, there is no single model that satisfactory describes all mechanisms and shapes. Langmuir and Freundlich models have been widely used to describe adsorption isotherms in wastewater treatment applications. The Langmuir isotherm [43] assumes uniform and constant binding of the sorbate on the surface of the adsorbent, which is usually described by:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{2}$$

where, as mentioned earlier, q_e (mg/g) is the equilibrium amount of solute adsorbed in mg per gram of solid, C_e (mg/l) is the equilibrium concentration of solute in solution, and q_m (mg/g) and b (l/mg) are temperature dependant parameters representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

Unlike the Langmuir isotherm model, the Freundlich isotherm (Eq. (3)) [44] does not have any thermodynamic basis and does not offer much physical interpretation of the adsorption data [36,45]. The model is not bound by a maximum uptake, and it does approach Henry's law at low concentrations.

$$q_e = a_F C_e^{1/n} \tag{3}$$

where, a_F ($\mathrm{mg}^{(1-1/n)}\,\mathrm{l}^{1/n}/\mathrm{g}$) and n are constants.

A combination of the Langmuir and Freundlich isotherms is expressed in the Sips isotherm (Eq. (4)) [46]. At low sorbent concentrations, the Sips isotherm approaches the Freundlich isotherm, whereas it approaches the Langmuir isotherm at high concentrations.

$$q_e = \frac{K_{LF} C_e^{n_{LF}}}{1 + (a_{LF} C_e)^{n_{LF}}} \tag{4}$$

where, K_{LF} (l/g), n_{LF} and a_{LF} (l/mg) are constants.

Another isotherm that has seen considerable applications is the Dubinin–Radushkevich shown in Eq. (5) [47]:

$$q_e = q_D \exp\left(-B_D \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \tag{5}$$

Where q_D (mg/g) is the D–R isotherm constant related to the degree of sorbate sorption by the sorbent surface and B_D ($\mathrm{mol}^2/\mathrm{kJ}^2$) is constant related to the free energy of sorption per mole of sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution [48]. The free energy is related to B_D as follows:

$$E = \frac{1}{\sqrt{2B_D}} \tag{6}$$

The shapes of various models isotherms depend on the type of adsorbate/adsorbent and the intermolecular interactions between the fluid and the surface [49]. The model that fits the experimental data most accurately can then be used to describe the system and predict the adsorption behavior for practical process design.

2.4.2. Adsorption kinetics

Adsorption kinetics describes reaction pathways and the time needed to reach the equilibrium, whereas chemical equilibrium gives no information about pathways and reaction rates [50]. Adsorption kinetics show large dependence on the physical and chemical characteristics of the adsorbent material which also influence the adsorption mechanism that can either be film or pore diffusion or a combination of both, depending on the system hydrodynamics. In order to examine the controlling mechanism, three kinetics models have been used at different experimental conditions.

2.4.2.1. Pseudo-first order model. The pseudo-first order equation of Lagergren [51,52] is given by;

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

Where q_t and q_e are the amounts of phenol adsorbed at time t and equilibrium (mg/g), respectively, and k_1 is the pseudo-first order rate constant for the adsorption process (l/min).

2.4.2.2. Pseudo-second order model. The pseudo-second order chemisorption kinetic rate equation is expressed as [53]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

Where k_2 is the equilibrium rate constant of pseudo-second order equation (g/mg min).

2.4.2.3. Elovich's model. Elovich's kinetic model is given by [54]:

$$\frac{dq_t}{dt} = a\exp(-bq_t) \tag{9}$$

Where a initial adsorption rate (mg/g min); b is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

2.5. Regeneration of DP-AC

The effectiveness of different regeneration techniques was investigated. These include thermal regeneration using steam and chemical regeneration using 1 M HCl, 1 M NaOH, ethanol (70%, 100%) and ethanol–NaOH–H_2O_2. An amount of 4 g of spent activated carbon was placed in 50 ml of the prepared solution or hot water (at 90 °C) and shaken for about 2 h; the regenerated DP-AC was then washed with distilled water and dried at 105 °C. For steam regeneration, the DP-AC was exposed to a continuous flow of saturated steam in a small packed column for 2 h and then dried at 105 °C.

The effectiveness of regeneration was evaluated by subjecting the regenerated DP-AC to a batch equilibrium experiment, similar to the one described in Section 2.3. The procedure was repeated for four cycles. For each cycle, the regenerated DP-AC was contacted with fresh wastewater until equilibrium is achieved. The adsorption capacity or equilibrium uptake is calculated by the following

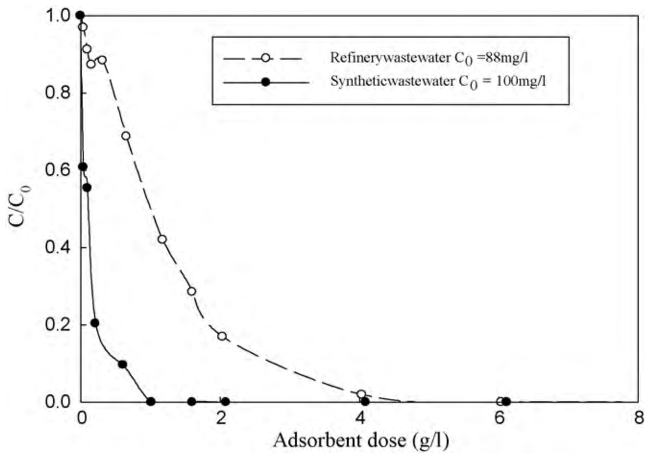

Fig. 2. Effect of adsorbent dose on phenol reduction at 25 °C.

equation:

$$q_{e,i} = \frac{(C_{o,i} - C_{e,i})V_i}{m} \tag{10}$$

where the subscript i represents the cycle number, $C_{o,i}$ and $C_{e,i}$ are the initial and equilibrium phenol concentrations, respectively V_i (l) is the volume of wastewater, and m (g) is the mass of DP-AC used in the batch test, which is the same for any additional regeneration cycles. The regeneration efficiency (RE%) is another important parameter for showing the effectiveness of the regeneration method, and it is defined as follows:

$$\mathrm{RE\%} = \frac{q_r}{q_e} \times 100\% \tag{11}$$

Where, q_e is the adsorption capacity of virgin activated carbon (mg/g) and q_r is the adsorption capacity of regenerated carbon after the re-adsorption equilibrium (mg/g).

3. Results and discussion

3.1. Effect of adsorbent dose

In any adsorption process, the amount of adsorbent plays an important role. In order to evaluate the effect of adsorbent dose (in grams of adsorbent per one liter of solution) on phenol adsorption, various amounts of DP-AC, in the range of 0–10 g/l, were contacted with aqueous and refinery wastewater samples having an initial phenol concentrations of 100 and 88 mg/l, respectively. The effect of adsorbent dose on the concentration of phenol, after 24 h of incubation, is shown in Fig. 2. It was found that the concentration of phenol decreased with an increase in adsorbent concentration. This is expected, as increasing the adsorbent concentration at a fixed phenol initial concentration provided more available adsorption sites for phenol and hence the removal is enhanced. This effect was stronger for aqueous wastewater than refinery wastewater for the same adsorbent dose. This is due to the existence of other compounds in the real refinery wastewater that compete with phenol on the adsorption sites, and hence lead to less amount of phenol adsorption. For the refinery wastewater an adsorbent dose of 4 g/l was sufficient to remove most of the phenol from the wastewater.

3.2. Effect of solution pH

It is well known that phenol adsorption onto activated carbon can occur via a complex interplay of electrostatic and dispersion interactions with three possible mechanisms [55]:

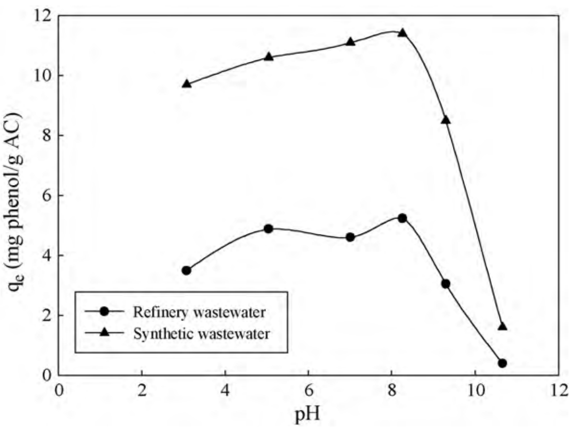

Fig. 3. Equilibrium uptake of phenol at different pH values at 25 °C and initial concentrations of 88 mg/l (refinery) and 100 mg/l (aqueous phenol solution).

- π–π dispersion interaction between the phenol aromatic ring and the delocalized π electrons present in the aromatic structure of the graphite layers.
- Hydrogen bond formation.
- Electron donor–acceptor complex formation at the carbon surface where the oxygen of the surface carbonyl group acts as the electron donor and the phenol aromatic ring as the acceptor [56].

In addition, electrostatic interactions can play a significant role if phenol is predominately in the phenolate ion form that can interact with the charged AC surface. Both aspects are determined by the solution pH [22]. Due to the amphoteric character of a carbon surface, its adsorption properties may be influenced by the pH value of the solution [57]. The effect of initial pH on the adsorption of phenol was also evaluated at 25 °C at different initial pH values in the range of 3–11 for initial concentrations of 88 and 100 mg/l for refinery and aqueous wastewater, respectively. The typical pH of the refinery wastewater was about 8, and it was adjusted to the desired value by the addition of few drops of 0.1 M HCl or 0.1 M NaOH. The equilibrium uptake as a function of pH for both refinery and aqueous wastewater, shown in Fig. 3, indicates that higher uptake is achieved for unbuffered wastewater. The decrease in phenol adsorption as the pH dropped from 8 to 3 is mainly due to the increased H^+ adsorption on the carbonyl sites, which suppresses phenol adsorption on these sites. On the other hand, the decrease in the phenol amount adsorbed as the pH increased to 11 is attributed to both greater solubility of dissociated phenol at $\mathrm{pH} > \mathrm{pKa}$ and increased repulsion forces between the dissociated form of the adsorbate and the carbon surface [1].

3.3. Adsorption kinetics

The phenol adsorption rate was determined by contacting both types wastewater with different initial phenol concentrations using an adsorbent dose of 4 g/l. The results shown in Fig. 4 indicate that most of the phenol removal takes place during the first 60 min. After that the phenol concentration remained almost unchanged, and equilibrium is reached.

In order to predict the adsorption kinetic model for phenol onto DP-AC, pseudo-first order, pseudo-second order and Elovich's kinetic models were applied to the data at different initial concentration of phenol. The straight line plots of $\ln(q_e - q_t)$ against time were tested to obtain the pseudo-first sorption rate constant. The pseudo-second order constants were determined by plotting t/q_t against t and the plot of q_t against $\ln(t)$ were used to determine the Elovich's model constant. Only the pseudo-second order

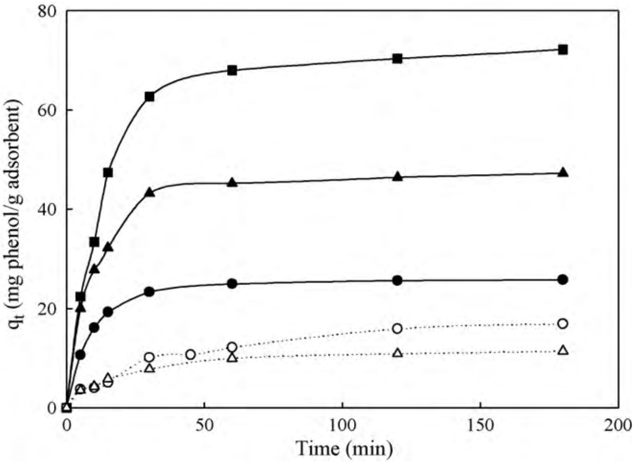

Fig. 4. . Kinetics of phenol uptake at 25 °C and different initial phenol concentrations (●) $C_o = 100$ mg/l, (▲) $C_o = 200$ mg/l, (■) $C_o = 300$ mg/l, (○) $C_o = 88$ mg/l (△) $C_o = 46$ mg/l (black) aqueous phenol solution and (white) refinery wastewater.

plots are presented in Fig. 5. The kinetic constants and correlation coefficients of these models were given in Table 3.

Although the R^2 values for the plots were in the range of 0.85–0.98 after applying the pseudo-first order model, the calculated q_e values obtained from this model do not give reasonable values (Table 3) which are low compared with experimental q_e values. This finding suggested that the sorption process does not follow the pseudo-first order adsorption rate expression. If the intercept value does not equal $\ln(q_e)$, the reaction is not likely to obey a pseudo-first order kinetics model, even if the plot has a high correlation coefficient [58].

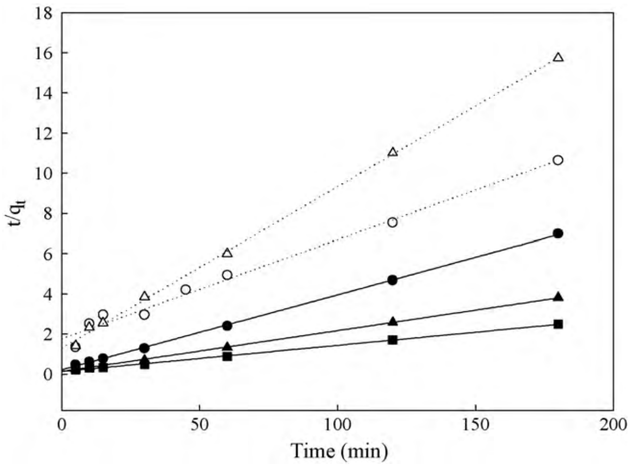

Fig. 5. t/q versus t according to the pseudo-second order at 25 °C and different initial phenol concentrations (●) $C_o = 100$ mg/l, (▲) $C_o = 200$ mg/l, (■) $C_o = 300$ mg/l, (○) $C_o = 88$ mg/l (△) $C_o = 46$ mg/l, (black) aqueous phenol solution and (white) Refinery wastewater.

The results showed that the adsorption system followed the pseudo-second order model for the entire adsorption period, with R^2 value of 1.00 for the concentration range used in this study. The calculated q_e values from the model were also in good agreement with the experimental values. The fact that the kinetics of phenol adsorption on DP-AC follows the pseudo-second order suggests that the rate-limiting step may be chemisorption [58,59]. This may indicate that the adsorption of phenol takes place via surface exchange reactions until the surface functional sites are fully occupied; thereafter phenol molecules diffuse into the AC network for further interactions (such as inclusion complex, hydrogen bonding, hydrogen phobic interactions) [60].

The constants of the Elovich equation for the same experimental data were obtained from the slope and intercept of the plot of q_t against $\ln(t)$ (plot not shown). In this case, a linear relationship was obtained with R^2 in the range of 0.88–0.97, which was lower than those of the pseudo-second order equation. The Elovich equation does not predict any definite mechanism, but it is useful in describing adsorption on highly heterogeneous adsorbents [60].

3.4. Intraparticle diffusion on DP-AC

The diffusion mechanism could be explained by using the intraparticle diffusion model [61]. Usually, the intraparticle diffusion depends on various factors such as the physical properties of adsorbent, the initial concentration of solution, temperature, and rotation speed in batch mode [61]. The intraparticle diffusion equation, suggested by Weber and Morris [62], can be expressed by:

$$q_t = Kt^{0.5} + C_b \tag{12}$$

Where q_t is the adsorbed quantity of phenol, K is the intraparticle diffusion parameter, and C_b is the thickness of the boundary layer. A plot of q_t versus $\sqrt{t}$ would give a straight line if intraparticle diffusion was the limiting process. However, the results in Fig. 6 show that this is not the case. The adsorption process exhibited multi-linear plots in which two straight portions were noticed. The first linear portion of the plot represents the external diffusion by macropore and mesopore; whereas the second portion of the plot indicates the micropore diffusion by the intraparticle diffusion [63].

The adsorption of phenol molecules on DP-AC is expected to proceed through the following sequence of steps: transport of phenol from the boundary film to the external surface of the adsorbent (film diffusion); transfer of phenol molecule from the surface to the intraparticular active sites; and uptake of phenol by the active sites of AC. In the initial stage of the adsorption process, the film diffusion is an important-rate controlling step. The change of phenol concentration with respect to time can be expressed as [63]:

$$\frac{dC}{dt} = -k_L A(C - C_s) \tag{13}$$

Where C and C_s are phenol concentration in the bulk and surface, k_L is the external mass transfer coefficient and A is the specific surface area for mass transfer. It is assumed that during the initial stages of adsorption, the intraparticle resistance is negligible and the transport is mainly due to film diffusion mechanism. At $t = 0$ the surface

Table 3
Fitted kinetics parameters for the adsorption of phenol onto DP-AC at 25 °C.

	C_o (mg/l)	Pseudo-first order			Pseudo-second order			Elovich model		
		q_e	k_1	R^2	q_e	k_2	R^2	a	b	R^2
Aqueous	100	12.6	0.0339	0.95	26.7	6.43×10^{-3}	1	21.6	0.245	0.88
	200	21.6	0.0216	0.85	49.0	3.13×10^{-3}	1	32.4	0.130	0.90
	300	39.71	0.0194	0.87	76.3	1.32×10^{-3}	1	19.9	0.071	0.90
Refinery	88	16.64	0.0099	0.94	20.3	1.37×10^{-3}	0.99	1.4	0.242	0.96
	46.3	8.7	0.0226	0.98	12.5	0.9×10^{-3}	1	1.9	0.417	0.97

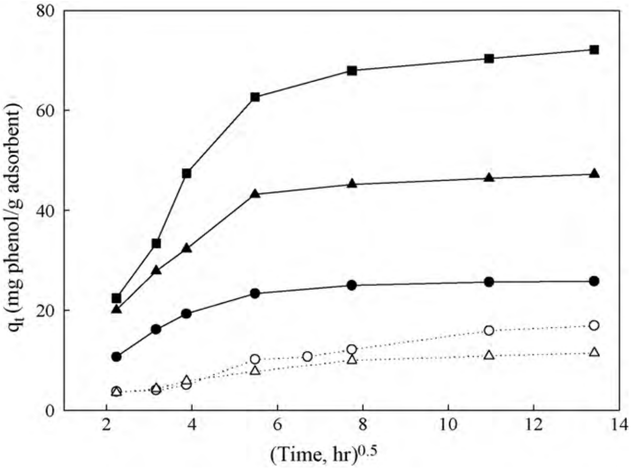

Fig. 6. q versus $\sqrt{t}$ according to the intraparticle diffusion model at 25 °C and different initial phenol concentrations (●) $C_o = 100$ mg/l, (▲) $C_o = 200$ mg/l, (■) $C_o = 300$ mg/l, (○) $C_o = 88$ mg/l (△) $C_o = 46$ mg/l, (black) aqueous phenol solution and (white) refinery wastewater.

concentration is negligible and $C = C_0$. With these assumptions, Eq. (13) can be simplified as:

$$\left(\frac{d(C/C_0)}{dt}\right) = -k_L A \qquad (14)$$

By plotting C/C_0 against t, the value of k_L may determined from the slope at $t = 0$. The kinetics data were fitted to determine the external mass transfer coefficients from the slopes as presented in Table 4. The results show that increasing initial phenol concentration resulted in a decrease in the initial rate. It is expected that external mass transfer resistance cannot be neglected even with high agitation, although this resistance is only significant for the initial period of adsorption time. Weber and Morries [62] found that for a process controlled by external diffusion, the initial rate will be directly proportional to the solute concentration.

For the second portion of the plot, adsorption intraparticle diffusion is the rate controlling step and the intraparticle diffusion rate was found from Weber and Morris model (Eq. (12)). The values of K (Table 4) increases with increasing initial phenol concentration, which may be due to the greater deriving force with increasing the initial concentration [63].

3.5. Adsorption Isotherms

The equilibrium adsorption isotherms of phenol were determined at different temperatures of 25, 40 and 60 °C at pH of 8, for both aqueous and refinery wastewater and the results are shown in Figs. 7 and 8, respectively. The experimental data were fitted to the Langmuir (Eq. (2)), Freundlich (Eq. (3)), Sips (Eq. (4)) and Dubinin–Radushkevich (Eq. (5)) isotherm models using SigmaPlot non-linear regression, which uses the Marquardt–Levenberg algorithm to find the parameters that gives the best fit between a set of data and a proposed non-linear equation. Values for the determined parameters of each isotherm are shown in Table 5, together with the respective R^2 value for each regression. The results show that the experimental data were best fit by the Sips model with R^2 values closest to 1.0. The results shown in Table 5 were used to determine the mean free energy of sorption (E), as calculated by Eq. (6), which was found to be 0.7 and 1.4 kJ/mol for refinery and aqueous wastewater at 25 °C, respectively. These values are relatively small compared to the typical range of bonding energy for ion-exchange mechanisms, which is 8–16 kJ/mol [64,65]. This indicates that ion-exchange does not play an important role in the uptake of phenol by DP-AC, and that physical and/or chemical adsorption are the only major contributor to the adsorption process.

Table 4
Effect of initial phenol concentration on the external mass transfer coefficients(k_L) and intraparticle diffusion rate constant (K).

C_0 (mg/l)	k_L (cm/min)	K (mg/g min$^{0.5}$)
100	0.156	0.293
200	0.143	0.487
300	0.099	1.129
46	0.059	0.255
88	0.025	0.855

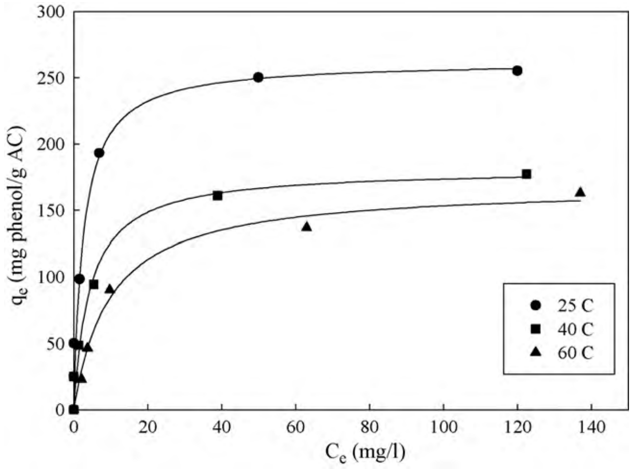

Fig. 7. Equilibrium isotherm data for the adsorption of phenol at different temperatures for aqueous phenol solution.

A comparison of the maximum phenol uptake in this study (q_m) with those reported in the literature for other adsorbents is presented in Table 6. It shows that the uptake capacity of DP-AC is comparable to other adsorbents, which proves that it can be considered as a low-cost alternative to commercial activated carbons for the removal of phenols from wastewater.

3.6. Thermodynamic parameters

Evaluation of the effect of temperature on the adsorption of phenol indicated that increasing the temperature from 25 to 60 °C decreased the uptake capacity by 36% and 56% for aqueous and

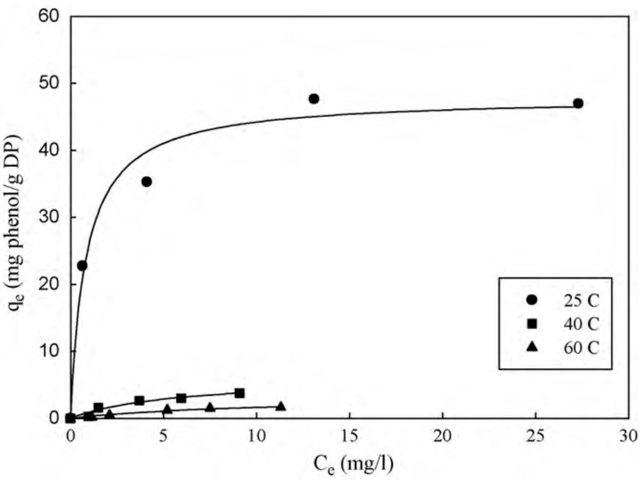

Fig. 8. Equilibrium isotherm data for the adsorption of phenol at different temperatures for refinery wastewater.

Table 5
Isotherm model parameters for the adsorption of phenol on DP-AC at different temperatures for both aqueous and refinery wastewaters.

Isotherm	Parameter	25 °C		40 °C		60 °C	
		Aqueous	Refinery	Aqueous	Refinery	Aqueous	Refinery
Langmuir	q_m (mg/g)	262.3	56.9	206	36.9	168.2	34.7
	b (l/mg)	0.385	1.19	0.21	0.17	0.102	0.009
	R^2	0.95	0.98	0.97	0.95	0.99	0.97
	ARE	0.012	0.04	0.059	0.08	0.094	0.09
Freundlich	a_F	118	26.64	59.96	1.638	33.08	0.315
	n	0.17	0.19	0.24	0.365	0.33	0.717
	R^2	0.92	0.98	0.95	0.99	0.96	0.94
	ARE	0.37	0.05	0.26	0.43	0.21	0.34
Sips (L-F)	n_{LF}	1.09	0.5613	0.78	0.402	1.12	2.15
	a_{LF}	0.39	0.6703	0.18	0.001	0.115	0.28
	K_{LF}	93.79	57.98	51.59	27.63	14.4	1.77
	R^2	0.99	0.99	0.99	0.99	0.99	1.0
	ARE	0.04	0.06	0.04	0.05	0.06	0.01
D-R	q_D (mg/g)	141.2	44.72	154.7	4.76	141.2	148.3
	B_D	2.55×10^{-7}	9.35×10^{-7}	7.8×10^{-7}	5.4×10^{7}	2.8×10^{-6}	5.4×10^{7}
	E (J/mol)	1392.8	731.3	798.8	9.7×10^{-5}	421.69	9.7×10^{-5}
	R^2	0.91	0.94	0.88	0.93	0.87	0.9
	ARE	0.42	0.4	0.7	0.4	0.75	0.52

ARE: average relative error: absolute value of [(experimental value – predicted value)/experimental value].

Table 6
Comparison of various adsorbents for the adsorption of aqueous phenol.

Adsorbent	Capacity (mg/g)	Reference
AC (Kraft black liquor)	227	[66]
AC (Corncob)	177.6	[67]
Commercial AC	322.5	[2]
Granular AC	350	[68]
Powdered AC	303	[69]
Olive stones	189	[2]
Petroleum coke treated with KOH	158	[2]
Red mud	59.2	[70]
Filtrasorb-400	205	[71]
HiSiv 1000	319	
Thermal sewage sludge	185	[72]
Coconut shell	205.8	[14]
Rattan sawdust	149.25	[73]
Clay	30.3	[74]
Date-pits	46.1	[41]
	262.3 (aqueous) 56.9 (refinery)	Present work

refinery wastewater, respectively, as shown in Table 5. Equilibrium experiments performed at different temperatures showed a decrease in the amount of phenol adsorbed, implying an exothermic nature of the adsorption process. Values for the Langmuir isotherm constant (b) obtained for the different temperatures were used to calculate thermodynamic parameters such as Gibbs free energy (ΔG), change in enthalpy (ΔH), and entropy (ΔS). Both energy and entropy are key factors to be considered in any process design. The Gibbs free energy change is the basic criterion of spontaneity and a negative value indicates that the reaction is spontaneous. The Gibbs free energy (ΔG), the enthalpy (ΔH) and the entropy change (ΔS) can be evaluated using the following equations [49]:

$$\Delta G = -RT \ln b \tag{15}$$

$$\Delta G = \Delta H - T\Delta S \tag{16}$$

$$\ln b = -\frac{\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{17}$$

where T is the temperature (K), R is the gas constant (8.314 J/mol K), and b is the Langmuir constant and can be expressed as:

$$b = b_0 \exp\left(\frac{-\Delta H}{RT}\right) \tag{18}$$

After substituting Eq. (18) into Eq. (2), ΔH and ΔS were calculated using Sigma Plot non-linear regression by fitting qe as a function of T and C_e. The values are shown in Table 7.

The ΔG values were then calculated using Eq. (16) and were found to range between −2.72 and −12.84 kJ/mol for the temperature range of 25–60 °C, which indicated the spontaneous nature of the adsorption process. The change in the enthalpy was found to be −66.7 and −83.7 kJ/mol for aqueous and refinery wastewater, respectively. The negative value of ΔH suggests the exothermic

Table 7
Thermodynamic parameters calculated from the Langmuir model for the adsorption of phenol onto DP-AC for both aqueous and refinery wastewater.

	Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol K)	R^2	ARE
Aqueous	298	−3.03	−66.7	0.23	0.9	0.3
	313	−6.54				
	333	−11.22				
Refinery	298	−2.72	−83.7	0.29	0.97	0.23
	313	−7.07				
	333	−12.87				

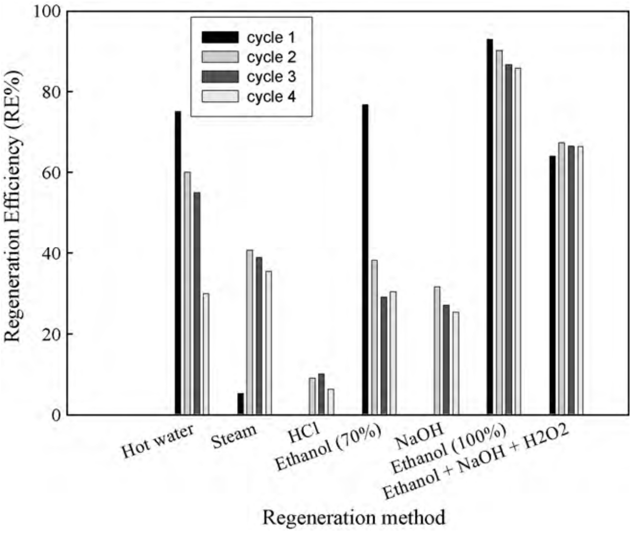

Fig. 9. Regeneration efficiency for batch experiments using different techniques for four cycles of regeneration.

nature of phenol adsorption onto DP-AC [75], while the positive ΔS values confirm the increased randomness at the solid–solution interface during adsorption.

3.7. Regeneration of activated carbon

The regeneration of spent DP activated carbon was evaluated for four cycles using different regeneration methods, and the results are shown in Fig. 9. Chemical regeneration using ethanol achieved the highest regeneration efficiency of 86% even after the fourth cycle. A combination of alcohol, alkali and oxidant, consisting of ethanol, NaOH and hydrogen peroxide, showed good regeneration efficiency reaching 66% after the fourth cycle. On the other hand, HCl and NaOH did not show any promising results for the regeneration of DP-AC.

Thermal regeneration with hot water (at 80–90 °C) reached 75% regeneration efficiency after the first cycle, which is believed to be due to the enhanced solubility of phenol in hot water. However, the regeneration efficiency dropped to about 30% after the fourth cycle. Similar behavior was observed when steam was used with 35% regeneration efficiency achieved after the fourth cycle. Fig. 9 shows that water and steam exhibit low regeneration efficiencies in the fourth cycle relative to the first cycle; whereas the regeneration efficiency with ethanol did not experience such reduction in the repeated cycles. This may be due to the fact that physical regeneration involves expansion of the DP-AC pores in each cycle, which may affect the characteristics of adsorbent after repeated cycles, leading to a drop in the regeneration efficiency.

4. Conclusions

The effectiveness of activated carbon locally prepared from date-pits (DP) for the uptake of phenol from refinery and synthetically prepared aqueous solution wastewater was evaluated. Kinetics and equilibrium data for the adsorption of phenol were obtained and fitted to different kinetics and isotherm models. The results show that the capacity of DP-AC is comparable to other adsorbents, which proves that it can be considered as a low-cost alternative to commercial activated carbons for the removal of phenols from wastewater. In addition, the utilization of DP can provide an excellent disposal option for the date palm industry. Kinetics data were best fitted by the pseudo-second order model, and the equilibrium data followed the Sips isotherm. High regeneration efficiency was achieved using pure ethanol.

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