Characterizing o- and p-nitrophenols adsorption onto innovative activated carbon prepared from date pits

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ABSTRACT

The production and performance of activated carbon prepared from date pits was investigated. Date pits are an abundant local waste product in many countries; converting them to a commercial product would increase the sustainability of this fruit crop. The date pit activated carbon was shown to have similar characteristics of pore size and surface functional groups as other commercial carbons. Batch experiments were conducted with o- and p-nitrophenol to evaluate the performance of this carbon. Results were analyzed according to Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherms. The adsorption capacity of o-nitrophenol was 142.9 mg/g while that of p-nitrophenol was 108.7 mg/g. The adsorption process was physical in nature. The position of the --NO2 group in the benzene ring has a considerable effect on the adsorption capacity and rate of uptake. The kinetic results showed that a pseudo second-order model appropriately describes the experimental data. The analysis of kinetic data revealed that the mechanism of adsorption is complex with both liquid film diffusion and intraparticle diffusion contributing to adsorption of both adsorbates.

Key words | activated carbon, adsorption, date pits, o-nitrophenol, p-nitrophenol

INTRODUCTION

Worldwide, wastewater containing phenolic compounds is produced by many industries, e.g., paper, solvent, plastic, and iron-steel industries. In addition, accidental spills of phenolic compounds contaminate waterways, as occurred when phenol-related chemicals polluted the Amur River in Russia to nearly 50% above permitted levels (Blagov 2006). In February 2012, China probed a chemical spill from a South Korean cargo ship that contaminated a Chinese water source with sufficient phenol to cause tap water to possess a pungent odor (WNAP 2011). The dangerous effects of phenols are due to both their toxicity and also the large volume disposed worldwide. For example, in Europe more than 2000 ton/year of phenolic compounds are released as indirect emission to the environment (EPER 2012).

Removal of pollutants from water can be conducted via different methods, e.g., biological processes, solvent extraction, chemical oxidation, ion exchange, incineration and adsorption (Potgieter et al. 2009). However, the treatment efficiency is different from one technique to another depending on factors including the nature of the pollutant and characteristics of water. Wastewater and drinking water must be treated to meet not only the increasingly stringent regulatory requirements, but also to minimize negative aesthetic effects. Sorption of aqueous contaminants onto activated carbon represents an important global approach to controlling water pollution and improving water quality. Activated carbon is widely applied for treating drinking water, wastewater, and also source waters to drinking water plants during chemical spills (Zhang et al. 2011). Activated carbon has high capacity and fast rate for adsorption of phenolic compounds from water (Derylo-Marczewska et al. 2010). The main disadvantage of activated carbon is the high cost associated with its manufacturing and regeneration (Koyuncu et al. 2011). Although many studies have been performed to investigate the removal of phenolic compounds by adsorption, this subject is still important to discuss due to the complex nature associated with this process (Haydar et al. 2003; Terzyk et al. 2008; Gao et al. 2011). Mechanisms suggested by different researchers include interaction of electron rich regions in graphenes layers with the π electrons of the aromatic ring of phenol; bonding of the aromatic ring to carbonyl groups in the surface of activated...
carbon; formation of hydrogen bonds between superficial carboxylic groups and the OH functional groups of phenol (Derylo-Marczewska et al. 2010).

Activated carbon can be prepared from many carbon sources. The use of local agricultural waste as a carbon source for preparing activated carbon is receiving emphasis as a sustainable solution to global environmental problems (Ioannidou & Zabaniotou 2007). The worldwide annual production of dried date is 3.1 million tons, primarily from countries in North Africa and the Middle East (Alshuaibi 2011). Saudi Arabia produces nearly one third of the worldwide production, or 986.000 tons (Alshuaibi 2011). Substantial agricultural waste is produced every year as a byproduct of date fruit processing (Altaher & ElQada 2011). Converting waste date pits into activated carbon represents a sustainable solution that is economical and provides a valuable means for water and wastewater treatment.

The aim of this research is to develop a date pit activated carbon that is effective for treating water. The objectives of this study were to: (1) prepare carbon from date pits and evaluate its physical and surface chemical characteristics; (2) evaluate date pit activated carbon for removal of o- and p-nitrophenolns from water to investigate the structural effect of the adsorbate on the sorption process; (3) apply kinetic models to evaluate the sorption processes.

METHODS

Adsorbates

Stock solutions of ONP and PNP were prepared by individually dissolving each solid substance in distilled water. Concentrations were determined spectrophotometrically (using UV mini-1240, Shimadzu) at 316 and 350 nm for p-nitrophenol and o-nitrophenol, respectively. The physical properties of the two adsorbates are presented in Table 1.

Preparation of date pit activated carbon

The date pits were washed using liquid detergent with good rubbing of the pits to remove all foreign materials, followed by rinsing three times with tap water, soaking in distilled water for ten minutes, and filtering to separate pits from water. The pits were dried at 105 °C overnight, and then crushed using a kitchen grinder. The dried pits were mixed with concentrated phosphoric acid in a mass ratio of 1:1. To activate, the pits were placed in crucibles positioned inside a muffle furnace containing a nitrogen gas atmosphere, and then heated to a temperature of 500 °C which was maintained for one hour. The carbonized samples were cooled to room temperature inside a desiccator. They were rinsed 10 times with distilled water, followed by neutralization with 0.1 N of NaOH or 0.1 N of H2SO4 to remove the activator. The rinsing process continued until the pH of the rinse water reached about 7. The activated carbon was oven-dried at 105 °C, cooled in desiccators, ground and sieved to different fractions and stored in sealed plastic bottles (Altaher & Khalil 2012). Activated carbon of particle size <250 μm was used in this research.

The Fourier transform infrared spectroscopy (FT-IR) spectra of date pits and prepared activated carbon were recorded in the range 4,000 to 400 cm−1 as KBr pellets on an infrared spectrophotometer (Varian, USA, FT-IR 800 Scimitar Series). The surface morphology of the date pits, activated carbon samples, and commercial charcoal was examined using scanning electron microscopy (SEM) (JEOL-JSM 5300) at different magnifications.

Sorption experiments

Batch experiments were applied to study factors that may affect the adsorption process. When testing one factor, the other factors were kept constant. For example, the mass of adsorbent was 0.12 g, rate of stirring was 300 rpm, initial concentration was 115 mg/l, time of shaking was 240 minutes for ONP and 503 minutes for PNP, and the

Table 1 | Physical properties of adsorbates (Morrison & Boyd 1992)

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Aqueous solubility, g/L</th>
<th>pK_a</th>
<th>Molecular size, Å</th>
<th>Boiling point, °C</th>
<th>Melting point, °C</th>
<th>Dipole moment, D</th>
</tr>
</thead>
<tbody>
<tr>
<td>ONP</td>
<td>2</td>
<td>7.24</td>
<td>8.1</td>
<td>216</td>
<td>46</td>
<td>3.74</td>
</tr>
<tr>
<td>PNP</td>
<td>16.9</td>
<td>7.16</td>
<td>6.7</td>
<td>297</td>
<td>113-114</td>
<td>5.7</td>
</tr>
</tbody>
</table>

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temperature was at room temperature (20 ± 2°C). A volume of 50 ml of solution was used in all experiments. Adsorbate and adsorbents were placed in 150 ml flasks and agitated using an IKA YellowLine shaker. After reaching equilibrium, the solid phase was separated from the liquid phase by filtration. The final concentration of the adsorbate was determined spectrophotometrically as previously described.

Adsorption isotherms

The experimental data were analyzed with three established isotherm models: Langmuir, Freundlich and Dubinin-Radushkevich (D-R). Descriptions of the models are provided in the Supplementary Material (available online at http://www.iwaponline.com/wst/069/522.pdf). The main difference between the first two models is the variation of heat of adsorption with the surface coverage. Langmuir assumes uniformity in the active site and consequently in the heat of adsorption, whereas the Freundlich model assumes logarithmic change. The D-R model was applied to investigate the type of adsorption; physical or chemical. If the magnitude of E (free energy; see Supplementary Material for explanation), is less than 8 KJ/mol, then the adsorption is physical; if it is between 8 and 16 KJ/mol, then the adsorption process is attributed to ion exchange; and greater than 16 KJ/mol indicates that the process is chemical adsorption.

Kinetic models

Information on the dynamics of sorption is required for selecting optimum operating conditions for the full-scale process. To examine the rate and mechanism of adsorption of adsorbates on the surface of activated carbon, five models were used (see Supplementary Material for detailed descriptions of the models). Pseudo first-order and second-order models determine the rate of the adsorption process and the adsorption capacity at the conditions tested. The Elovich model assists in predicting whether the nature of the adsorption process is physical adsorption or chemisorption. Intraparticle diffusion model and the Boyd model estimate the mechanism of adsorption and determine the rate limiting step.

RESULTS AND DISCUSSION

Characteristics of date pit carbon

Figure 1 represents the morphology of date pits before and after the carbonization process. Scanning electron microscope images confirm that chemical activation with H₃PO₄ promotes porosity in carbon, thereby increasing its contaminant removal efficiency.

The FT-IR spectra (not shown) displayed bands at 3,360–3,350 and 2,925–2,850 cm⁻¹, which arise from the O-H and aliphatic C-H, respectively. Bands were also present at 1,610, 1,700 cm⁻¹, arising from the C=O in ketone, aldehyde, lactone or carboxyl groups (Yakout & Sharaf El-Deen 2012); 3,050–3,100 cm⁻¹ arising from the aromatic C-H and 2,300–2,400 cm⁻¹ representing ketone group. Two peaks were observed at 1,075 and 1,180 cm⁻¹. The first peaks may be assigned to ionized linkage P-O in acid phosphate ester and to symmetrical vibration in P-O-P chain (Bourbigot et al. 1995). The later peak may be assigned to the stretching mode of hydrogen bond P=O, to O-C stretching vibration in P-O-C and to P=OOH (Yakout & Sharaf El-Deen 2012). The OH groups of nitrophensols and surface OH groups of activated carbon may interact with each other through a hydrogen bond (Öztürk

Figure 1 | Scanning electron micrographs of: (a) dates pits (>7500 magnification), (b) activated carbon (>7500 magnification), and (c) activated carbon (<1000 magnification).
et al. 2009). Carboxylic and carbonyl groups may also play an important role in the removal of nitrophenols (Terzyk et al. 2008, Suresh et al. 2013).

Adsorption equilibrium for nitrophenols

The goodness of data fitting to the adsorption models was verified using linear regression represented by correlation coefficient value ($R^2$) in Table 2 and by comparing the experimental data to the calculated data obtained from the models as illustrated by Figures 2(a) and 2(b). The correlation coefficient value determined for each isotherm indicates that the Freundlich model effectively fits the experimental data better than other models. The value of exponent ($n$) for both systems, being greater than 1, indicates favorable adsorption condition. Figures 2(a) and 2(b) support this result. The two curves representing the experimental data and calculated data (using Freundlich) almost coincide.

The adsorption capacities of ONP and PNP were found to be 142.9 and 108.7 mg/g, respectively, based on the Langmuir equation. As depicted in Table 3, the adsorption capacity of date pit activated carbon is comparable to other activated carbons.

\begin{table}[h]
\centering
\small
\caption{Adsorption and kinetic parameters for the applied adsorption models}
\begin{tabular}{|l|c|c|}
\hline
Parameter & ONP & PNP \\
\hline
Langmuir & $R^2$ & 0.897 & 0.976 \\
& $q_m$ & 142.9 & 108.7 \\
& $k_L$ & 0.034 & 0.145 \\
& $R_L$ & 0.171 & 0.042 \\
Freundlich & $R^2$ & 0.970 & 0.998 \\
& $n$ & 2.089 & 2.860 \\
& $k_f$ & 12.79 & 18.52 \\
Dubinin-Radushkevich (D-R) & $R^2$ & 0.811 & 0.877 \\
& $q_m$ & 51.84 & 19.65 \\
& $B$ & $4 \times 10^{-6}$ & $8 \times 10^{-6}$ \\
& $E$ & 0.354 & 0.250 \\
Pseudo first order & $R^2$ & 0.804 & 0.964 \\
& $k_1$ & 0.014 & 0.033 \\
& $q_e$ & 13.76 & 17.56 \\
Pseudo second order & $R^2$ & 0.999 & 1.000 \\
& $k_2$ & 186.3 & 1269 \\
& $q_e$ & 38.91 & 50.00 \\
Elovich & $R^2$ & 0.902 & 0.892 \\
& $B$ & 0.200 & 0.338 \\
& $\alpha$ & 58.84 & 336100 \\
Intraparticle diffusion & $R^2$ & 0.665 & 0.558 \\
& $k_p$ & 1.782 & 0.634 \\
& $c$ & 15.29 & 39.70 \\
Liquid film diffusion & $R^2$ & 0.870 & 0.965 \\
& $k_{ld}$ & 0.029 & 0.016 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\small
\caption{Adsorption capacities of ONP and PNP onto different activated carbons}
\begin{tabular}{|l|c|c|}
\hline
& ONP & PNP \\
\hline
1 & – & 251–573 \\
2 & 66–242 & 250 \\
3 & 66–242 & 250 \\
4 & 60–240 & 250 \\
5 & 56.41 & 50.00 \\
6 & 142.9 & 108.7 \\
\hline
\end{tabular}
\end{table}

$E$ values for o- and p-nitrophenol, calculated from the D-R model, was <8 kJ/mol which suggests physical interaction between adsorbent and adsorbate for both systems. The position of the nitro group plays an important role in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Application of different adsorption models to data for: (a) o-nitrophenol, and (b) p-nitrophenol.}
\end{figure}
sorption as the ortho position hinders the possibility of the hydrogen bonding between the solute and the solvent water (Singh & Yenkie 2006). ONP has lower solubility in water due to the formation of intramolecular hydrogen bonds which limits H-bonding to water molecules, whereas PNP can form intramolecular H-bonds with water or other molecules. The affinity of activated carbon for adsorbates is attributed to pKa and solubility (Gao et al. 2014) as well as polarity (Potgieter et al. 2009). The lower adsorption capacity of PNP may be attributed to polarity/dipole moment and water solubility of this molecule compared to ONP (Table 1 and Table 2). These results are in agreement with that of Hu et al. (2000).

The difference in adsorption behavior of ONP and PNP may also be due to the different Van der Waals interactions and hydrogen bond interaction between functional groups on the surface of activated carbon and the adsorbate (Singh & Yenkie 2006). The carboxyl groups present on the carbon surface may be also responsible for the uptake of phenols by donor-acceptor complex mechanism. The substitution of an electron withdrawing group like nitro in phenol lowers the electron density in the pi-system of the ring, which acts as an electron acceptor, and carboxyl group acts as an electron donor.

The surface chemistry of adsorbents is determined by the acidic and basic character of their surface. The FT-IR data indicate the presence of acidic oxygen-containing functional groups (e.g., hydroxyl, $P = O$) on the surface of date pit activated carbon. When phosphoric acid was used as an activator for olive stone activated carbon, various surface acidic functional groups (oxygen- and/or phosphorus-containing groups) developed on the surface while developing required porosity. Phosphoric acid promoted bond cleavage reactions, plus formation of cross-linkages through cyclization, condensation, and/or phosphate and polyphosphate bridges with organic species (Yakout & Sharaf El-Deen 2012). Some researchers (Deng et al. 2010, Yakout & Sharaf El-Deen 2012) suggested that the mechanism of formation of pores is through the evaporation of the activating during carbonization of lignocellulosic materials, creating pores in the space previously occupied by the activating agent. Like olive stones, date pits are lignocellulosic materials. Therefore, the mechanism of phosphoric acid activation is likely to be the same for date pits as it is for olive stones.

**Kinetic study**

In the kinetic models, the adsorption rate of the solute onto the carbon surface is considered the only factor controlling the overall rate of adsorption. In this case, both intraparticle diffusion and external mass transfer are neglected. The latter two are considered by the diffusion model. The parameters of the kinetic models are presented by Table 2 and Figures 3(a) and 3(b). Figures 3(a) and 3(b) demonstrate that both adsorbate systems follow pseudo second-order reaction. This result is expected since pseudo second order describes data related to adsorption on heterogeneous and/or porous systems or energetically homogeneous adsorbents (Derylo-Marczewska et al. 2010; Marczewski 2010). The poor fitting of data to Elovich model assures the physical nature of the adsorption process which support the results obtained from D-R isotherm. The rate of adsorption of PNP was found to be much higher than that of ONP. This result is supported by Derylo-Marczewska et al. (2010).

![Figure 3](https://iwaponline.com/wst/article-pdf/69/1/31/471851/31.pdf)
whose results demonstrated that adsorption of PNP was much faster than that of ONP and m-nitrophenol.

Examining Figures 3(a) and 3(b) indicates that three adsorption steps occurred. The first step is very fast and characterized by rapid adsorption of both ONP and PNP on the activated carbon surface. This may be due to the large number of vacant surface sites available for adsorption in the initial stage. No competition takes place between the adsorbate molecules. The adsorbate is rapidly accumulated on the adsorbent surface within the first 20 minutes. The second step is slow and attributed to the repulsive force between attached and non-attached solute molecules in conjunction with a reduced concentration gradient in the solution (Srivastava et al. 2006). The third step is the equilibrium stage where the adsorption reaches a plateau.

To investigate the diffusion mechanism, the model of Weber and Morris (Santhi et al. 2010) was applied. As indicated by Figure 4, the data for both ONP and PNP deviate from linearity and the lines do not pass through the origin which indicates that the pore diffusion is not the rate controlling step for both compounds (Boparai et al. 2011). The initial rapid uptake may be explained by sorption to the readily available active sites on the surface of date pit carbon, whereas the second slower-uptake phase may be attributed to the adsorption on the remaining sites which are difficult to access.

The data presented in Table 3 and Figure 4 indicate that PNP has a higher rate of adsorption than ONP. PNP is more water soluble and has a smaller molecular size than ONP. It would be expected that the smaller the molecular size, the faster is the mass transfer (Do 1998). Taking into account the higher solubility of PNP in water, this implies the higher mobility of PNP molecules. Also, the contribution of surface diffusion decreases with smaller molecules because these molecules are not easily condensed and absorbed. The higher the density of the adsorbate molecules, the easier will be their condensation on the surface of the adsorbent, hence their adsorption (Brasquet et al. 1997; Do 1998).

The liquid film diffusion model is used to predict the effect of the boundary layer around the adsorbent surface on the adsorption process. If the plot of \(-\ln (1-(q_t/q_e))\) versus \(t\) is linear and passes through the origin, then the transport of the adsorbate through the liquid film surrounding the adsorbent is a rate limiting step. The high value of intercept indicates the high thickness of the boundary layer (Boparai et al. 2011). However, the higher correlation coefficient value in the case of PNP suggests that liquid film diffusion model might have some role to play in the kinetics of adsorption.

**CONCLUSIONS**

Activated carbon prepared from date pits with phosphoric acid as a chemical activator was found to have similar physical and chemical characteristics to other activated carbons used to treat water. Date pits carbon was shown to be effective for removal of ONP and PNP from aqueous solution and consistent with performance of other chemical activated carbons. The adsorption capacity of ONP was higher than that of PNP. The rate of adsorption of PNP was faster than that of ONP. Both adsorbate systems are fast at initial stages and became slower near equilibrium. The mechanisms of adsorption for these phenolic compounds may be explained by both liquid film diffusion and intraparticle diffusion models. The \(-\text{NO}_2\) group in the ortho position increased the adsorption capacity while in the para position it increased the adsorption rate.

**REFERENCES**


