ABSTRACT: The present work was carried out to evaluate the removal of p-nitrophenol by adsorption onto olive cake based activated carbon having a BET surface area of 672 m²/g. The batch adsorption experimental results indicated that the equilibrium time for nitrophenol adsorption by olive cake-based activated carbon was 120 min. The adsorption data was modeled by equilibrium and kinetic models. The pseudo-first and second order as well as the Elovich kinetic models were applied to fit the experimental data and the intraparticle diffusion model was assessed for describing the mechanism of adsorption. The data were found to be best fitted to the pseudo-second order model with a correlation coefficient ($R^2 = 0.986$). The intraparticle diffusion mechanism also showed a good fit to the experimental data, showing two distinct linear parts assuming that more than one step could be involved in the adsorption of nitrophenol by the activated carbon. The equilibrium study was performed using three models including Langmuir, Freundlich and Temkin. The results revealed that the Temkin equilibrium model is the best model fitting the experimental data ($R^2 = 0.944$). The results of the present study proved the efficiency of using olive cake based activated carbon as a novel adsorbent for the removal of nitrophenol from aqueous solution.

KEYWORDS: Activated carbon; Adsorption; Equilibrium; Intra-particle diffusion; Olive cake; p-nitrophenol (PNP)

INTRODUCTION

The removal of organic pollutants from wastewater is a very important challenge. Organic pollutants are widely used in several industries and many of them are released into water systems. Phenolic compounds represent a major class of harmful organic pollutant due to their toxic effects. Among phenolic compounds, the US Environmental Protection Agency denotes p-Nitrophenol (PNP) as one of the toxic chemicals, non-degradable and bioaccumulative (Tang et al., 2007). Nitrophenols can be found in different industrial effluents such as those generated from the iron and steel, coke, petroleum, pesticide, paint, solvent, pharmaceutics, wood preserving chemicals, as well as paper and pulp industries (Ahmad et al., 2011).

Although several techniques have been proposed to remove organic pollutants from wastewater, but still the adsorption technique offers more advantages. Adsorption can remove both soluble and insoluble organic pollutants with a high removal capacity (Ali et al., 2012). It has been generally agreed that the most important factor for successful adsorption is the selection of adsorbent (Mittal et al., 2009). Adsorption methodology employing activated carbon is a proficient and hopeful approach in the wastewater treatment practices (Gupta et al., 2011). In the recent years, activated carbon has proven high adsorption efficiency and its use as adsorbent for organic pollutants. Activated carbons have unique characteristics owned to their high surface area, surface acid groups, micro
and mesoporous structure and large sorption capacities (Dural et al., 2011; Isoda et al., 2014). Activated carbons have been successfully used as adsorbent for the removal of synthetic and naturally occurring organic pollutants from water and wastewater (Ifelebuegu et al., 2015).

Unfortunately, the high cost of activated carbon production hinders its extensive use (Mittal et al., 2010). Usually, the precursor materials used for the industrial preparation of activated carbon are coal, wood and coconut shell (Baccar et al., 2009). For developing countries it is a necessity to find cheap alternatives for these expensive precursors (Baccar et al., 2009). The use of agro-industrial wastes as starting material to produce activated carbon has been recently attracting scientists’ attention. The use of these wastes for producing activated carbon have both economic and environmental impacts as it helps converting unnecessary, low-value waste material into a valuable adsorbent (Abdel-Ghani et al., 2015).

Olive trees are cultivated in Egypt and are widely abundant in many countries in Africa. Large amounts of olive-waste cake are generated as by-products of oil extraction process (Baccar et al., 2009). In order to get benefit of this waste, several attempts were made to use olive cake as a precursor material for the production of activated carbon. In our previous work, we have prepared a novel activated carbon from olive cake waste after optimizing the preparation procedure via factorial experimental design (Abdel-ghani et al., 2015).

The aim of the present study was to evaluate the removal of p-nitrophenol by adsorption using a novel activated carbon prepared from olive cake waste. The adsorption experiment was modeled by equilibrium and kinetic models to get a clear view about the processes governing the adsorption of p-nitrophenol by olive cake based activated carbon.

The present work was performed in the Regional Center for Food and Feed (RCFF) at Agricultural Research Center, Giza, EGYPT during 2015.

MATERIALS AND METHODS

Materials

A detailed method of preparation of OCAC and its full characterization is given in our previous work (Abdel-ghani et al., 2015). Olive cake activated carbon (OCAC) used in this study was prepared after optimization of the preparation conditions using a full factorial 2³ factorial design. The preparation conditions were: impregnation ratio of (1 Charcoal: 2KOH), activation time (1h.) and activation temperature at 600°C with Brunauer, Emmet, and Teller (BET) surface area of 672 m²/g.

The adsorbate used in the present work (p-nitrophenol (PNP)) was supplied from Sigma Co.

Preparation of PNP solutions

1g of PNP powder was dissolved in 1000 mL of deionized water to prepare the concentration of 1 g/L PNP solution. Solutions of different initial concentrations of PNP were prepared by diluting the initial stock solution using deionized water.

Determination of PNP concentration

Double-beam UV-visible spectrophotometer (Model SPECORD® PLUS spectrophotometer, Analytik Jena) was used to measure the concentration of PNP during the experiments. The maximum wavelength of the PNP was determined as 400 nm. A calibration curve of PNP was prepared using different PNP concentrations that cover the concentration range used in this work.

Batch equilibrium studies

Batch equilibrium studies were used to determine the adsorption of PNP on OCAC.

The adsorption at equilibrium qₑ (mg/g) was calculated as Eq. 1:

$$qₑ = \frac{(C₀ - Cₑ)V}{W}$$

Where C₀ (mg/L) and Cₑ (mg/L) are the initial and equilibrium concentrations of PNP, respectively, V(L) is the volume of the solution and W (g) is the mass of activated carbon used.

The effect of contact time on p-nitrophenol removal by OCAC was studied in the range from 15 to 180 minutes in order to determine the equilibrium time of adsorption. The effect of PNP initial concentration was studied using PNP solutions at various initial concentrations of 5, 7.5, 10 and 15 ppm were placed in an isothermal water bath shaker. All measurements were done at room temperature and pH 7.

Equilibrium and kinetic studies

Adsorption isotherm equilibrium studies were carried out by applying the Langmuir (Langmuir, 1918),
Freundlich (Freundlich, 1906) and Temkin (Temkin and Pyzhev, 1940) equations to the experimental data.

The kinetics of the adsorption was investigated using the pseudo-first order model (Lagergren, 1898), pseudo-second-order model (Ho and McKay, 1998) and Elovich's model (Zeldovich, 1946). The intra-particle diffusion equation (Weber and Morris, 1963) was also applied to the adsorption data.

RESULTS AND DISCUSSION
The effect of contact time and equilibrium kinetics
The effect of contact time on p-nitrophenol (PNP) removal by OCAC at different concentrations is shown in (Fig. 1). A variation in the removal percentage of PNP was generally observed in the initial adsorption period (during the first 60 min.), then the removal started to be constant indicating that equilibrium is attained after 120 min. The kinetics of p-nitrophenol adsorption onto OCAC was investigated by applying three kinetic models including the 1st order kinetics model, 2nd order kinetics model and the Elovich's kinetics model. The results are presented graphically in Fig. 2 (a, b and c) and the regression coefficients as well as the models’ constants are presented in Table 1.

The pseudo first-order model (Lagrgren model) is one of the most broadly utilized kinetic models for describing the adsorption of solute from a solution. The linear form of the model is given by Eq. 2, (Lagergren, 1898).

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

Where \( k_1 \) is the kinetic constant of pseudo first-order adsorption (1/min), and \( q_e \) and \( q_t \) (mg of PNP/g adsorbate) represent the amounts of adsorbed PNP at equilibrium and at time \( t \) in min., respectively (Fierro et al., 2008). When this equation applies, a plot of \( \log (q_e - q_t) \) versus \( t \) gives a straight line from which \( k_1 \) and \( q_e \) can be determined. As can be seen from Fig. 2 and Table 1, the regression coefficient \( R^2 \) was found to be 0.93 indicating that this model may not be the best model for fitting the present study data.

The pseudo second order kinetic rate is given as Eq. 3, (Ho and McKay, 1998).

\[
t/q_t = 1/K_2q_e^2 + t/q_e
\]

In this equation, \( q_t \) and \( q_e \) are as previously indicated in the pseudo-first order equation and \( K_2 \) is the rate constant of second-order model (g/mg min). When this equation applies, then a plot of \( t/q_t \) versus \( t \) should give a straight line from which \( q_e \) and \( K_2 \) can be determined. As it can be seen from Fig. 3 and Table 1, the high \( R^2 \) value was obtained (0.98) assuming the suitability of the pseudo-second order model to fit the present data. The Elovich’s equation was established by Zeldovich in his work concerning the adsorption of carbon monoxide on manganese dioxide (Zeldovich, 1946). The Elovich’s equation was then employed for relating the adsorption of contaminants from aqueous solutions. Elovich’s equation is expressed as Eq. 4.

\[
q_t = (1/\beta) \ln (\alpha \beta) + (1/\beta) \ln (t)
\]
Where $\alpha$ is the initial adsorption rate (mg/g min), and the parameter $1/\beta$ (mg/g) is related to the number of sites available for adsorption. If this equation applies, it should lead to a straight line by plotting $q_t$ as a function of $\ln (t)$ with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln (\alpha \beta)$, (Fierro et al., 2008). It is clear from Fig. 4 and Table 1, that the Elovich’s model did not fit adequately the present work data ($R^2 = 0.91$).

Based on the kinetic study results, it can be concluded that in the present study the adsorption of p-nitrophenol onto OCAC is best described in terms of the pseudo-second order kinetics model. The second-order model suggests that the adsorption process is governed by “chemisorptions” which involves the establishment of valency forces by sharing or exchanging electrons between adsorbents and
adsorbates (Deng et al., 2009). These results are in accordance with the results of (Tang et al., 2007) for the adsorption of p-nitrophenol onto activated carbon fibers and the results of (Ahmaruzzaman and Laxmi Gayatri, 2010) for the adsorption of nitrophenol by jute stick char.

In order to get more information concerning the adsorption mechanism, the data were further investigated by applying the intraparticle diffusion mechanism. The possibility of intra-particle diffusion was explored by applying the intra-particle diffusion model (Weber–Morris model) to the present work data. The intraparticle model (Weber and Morris, 1963) is expressed as: 

\[ q_t = k_i t^{1/2} + C_i \]

where \( k_i \) is the intraparticle diffusion rate constant (mg/g.min) and \( C_i \) is a constant related to the thickness of the boundary layer: large the value of \( C_i \) suggest high boundary layer effect (Itodo et al., 2010). The slope of the plot: \( q_t \) versus \( t^{1/2} \) is defined as a rate parameter, characteristic of the rate of adsorption in the region where intra-particle diffusion is rate controlling step. If the Weber-Morris plot of \( q_t \) versus \( t^{1/2} \) is linear, this means that intra-particle diffusion is rate controlling step. If the Weber-Morris plot of \( q_t \) versus \( t^{1/2} \) gives a straight line passing by the origin, this means that intra-particle diffusion is the only mechanism controlling the sorption process. On the other hand, if multi-linear plots are obtained then two or more steps are involved in the sorption process (El-Said, 2010). Fig. 5 presents the plots of p-nitrophenol uptake versus \( t^{1/2} \). The plots consisted of two linear sections indicating that two steps contribute to the adsorption process. Step “one” is
the diffusion through the solution to the external surface of the adsorbent or the boundary layer diffusion of solute molecules. While step “two” corresponds to the ongoing adsorption stage, where intraparticle diffusion is the rate-limiting step (Abdel-Ghani et al., 2015).

The calculated parameters of the model are summarized in Table 1. The diffusion was characterized by the specific rate parameters, $k_{d1}$ and $k_{d2}$. The value of $k_{d1}$ were higher than that of $k_{d2}$ which could be attributed to limitation of the available vacant sites for diffusion in and pore blockage (Yaneva et al., 2013).

Adsorption equilibrium modeling

The adsorption of PNP by OCAC was further investigated by applying the adsorption equilibrium models to the experimental data. The studied models were Langmuir, Freundlich and Temkin models. The three models differ from one another based on the way by which the heat of adsorption varies with the surface coverage: Langmuir assumes no decrease in heat of adsorption with increase in surface coverage; Freundlich assumes a logarithmic decrease, whereas Temkin assumes a linear decrease.

The Langmuir adsorption model depends on the presumption that a maximum extreme restricting uptake exists, related to the formation of a saturated monolayer of adsorbate molecules at the adsorbent surface. In this model, all the adsorption sites have the same sorption activation energy (Gottipati, 2012).

The Langmuir equation 5 can be indicated as:

$$
\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}
$$

Where $q_e$ is the amount of nitrophenol adsorbed per unit mass of activated carbon (mg/g), $k_L$ is the Langmuir constant related to the adsorption capacity (L/g), $C_e$ is the concentration of adsorbate in the solution at equilibrium (mg/L), $q_m$ is the maximum uptake per unit mass of carbon (mg/g).

When the Langmuir model applies, the efficiency of the adsorption process could be interpreted using the Langmuir parameter ($K_L$): the adsorption is considered as irreversible;
Table 2: Equilibrium models and their calculated parameters

<table>
<thead>
<tr>
<th>Equilibrium model</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
<td>$K_L$ (L/g)</td>
<td>0.310</td>
</tr>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>1.550</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.760</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td>$K_F$ (L/g)</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>5.180</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.350</td>
</tr>
<tr>
<td></td>
<td>$A_F$</td>
<td>2.500</td>
</tr>
<tr>
<td>Temkin isotherm</td>
<td>$B_T$ (L/g)</td>
<td>1.251</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.944</td>
</tr>
</tbody>
</table>

when $K_t = 0$, favorable when $0 < K_t < 1$, linear when $K_t = 1$, and unfavorable when $K_t > 1$ (Abdel-Ghani et al., 2009).

The Langmuir plot of PNP removal by OCAC is shown in Fig. 6 and the model’s calculated parameters are given in Table 2. As it can be seen from Table 2, the values of $R^2$, $K_t$, and $q_m$ were 0.76, 0.3096 (L/g), 1.55 mg/g, respectively. The data showed very low correlation coefficient and very low maximum uptake capacity which suggests that the Langmuir model is not suitable for fitting the present study data.

The Freundlich adsorption isotherm assumes that adsorption happens on a heterogeneous surface through a multilayer adsorption system, and that the adsorbed quantity increases with the concentration according to the Eq. 6, (Gottipati, 2012).

$$\log q_e = \log K_F + \frac{1}{n} \log C$$

(6)

Where $n$ and $q_m$ have the same meaning as in the Langmuir isotherm $K_F$ is the Freundlich constant and (n) is the empirical parameter representing the energetic heterogeneity of the adsorption sites (dimensionless).

The Freundlich plot of PNP adsorption onto OCAC is given in Fig. 7. Table 2 shows the Freundlich parameters, $k_F$, and $n$, together with the correlation coefficient ($R^2$). According to Table 2, the $R^2$ value of the model is very low (0.35), indicating that the adsorption of PNP by the studied adsorbent cannot be modeled by the Freundlich Eq. 6.

The Temkin isotherm equation suggests adsorbent–adsorbate interactions which causes a decrease in the heat of adsorption of all the molecules in the layer to decrease linearly with coverage, and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy (El-Sadaawy and Abdelwahab, 2014).

The Temkin model’s is given by Eq. 7:

$$q_e = B_T \ln A_T + B_T \ln C$$

(7)

Where $B_T$ is related to the heat of adsorption (L/g), and $A_T$ is the dimensionless Temkin isotherm constant. The present work data were fitted to the Temkin model as shown in Fig. 8. The Temkin parameters, $B_T$ and, together with the correlation coefficient $R^2$, corresponding to each OCAC is shown in Table 2. The value of $R^2$ is the highest one (0.944), indicating that Temkin isotherm is the most suitable model for fitting the experimental data. The applicability of the Temkin model indicates a chemical adsorption of PNP onto OCAC.

CONCLUSION

The present study has described the adsorption of p-nitrophenol by adsorption by a novel activated carbon prepared from olive cake. The suggested adsorbent showed promising results in removing nitrophenol from synthetic wastewater under the studied conditions. The adsorption was found to follow the pseudo-second order kinetic model and the Temkin equilibrium model indicating chemisorption process. Further studies could be addressed to finding the possible application of olive cake based activated carbon for the removal of other organic pollutants.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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Adsorption of p-nitrophenol from wastewater using olive cake-based activated carbon


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