Bio-adsorption of phenol from wastewater applying local Jordanian *Eucalyptus* leaves: parametric, kinetics, adsorption isotherms, and surface analysis

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**Abstract**

Phenol is a chemical compound that is naturally synthesized or manufactured and often found in the effluent of many industrial plants. It is highly toxic and carcinogenic, therefore, should be removed prior to discharging the wastewater. In this work, local Jordanian *Eucalyptus* leaves are utilized as an adsorbent for the removal of phenol from artificial wastewater for the first time. The morphology of the leaves was studied using scanning electron microscope. Effects of the phenol initial concentration, adsorbent concentrations, temperature, pH of the solution, and contact time on the efficiency of adsorption were investigated. A removal percentage of 95% to 59% was achieved upon using phenol concentration in the range of 50–400 mg/L, neutral solution, a temperature of 25°C, 0.2 g of adsorbent and a contact time of 3 h. The pseudo-first order reaction rate exhibited better representation of the results than the other rates tested with a correlation coefficient ($R^2$) greater than 0.93. Langmuir and Freundlich adsorption isotherms did fit the adsorption results very well with a favorable physical exothermic adsorption process with the heat of reaction of $-2.4$ kJ/mole. Therefore, *Eucalyptus* leaves exhibited good adsorption capacity toward phenol within the experimental conditions utilized.

**Keywords:** Phenol batch adsorption; Local Jordanian *Eucalyptus* leaves; Parametric optimization; Adsorption kinetics and isotherms; Removal performance; Surface morphology

1. Introduction

The management of water resources and their quality is one of the major supports for the sustainability of human, animals, and plants. The important aspect of this is not only to preserve water resources but also to treat polluted wastewater. This is very important to meet the enormous increase in the demand for freshwater and industrial water as a result of the fast increase in the world population, global development, and industrialization. Water contamination is primarily caused by man, and infrequently by nature. Man-made contamination is mainly due to the industrial activities that generate wastewater effluents, the application of fertilizers and pesticides, in addition to using disinfectants, and other activities [1]. As a result, different types of contaminants were found and identified in the wastewater. Industrial effluents usually contain significant levels of organic and inorganic pollutants. Depending on the nature of contaminants, different treatment methods are often recommended and studied to eliminate them or reduce their levels [2,3].

Phenol and its derivatives are the most common pollutants usually found in the effluent of chemical plants and industries such as petroleum, petrochemical, fiberglass, olive mills, textiles, pharmaceutical and many more at different levels depending on the source. They are highly toxic, carcinogenic and have negative effects on the bio-systems of human, plants and microorganisms. They form toxic byproducts, cause water turbidity when degraded, and are considered as a priority pollutant according to
the environmental protection agency. They may enter the human body through skin and respiratory system, when it is in the vapor phase, and digestive system. Long-time exposure would cause serious health problems and damage to the kidneys, lungs, and liver. The World Health Organization sets the limits of the concentration of phenol in drinkable water to 0.001 mg/L [4,5].

The treatment of wastewater polluted with phenol is essential and attracted the attention of many researchers. Steam and solar distillation were investigated for the purification of water from phenolic compounds [6,7]. Liquid–liquid extraction was used to remove phenol using cumene and other solvents [8,9]. Treatment of phenol using catalytic and non-catalytic oxidation was also investigated [10]. Furthermore, biodegradation and reverse osmosis were applied by different researchers to reduce the levels of phenol in wastewater [11,12]. Therefore, the removal of phenol from the wastewater imposes a great duty on the researchers to get on unpolluted safe water.

Adsorption is extensively studied and applied for the removal of different types of pollutants from wastewater [13]. It has been found to be effective since it can deal with contaminations from very small concentrations to percent ones. Besides, it is easy to design and carry out. In this aspect, different adsorbents were applied and tested; activated carbon is the most widely used adsorbent, although it is expensive, it was found to be efficient [14,15]. The search for low cost, effective, abundantly available, and environmentally friendly adsorbent, to remove phenol and its compounds from polluted water, is a going process [16–18]. Different materials and compounds have been studied by researchers to reduce phenol levels in water such as bamboo biochar, carbonaceous activated carbon, oak wood biochar, mesoporous carbon, Luffa fibers, porous clay, and zeolite [19–21].

This work aims to investigate the possibility of removing phenol from the wastewater using local Jordanian Eucalyptus leaves as an adsorbent for the first time. The Jordanian Eucalyptus trees were selected based on their availability in Jordan, their growth rate is very fast, leaves features, and surface porosity of the leaves. Batch adsorption experiments will be performed by varying the initial phenol concentration, adsorbent dosage (g), temperature, pH of the solution, and the contact time. Results will be analyzed using the well-known Langmuir and Freundlich isotherms, pseudo-first order kinetics, and pseudo-second order kinetics.

2. Materials and methods

Eucalyptus leaves were collected from the north of Jordan. Cleaned of dust and other impurities then washed with warm distilled water several times to avoid leaching of color. They were dried in an oven at 60°C then left to dry over night at 80°C, higher temperatures resulted in burning some parts of the leaves. Dried leaves were ground, sieved and classified into groups based on the mesh size using standard Tyler series size analysis. A micrograph of the leaves powder, taken by a scanning electron microscope, model FEI COUNTA 450, is exhibited in Fig. 1. Irregular morphological surface characteristics, which will have a positive effect on adsorption, can be clearly observed.

Phenol solutions preparation and analysis were performed according to standard methods for the examination of water and wastewater using UV-spectrophotometry (JASCO V-700 serie, Mafraeq-City, Jordan) at 270 nm [2,22,23]. A stock solution (1.00 mg/L) of phenol in distilled water was prepared. It was then used to prepare solutions with lower concentrations, via dilution with distilled water, as required. The pH was adjusted using 0.1 N solutions of HCl and NaOH. All chemicals used in this study were pure and reagent grades (Sigma-Aldrich, Mafraeq-City, Jordan). A water bath shaker (JISICO Water Bath, Mafraeq-City, Jordan), with a rotation speed of 150 rpm, was used in preparing the solutions. The temperature was kept at 25°C unless otherwise is stated. A calibration curve was prepared and used to measure phenol concentration for the different experiments. The adsorption experiments were all conducted in a batch mode. Analysis of a blank sample was always conducted prior to testing solution samples. The effect of some parameters such as adsorbent dosage (g), pH of the solution, initial phenol concentration, temperature and contact time on the adsorption of phenol into the surface of Eucalyptus leaves were investigated.

2.1. Adsorption isotherms and kinetic tests

Known concentration of phenol solutions were placed in 100 mL Erlenmeyer flasks, adsorbent was accurately weighed and added to each flask. The flasks, containing the phenol solution and adsorbent, were placed on the shaker for a specified time and speed to carry out the adsorption process. After the specified time has passed, adsorbent was separated, and the solution was tested for the residual phenol using a spectrophotometer. To find the optimum adsorption capacity of the Eucalyptus leaves, the experiment was repeated for different initial phenol concentration, adsorbent dosage, pH, temperature, and contact time. Removal percentage and the phenol uptake or the adsorption capacity (q, mg/g) was calculated using the following equations:

\[ q = \left( C_0 - C_t \right) \frac{V}{m} \]  

(1)
while

\[
\text{Percentage(\%)} = \left(1 - \frac{C_t}{C_0}\right) \times 100
\]  

(2)

where \(V\) is the volume of solution in L; \(m\) is the mass of adsorbent (g); \(C_0\), \(C_t\), and \(C_e\) are phenol initial concentration, phenol concentration at time \(t\), and phenol concentration at equilibrium in mg/L, respectively. At equilibrium, adsorption capacity \((q_e)\) and equilibrium concentration of phenol \((C_e)\) is used in Eq. (1) [23].

3. Results and discussions

3.1. Effect of adsorbent mass

Effects of the amount of adsorbent (Eucalyptus leaves) on the phenol removal from water are illustrated in Fig. 2. The only parameter that was varied, in this experiment, is the mass of adsorbent in grams (g) while other parameters were kept the same throughout the experiment time; initial phenol concentration of 100 mg/L, neutral pH of 7, a temperature of 25°C and 100 mL of the solution. Evidently, increasing the amount of adsorbent, from 0.05 to 0.2 g, resulted in a gradual increase in the phenol percentage removal; nevertheless, it remained almost constant beyond this value. These findings are not unusual and in line with a previously done work. This behavior is attributed to the availability of more adsorption sites as a result of increasing the adsorbent mass dosage while using the same solute concentration [24,25].

3.2. Effect of pH

Effect of pH on the adsorption of phenol using the ground Eucalyptus leaves is depicted in Fig. 3. Phenol uptake by the adsorbent (mg/g) was calculated at different pH values while keeping the phenol solution concentration at 200 mg/L and using a 0.2 g of adsorbent. The original pH of the solution, without adjustment, was 6.5. Fig. 3 shows a slight increase in the phenol removal uptake with decreasing the acidity (increasing the pH value) until it reached 7, which is the point at which the solution became neutral. Beyond a pH value of 7, the phenol removal has decreased with increasing the pH value, or inversely proportional. Therefore, it can be noticed that the adsorption is favored with a neutral to near neutral acidity (pH 6–7) solutions. In the neutral medium, phenol exits in the molecular form while in the basic medium it exits in the ionic state since the pKa of phenol is 9.89 at 298 K. As a result, the adsorption affinity turns into lower values in the basic solution [26].

3.3. Effect of contact time

Fig. 4 illustrates effects of the contact time on the phenol uptake using the Eucalyptus leaves for three different phenol initial concentrations (100, 200 and 400 mg/L). The temperature and pH value were both held constant at 25°C and 7, respectively. The phenol uptake (mg/g) exhibited high initial rate of increase for up to about 50 min of adsorption time, beyond that it kept rising but at a slower rate up to an adsorption time of about 180 min then stayed flat for the rest of the experiment time (220 min). The drop in the uptake rate is due to the continuous decrease in the concentration difference that resulted in lower mass transfer driving force. The behavior was identical for the three
phenol initial concentrations, nevertheless higher uptake and uptake rate was observed for the larger phenol initial concentration as it was increased from 100 to 400 mg/L. increasing the uptake with increasing the initial phenol concentration reflects an increase in the mass transfer driving force, which is proportional with the concentration difference between the solution and that on the solid surface of the ground leaves. The maximum phenol removal was observed for 3 h after starting the experiment, which was considered the equilibrium time for the adsorption process within the specified experimental conditions utilized.

3.4. Adsorption isotherms

To optimize the use of a certain adsorbent, the batch adsorption results were fitted using adsorption isotherm models. Knowing the isotherm that best fits the data helps in the determination of adsorbent capacity, consumption, and bonding of solutes with the adsorbent. The well-known isotherms that were used in this study are the multi-layer Freundlich model and the single-layer Langmuir model.

The linearized Langmuir model is given by:

$$\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}}k_L C_e}$$

While the linearized Freundlich model is given by:

$$\ln q_e = \ln(k_f) + \frac{1}{n} \ln(C_e)$$

where $q_e$ is the uptake capacity or the adsorption uptake at equilibrium (mg/L), $q_{\text{max}}$ is the uptake capacity or the maximum adsorption uptake in mg/g, $k_L$ is the Langmuir adsorption constant (L/mg), $1/n$ is the exponent of non-linearity, and $k_f$ is the Freundlich adsorption constant [27,28].

The phenol uptake by the adsorbent gradually increased with time and no changes were observed after 3 h as given in Fig. 4. Higher number of available vacant sites on the adsorbent surface for the early time could explain this result. The equilibrium time was taken as 3 h for further analysis at equilibrium. Adsorption data were fitted using the Langmuir and Freundlich isotherms. Fig. 5 depicts a plot of $1/q_e$ vs. $1/C_e$ and is representing Langmuir model. The application of Freundlich model is illustrated by plotting $\ln(q_e)$ vs. $\ln(C_e)$ as presented in Fig. 6. Higher number of available vacant sites on the adsorbent surface for the early time could explain this result. The equilibrium time was taken as 3 h for further analysis at equilibrium. Adsorption data were fitted using the Langmuir and Freundlich isotherms. Fig. 5 depicts a plot of $1/q_e$ vs. $1/C_e$ and is representing Langmuir model. The application of Freundlich model is illustrated by plotting $\ln(q_e)$ vs. $\ln(C_e)$ as presented in Fig. 6. Although Langmuir isotherm exhibited higher correlation coefficient ($R^2 > 0.99$) than Freundlich ($R^2 > 0.96$), both isotherms can be considered to provide excellent fitting for the adsorption data and this was clearly demonstrated by the high values of the correlation coefficients. Fitting parameters of both models are summarized in Table 1. Langmuir isotherm represents monolayer adsorption with no lateral interaction between adsorbed molecules. On the other hand, the multi-layer heterogeneous adsorption due to the diversity of adsorption sites or the diverse nature of the adsorbent, free, or hydrolyzed species is proposed by the Freundlich isotherm. Therefore, the excellent fitting presented by both isotherms indicates that mono and multi-layer adsorption mechanisms were both taking place.

3.5. Effect of temperature

To investigate effect of temperature on the adsorption of phenol, two-temperature levels 25°C and 50°C were utilized; results are presented in Figs. 5 and 6. It can be seen that the removal of phenol by the adsorbent was higher for the lower temperature than that for the higher temperature. Therefore, the phenol uptake was inversely proportional with temperature. The adsorption capacity constants given by $K_f$ and $K_L$ values, listed in Table 1, decreased with temperature, which indicates the exothermic nature of the adsorption process. The value of $n$ in Table 1 is greater than 1 suggesting S-type adsorption [29]. Based on the obtained parameters from the different adsorption isotherms, Table 1, and using the equation $\ln K_f = \frac{-\Delta H}{RT} + A$, where $R = 8.314$ J/mol K, and $T$ is the temperature in Kelvin (K), the calculated value of the heat of reaction ($-\Delta H$) was 2.4 kJ/mol. The negative value of the heat of reaction is
another indication that the adsorption process is exothermic and spontaneous. Also, the $R_L$ is 0.1 from $R_L = 1/(1 + K_L \cdot C_0)$, which means a favorable adsorption process [2,17,28].

3.6. Kinetics of adsorption

To analyze kinetics of the adsorption process, the following correlations were used:

$$\log \left( \frac{1 - q_t}{q_e} \right) = -\frac{K_1}{2.303} t$$

(5)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e}$$

(6)

$$q_t = k_p t^{0.5} - C$$

(7)

where Eq. (5) is the pseudo-first order kinetics model with a constant $K_1$, and Eq. (6) is the pseudo-second order kinetics model with a constant $K_2$. Eq. (7) is the modified intra-diffusion model with correlation constants $k_p$ and $C$ [30]. Fitting the adsorption results using Eqs. (5)–(7) at different initial concentrations of phenol is illustrated in Figs. 7–9, respectively. The fitting parameters for the pseudo-first order and the pseudo-second order kinetics are summarized in Table 2. It can be seen that both models did fit the adsorption data perfectly based on the high values of the correlation coefficients ($R^2$). However, the calculated values of the equilibrium adsorption uptake ($q_e$ [mg/g]) based on pseudo-second order kinetics have a relative error of 22%–27% compared with a relative error of 4%–10% provided by the pseudo-first order model. Consequently, based on the previous findings and the higher $R^2$, the pseudo-first order model presents better fitting for the data. This would suggest the dominance of the physical adsorption process [17,25]. These findings would support that the physical adsorption is favored over the chemical adsorption [27,28]. Also, from Table 2, it can be seen that the rate constant for the pseudo-first order kinetics is almost independent of the initial phenol concentration while the pseudo-second order constant is decreasing with increasing initial phenol concentration. These results are consistent with previous works [17,22,30].

To get on more perception of the adsorption mechanism, fitting of the adsorption results to the modified intra-diffusion model was conducted and the outcomes are presented in Fig. 9 parts a and b in addition to Table 3. As it can be seen in Fig. 9, the intra-diffusion model provided excellent fitting for the data obtained with a correlation coefficient over 0.92 with relative error values between 9.1% and 13.8% for the three initial phenol concentrations. Part b of Fig. 9 exhibits more insight into the mechanism of adsorption where a three-step adsorption process is obtained. The early step is a fast one representing solute adsorption on the vacant-surface adsorbate sites due to electrostatic forces, the second step is a slower one related to intra-particle diffusion, and the last one is the equilibrium step where most of the sites in the adsorbent are occupied by the solute and the adsorption process stops [30].

The results obtained demonstrate the capacity of the adsorbent prepared from *Eucalyptus* leaves to efficiently treat wastewater containing phenol. Table 4 lists different adsorbents found in the literature to remove phenol from wastewater carried out at different experimental conditions. Most of the work that resulted in high removal efficiency of phenol relied on converting the available adsorbent into activated carbon or by direct burning of the adsorbent. For example, when oak wood is converted to activated carbon, 66.0 mg/g of phenol was attained at equilibrium starting with 10 mg/L phenol. Also activated carbon prepared from coconut husk could remove 95% of the 25 mg/L phenol in water. Other adsorbents prepared from other materials such as tendu leaf, *Aspergillus niger*, *Luffa cylindrica* fibers offered 48%–98%, 66% and 85% removal, respectively. Another adsorbent prepared from porous acrylic ester polymer resulted in 35.0 mg/g phenol uptake. In this
work, the removal efficiencies ranged from 94.0% to 59.0% for 50–400 mg/L initial phenol concentration with phenol uptake at equilibrium reaching 45.0–118.0 mg/L (Table 4). The results are promising for this available, eco-friendly, low-cost adsorbent compared with other adsorbent.

4. Conclusions

The application of the available local Jordanian Eucalyptus leaves as an adsorbent for the removal of phenol from wastewater was investigated at the selected experimental conditions for the first time. The achieved results document the ability of the leaves, ground and treated, to remove phenol from water effectively with good adsorption capacity in a practical method at a reasonable time. The adsorption of phenol into the surface of Eucalyptus leaves, in the range of the batch experimental conditions utilized, indicated that the phenol removal percentage was directly proportional with the initial phenol concentration, adsorbent concentration and contact time; whereas it was inversely proportional to the temperature. Equilibrium was reached after 3 h. The adsorption process was spontaneous and exothermic, which was proved by the negative heat of reaction obtained. The optimum phenol uptake

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**Table 1**

Adsorption isotherm parameters for phenol

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_m ) (mg/g)</td>
<td>( K_L ) (L/g)</td>
</tr>
<tr>
<td>25</td>
<td>100.00</td>
<td>0.1044</td>
</tr>
<tr>
<td>50</td>
<td>89.53</td>
<td>0.0559</td>
</tr>
<tr>
<td>( \Delta H ) (kJ/mol)</td>
<td>-2.4</td>
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</table>

**Table 2**

Adsorption kinetic parameters from the pseudo-first order and the pseudo-second order fittings

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>( q_e ) (mg/g) experimental</th>
<th>Pseudo-first order kinetics</th>
<th>Pseudo-second order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_1 ) (min(^{-1}) )</td>
<td>( q_e ) (mg/g) calculated</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>100</td>
<td>45.0</td>
<td>0.024</td>
<td>41.3</td>
</tr>
<tr>
<td>200</td>
<td>77.0</td>
<td>0.020</td>
<td>69.4</td>
</tr>
<tr>
<td>400</td>
<td>118.0</td>
<td>0.031</td>
<td>123.4</td>
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</table>

**Table 3**

Adsorption kinetic parameters from the modified intra diffusion model

<table>
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<th>Initial concentration (mg/L)</th>
<th>( q_e ) (mg/g) experimental</th>
<th>Pseudo-first order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_1 ) (mg/g min(^{-1}) )</td>
<td>( % ) Error in ( q_e )</td>
</tr>
<tr>
<td>100</td>
<td>45.0</td>
<td>3.75</td>
</tr>
<tr>
<td>200</td>
<td>77.0</td>
<td>6.40</td>
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<tr>
<td>400</td>
<td>118.0</td>
<td>10.08</td>
</tr>
</tbody>
</table>
was achieved at a pH value between 6 and 7 beyond which (basic medium) did decrease. For phenol initial concentrations of 100, 200 and 400 mg/L, the corresponding uptake was 45, 77 and 118 mg/L, respectively. Langmuir and Freundlich isotherms fitted the equilibrium adsorption results very well with $R^2$ value greater than 0.95 revealing a mono- and multi-layer adsorption. The adsorption process was spontaneous and exothermic, which was proved by the negative heat of reaction obtained. The pseudo-first order kinetics provided the best exemplification for the adsorption kinetics. The modified intra-diffusion showed a three-step adsorption process. The results are promising and pave the way for more research using this low cost, available, bio-friendly adsorbent.

References


