Phenol Adsorption from Aqueous Solutions onto Activated Carbon Produced from Iraqi Date-Stones.

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date-stone.

ABSTRACT

This study is conducted to synthesize an activated carbon from date-stones using different concentration (20%,35%,50%) of phosphoric acid as activater. The carbon was soaked for 72 hours followed by carbonization at (500°C) for two hours. Specific surface area and pH were measured. The adsorption of phenol at different temperatures (283K, 293K, 313K, 333K) from aqueous solutions onto activated carbon was investigated. The determination of phenol concentration at equilibrium solution was measured using U.V. spectrophotometer with an absorbance wavelength of (211nm). The activated carbon exhibited high ability to adsorbe phenol from aqueous solutions. The maximum adsorption rates were 98.76%, 98.9% and 97.5% at an initial concentration of (240 mg/l) of phenol and at 333K for activated carbon, (20%,35% and 50%) respectively. Adsorption isotherm was studied using Langmuir and Freundlich isotherm models. The characteristic parameters for each isotherm and related correlation coefficient have been determined. The results showed that the adsorption process of the synthetic activated carbon fits very well with the Freundlich isotherm model and in a lesser degree with Langmuir isotherm model. Thermodynamic parameters such as ΔG°, ΔH° and ΔS° have also been evaluated and it has been found that the sorption process was feasible, spontaneous and endothermic.

Introduction

Phenols at low concentration are considered as priority pollutants, since they are harmful for humans and animals. However, phenols might be classified as hazardous pollutants, because of their high potential harm for human health (1-3). Phenols have high instant solubility in water which cause great bad effects on drinking water (4,5). Many techniques have been considered for removing phenols from aqueous solutions such as solvent extraction, precipitation, adsorption and ion-exchange (6-8).

Adsorption is a powerful and well established technique for treating industrial and domestic wastes (9,10). Adsorption onto the surface of activated carbon is the most widely used method in water treatment (11,12).

Organic materials that rich in carbon are used for the production of activated carbon, such as data-stones, rice huck, wood, cornstalk and peat (13).

The preparation of activated carbon with different pore sizes can be divided into two processes, physical or chemical activations. Physical activation uses oxidizing gases such as CO2, NO2 and O2. This activation normally takes place at temperatures between (700°C-800°C). In the chemical activation process, chemicals such as zinc salts or phosphoric acid are added to the carbon precursors at some intermediate temperatures (400°C -700°C) to produce the activated carbon (14,15).

In this study we had prepared activated carbon (AC) invented from date-stones by using a chemical activation agent with phosphoric acid as a vital activator element. The capacity of adsorption with activated carbon for phenol from aqueous solution was studied.

Methods

Materials.

Ortho phosphoric acid (%85), ethylene glycol monoethyl ether, anhydrous calcium chloride and phenol were purchased from BDH chemicals LTD, England.
Precursors used for the production of activated carbon (AC) was date_stone collected from Heet city in Al-Anbar-Iraq.

**Method of preparation**

**Preparation of Activated Carbon (AC).**

Samples of dried date-stone were washed thoroughly with distilled water and then dried again in oven at (383K). After cooling to room temperature, they were cut into small pieces with blender and soaked for (72h.) in various concentrations of phosphoric acid (20%, 35%, 50%). The treated stones were then carbonized at a temperature of (500°C) for (2h.), using muffle furnace.

The activated carbon (AC) was washed with bidistilled water. The sample was then dried at (383K) overnight and finally kept in disecators for subsequent use.

The weight of content is expressed as follows:

\[ \text{Total AC\%} = \frac{W1}{W2} \times 100 \]

Where:

- W1 = weight of sample (g)
- W2 = weight of AC (g)

**Measurements**

- **Determination of surface area.**
  
  The specific surface area was measured using ethylene glycol monoethyl ether method (EGME) (16).

- **pH measurements.**
  
  Determination of pH was performed by mixing (1g) of sample with (10 ml) distilled water, then measured by pH meter.

**Adsorption Equilibrium.**

The phenol stock solutions of concentration 1000 ppm was used to prepare different concentrations (40,80,120,160,200,240) ppm for adsorption isotherm.

An aqueous solution of phenol were added to activated carbon, shaking for (2h.) by shaker and stand for (24h.) until equilibrium reached at different temperatures (283 K, 293 K, 313 K, 333 K). The extract was then measured using U.V. spectrophotometer with wavelength of (211nm).

The quantity of adsorption was calculated by using the following equation:

\[ Qe = \frac{\text{Vsol}(\text{Co} - \text{Ce})}{M} \]

Where:

- Qe = quantity of adsorbate (mg/g)
- Vsol = Total volume of adsorbate solution (l)
- Co = Initial Concentration of adsorbate solution (mg/l)
- Ce = Concentration of adsorbate solution at equilibrium (mg/l)
- M = Weight of activated carbon (g).

While the Removal percentage was calculated by using the following equation:

\[ Qe\% = \left( \frac{\text{Co} - \text{Ce}}{\text{Co}} \right) \times 100 \]

Where:

- Qe% = Adsorption percentage.

**Results and discussion**

**Adsorption Isotherms**

Isotherm information is significant in order to advance an equation that correctly explains the results and could probably be used for design aims.

The carbon surface specialty and adsorption can affinity be identified by equilibrium studies, with enough information on the capacity of the adsorbent.

The Langmuir equation relates the solid phase adsorbate concentration (Qe) or uptake to the equilibrium liquid concentration (Ce) as follows:

\[ Qe = \frac{bC_e}{1 + aC_e} \]

Where a and b are the Langmuir constants, representing the maximum capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively (Table 1). This can be seen from figures (1 - 3).

The adsorption isotherms in figures (4 - 6) represent the Freundlich model with high correlation coefficient \( R^2 = 0.98 \).

The linear form of the Freundlich isotherm model is given by the following relation.

\[ \log Qe = \log K_f + \frac{1}{n} \log C_e \]

Where: Qe is the amount adsorbed of equilibrium (mg/mg), \( C_e \) is the equilibrium concentration of the adsorbate (mg/l).

\( K_f \) and \( 1/n \) are the Freundlich constants related to adsorption capacity and adsorption intensity respectively, of the sorbent (Table 1).

The values of \( K_f \) and \( 1/n \) can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of \( \log Qe \) versus \( \log C_e \).
This isotherm is usually used in special cases for heterogeneous surface by multilayer adsorption and the amount of adsorbate increases infinitely with increases in concentration, where it is characterized by the heterogeneous factor 1/n. The heterogeneous factor (n) was calculated and the estimated value ranged between (2.4 to 12.5). It is known that when the n value is greater than 1.0, the conditions are favorable to adsorption (17).

Thermodynamic Study

Thermodynamic parameters such as entropy (ΔS°), the free energy (ΔG°), and enthalpy (ΔH°) changes during adsorption can be evaluated from the following Equations (3, 4 and 5)

\[
K_c = \frac{C_A}{C_e} \text{ ..........3}
\]

\[
\Delta G^o = -RT \ln K_c K_c \text{ ..........4}
\]

\[
\ln K_c = \Delta S^o/R - \Delta H^o/RT \text{ ..........5}
\]

Where \(K_c\) is the equilibrium constant, \(C_e\) is the equilibrium concentration in solution (mg/l) and \(C_A\) is the solid-phase concentration at equilibrium (mg/l). \(\Delta G^o\), \(\Delta H^o\) and \(\Delta S^o\) are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. \(R\) is the gas constant (8.314J/mol/K) and \(T\) is the absolute temperature (K). The values of \(\Delta H^o\) and \(\Delta S^o\) were determined from the slope and the intercept of the plots of \(\ln K_c\) versus 1/T (figure7). The \(\Delta G^o\) values were calculated using Equation (4). The plots were used to compute the thermodynamic parameters (Table 2). The values of the enthalpy change (\(\Delta H^o\)) and the entropy change (\(\Delta S^o\)), in this work they were 83.3 J/mol and 16.462kJ/mol/K, respectively, for phenol concentration (160 mg/l). The negative \(\Delta H^o\) value indicates the exothermic nature of adsorption.

Surface Area:

Table (3) shows that the values of the surface area increased with the addition of phosphoric acid until 35%, and then decreased. The maximum values could be obtained at 35% of acid.

Conclusions:

1. The activated carbon prepared from date stones exhibits high adsorption abilities for phenol from their aqueous solution.
2. The adsorption process is exothermic.
3. The equilibrium sorption data fitted the Freundlich isotherm model better than the Langmuir model.
4. Activated carbon showed high adsorption capacities, and can be successfully used for the removal of phenol from waste water.

References:
Sci. Techno, 23:55


Fig 1: The linearized langmuir adsorption isotherm for phenol with date-stones activated carbon %20

Fig 2: The linearized langmuir adsorption isotherm for phenol with date-stones activated carbon %35.

Fig 3: The linearized langmuir adsorption isotherm for phenol with date-stones activated carbon %50.
Fig 4: The linearized freundlich adsorption isotherm for phenol with date-stones activated carbon %20

![Graph](image1)

Fig 5: The linearized freundlich adsorption isotherm for phenol with date-stones activated carbon %35.

![Graph](image2)

Fig 6: The linearized freundlich adsorption isotherm for phenol with date-stones activated carbon %50.

![Graph](image3)
Fig. 7: Relation shipe between ln kc and 1/t for date-stones activated carbon %20.

Fig. 8: Relation shipe between ln kc and 1/t for date-stones activated carbon %35.

Fig. 9: Relation shipe between ln kc and 1/t for date-stones activated carbon %50.
Table1: Parameters of freundlich and langmuir isotherm models.

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>Langmuir isotherm</th>
<th>Freundlich Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (mg/mg)</td>
<td>b (l/mg)</td>
</tr>
<tr>
<td>AC. With %20 phosphoric acid</td>
<td>-0.54</td>
<td>-1.05</td>
</tr>
<tr>
<td>AC. With %35 phosphoric acid</td>
<td>-0.33</td>
<td>-0.578</td>
</tr>
<tr>
<td>AC. With %50 phosphoric acid</td>
<td>-0.038</td>
<td>-0.171</td>
</tr>
</tbody>
</table>

Table2 Thermodynamic parameters for the adsorption of phenol onto date-stones activated carbon

<table>
<thead>
<tr>
<th>Initial phenol conc.(mg/l)</th>
<th>Activated carbon</th>
<th>ΔHº (kJ/mol)</th>
<th>ΔSº (J/mol/K)</th>
<th>....ΔGº (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>283K</td>
<td>293K</td>
<td>313K</td>
</tr>
<tr>
<td>160</td>
<td>20%</td>
<td>16.46</td>
<td>83.3</td>
<td>-7.97</td>
</tr>
<tr>
<td></td>
<td>35%</td>
<td>24.32</td>
<td>112.66</td>
<td>-3.63</td>
</tr>
<tr>
<td></td>
<td>50%</td>
<td>6.76</td>
<td>48.58</td>
<td>-7.16</td>
</tr>
</tbody>
</table>

Table3 Characteristics of activated carbon

<table>
<thead>
<tr>
<th>Phosphoric acid conc.(v/v)</th>
<th>Surface areas (m²/gm)</th>
<th>PH</th>
<th>C% (W/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>401.57</td>
<td>5.5</td>
<td>60.5</td>
</tr>
<tr>
<td>35%</td>
<td>1012.1</td>
<td>4.1</td>
<td>80.8</td>
</tr>
<tr>
<td>50%</td>
<td>335.45</td>
<td>3.0</td>
<td>70.8</td>
</tr>
</tbody>
</table>

Table4 Adsorption percentage of phenol onto activated carbon

<table>
<thead>
<tr>
<th>c₀ of phenol mg/l</th>
<th>AC with H₃PO₄ 20%</th>
<th>AC with H₃PO₄ 35%</th>
<th>AC with H₃PO₄ 50%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q, %</td>
<td>Q, %</td>
<td>Q, %</td>
</tr>
<tr>
<td>283K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>89.25</td>
<td>92.9</td>
<td>96.37</td>
</tr>
<tr>
<td>80</td>
<td>94.29</td>
<td>95.6</td>
<td>97.7</td>
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<tr>
<td>120</td>
<td>95.99</td>
<td>96.8</td>
<td>97.95</td>
</tr>
<tr>
<td>160</td>
<td>96.75</td>
<td>97.3</td>
<td>98.5</td>
</tr>
<tr>
<td>200</td>
<td>96.95</td>
<td>97.59</td>
<td>98.2</td>
</tr>
<tr>
<td>240</td>
<td>97.33</td>
<td>97.73</td>
<td>98.5</td>
</tr>
</tbody>
</table>

نتيجة الدراسة: 

تم في هذه الدراسة تحضير مادة الكربون المنشط من نوى التمر. استخدمت الطريقة الكيميائية التي يتم استخدامها في تحليل الفسفور ويتراكيز مختلفة كعامل نشط في مدة زمنية مدارها (72) ساعة لكل تركيز، اجريت بعد ذلك عملية التربينة بدرجة حرارة (500) درجة مئوية لمدة ساعتين. تم دراسة سعة الكربون المنشط على الامتصاص والتي تم اختبارها بمواد الفينول ودرجات حرارية متفاوتة (283, 293, 313، 333 درجة مئوية. تم قياس الامتصاصية لمحاولات توازن في الفينول قبل وبعد الامتصاص عند طول موجي (211) نانومتر. وكانت نسبة امتصاص الفينول (76, 98.9%) على سطح الكربون المنشط (20%, 35%, 50%) بالرغم من أن الكربون الكتبي الكتبي للفينول (240) ملم/المتر. وقعت درجة حرارة (333 درجة مئوية. تم استخدام معادلة لانكر وفريندشتل لحساب الامتصاص الإجمالي. وينت بنتائج تطابق أكبر مع معادلة فريندشتل. كما تم قياس القدة الحامضية والمطابقة السطحية للكربون المنشط. تم حساب الدوال الترموديناميكية مثل الانتروري والالتشامي ودالة كبس ونتائج ان التفاعل تلقائي ماس للحراة.

فيهمي عبد الرحمان

التفسير: 

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الخلاصة: