Removal of Polycyclic Aromatic Hydrocarbons from Water Utilizing Activated Carbons

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Abstract: Activated Carbon(AC), produced from agricultural wastes (corn cob), was utilized in the adsorption of (PAHs) compounds from wastewater. All lab experiments were applied at environmental conditions of atmospheric pressure and temperature of 24±2°C. The impact of adsorbent additive dose, initial PAHs concentration, contact time and pH were the main objectives of this work to know the adsorption efficiency. The obtained results showed that the impact of removal PAHs was achieved after two hours at pH seven with 0.5 g of AC / 500 ml. Increasing the concentration of the adsorbent leads to increase of the PAHs removal up to concentration of 0.5 g adsorbent/L and the adsorption became notably larger with increasing the contact time and initial PAHs concentrations. Another finding was that adsorption and equilibrium conditions well fitted by Freundlich adsorption isotherms (R²~0.9-0.99). The obtained data showed a big direct correlation between adsorption processes and the Freundlich model however Langmuir theory showed a weak association.

Key words: Adsorption • PAHs • Langmuir • Freundlich • Activated Carbon and Bio char

INTRODUCTION

PAHs created from the inadequate combustion of fossil fuels, burning of biomass and organic compound production [1]. Because of their lower solubility in water, low volatility and their slow biodegradability they're steady and extended inside the atmosphere [2]. Due to the hazard effects of PAHs the United States Environmental Protection Agency categorized [3]. The remediation of wastewater polluted with PAHs is currently performed by physico-chemical and biological treatments [4]. PAHs removal process generally needs much more time to digest pollutants to an acceptable level of PAHs [5].

Furthermore, PAHs are not efficiently removed by classical wastewater treatment processes such as sedimentation, coagulation, flocculation and filtration. Adsorption method is a process to remediate PAHs in a low cost and environmental protection manner [6-8].

Activated carbon produced from rice peel has higher adsorption efficiency than adsorbent made from other agricultural and industrial materials [5].

It is the most used adsorbent applying in removal of PAHs [9]. It is produced from several precursor substances such as shells and sewage sludge [10-12]. It is also synthesized in forms such as granules or powder according to its application. Practically, powder (PAC) and granular (GAC) activated carbons are the famous forms for PAHs adsorption [13, 14]. The best removal efficiency of naphthalene and phenanthren on activated carbon that is produced from rice agriculture wastes [15]. The PAHs adsorption efficiency on activated carbon depend on some important factors such as initial PAHs concentration, in water/wastewaters, contact time, material type and the adsorbent dose etc.

The main target of this work is to study the activated carbon usage for removal of eight types of PAHs from aqueous solution. United States Environmental Protection Agency (US- EPA) specified allowable limits for the sixteen PAHs according to their priority [16]. The exposure to high levels of pollutant mixtures containing PAHs results in symptoms such as nausea, eye irritation, vomiting and confusion [17]. Petroleum wastes contain several PAHs which can be
carcinogenic or threatens the coastal region through untreated sewage, oil spillage, oil transport, ballast water and industrial wastewaters [18].

The factors affecting the adsorption of PAHs on activated carbon as the impact of pH, time and the doses of activated carbons will be studied and isotherms adsorption models will be considered by applying the measurements on the Langmuir and Freundlich models.

**MATERIALS AND METHODS**

**Chemicals:** PAHs solutions of 250 mg/l containing eight compounds (Naphthalene, Fluoren, Anthracene, Pyren, indeo (1, 2, 3, c, d) pyren, Benz (a) pyren, dibenz (a, h) anthracene and Benz (a)anthracene) prepared by dilution with n-Hexane (HPLC grade) of corresponding PAHs solution purchased as certified standard from Aqua standard. All spikes used in this paper were prepared using Millis-Q water spiked with PAHs stock solutions. Other necessary materials, anhydrous sodium sulfate extra pure and glass wool were purchased from Fisher chemicals.

**Adsorbent:** Agricultural waste (corn cob) was collected from Egyptian farms. These waste materials were washed with deionized water and dried then crushed and grinded into small pieces then treated with phosphoric acid, ignited at 400°C finally it was washed until reached pH 7 and used as adsorbent. Physical properties of activated carbon were measured [19].

**PAHs Extraction method:** The concentrations of poly aromatic hydrocarbons in the solution before and after the adsorption experiment was determined by liquid-liquid extractions [20]. PAHs extracted with n-Hexane 3 times in a separating funnel before and after the treatment with AC. The organic phase containing the PAHs was separated and dried using Na$_2$SO$_4$ anhydrous. The final extract was prepared through concentration using the rotary evaporator apparatus to a volume of 5 ml and then to 1 ml under flow of clean nitrogen.

**Sample Analysis Using GC-FID:** PAHs concentrations were carried out using Agilent gas chromatography model 7980 with Flame Ionization Detector (FID). HP5 column (30 m x 0.25 mm i. d x 0.25 µm film thickness); Helium is the used gas at a flow rate of 1.6 mL/min. Injections were made in the split less mode at an injector temperature of 25°C. The FID working condition was: temperature 300°C Hydrogen flow (30 ml min$^{-1}$), Air flow (400 ml min$^{-1}$) and Make up N$_2$ (25 ml min$^{-1}$). The temperature program employed was initial oven temperature at 60°C (holding time 1 min) to 175°C at 6 °C min$^{-1}$ (holding time 4 min) to about 235 °C at 3 °C min$^{-1}$ and finally to 300 °C at 8 °C min$^{-1}$, keeping the final temperature constant for 5 min. 1µL injections of the final extracts were auto-injected into the GC system [21].

**Adsorption Studies:** Batch experiments were implemented by spiking known concentrations of standards solutions of PAHs in deionized water. The adsorption studies illustrated the effect of pH, time, activated carbon dose and the different concentrations of PAHs on the adsorption processes.

**Contact Time Effect Study:** The experiment was conducted to estimate the time required to reach equilibrium. In a conical flask 0.5 g of activated carbon added to 500 ml organic free water spiked with PAHs standard solution at concentration of 100 µg/L. The solutions stirred at 12 round per minute for 10, 30, 60, 120, 180 minutes at room temperature. PAHs residues in the solution extracted and analyzed using the previously mentioned procedure.

**pH Effect Study:** The PAHs adsorption on corn cob activated carbon was studied at pH 1.5, 3, 4, 5 and 7 to detect the optimum pH for the adsorption of these PAHs. In a conical flask 0.5 g of activated carbon added to 500 mL water which organic free spiked with PAHs standard solution at concentration of 100 µg/L. The PAHs solutions were adjusted to the needed pH using concentrated HNO$_3$ or NaOH then stirred at 12 round per minute for six hours in a rotation mixer (Heidolph Reax 20) at room temperature. The samples were then centrifuged (Medtronic BL-S) and the supernatant were separated by decantation, see section 2.3 and 2.4.

**Adsorbent Dose Effect Study:** The optimum adsorbent amount was studied on PAHs removal from aqueous solutions by adding different amounts of activated carbon from 0.1 to 1 g while keeping other conditions constant pH=7, temperature = 25 °C, initial concentrations of PAHs =100 µg/L for each PAHs individual and 2 h as contact time.
The efficiency of adsorption calculated before and after PAHs removal can be calculated from the following Equation (1):

\[ q_e = \frac{(C_0 - C_e)V}{W} \]  

(1)

where \( q_e \) is the adsorbed quantity in (µg/g); \( C_0 \) and \( C_e \) are the amount before and after adsorption experiment (µg/l); \( V(\text{ml}) \) volume of the solution and \( W(g) \) amount of the adsorbent. The relation between the adsorption capacities and the concentrations of PAHs were illustrated using the linear form of both Langmuir Freundlich adsorption isotherms equations.

**Effect of Initial Concentration of PAHs:** Different PAHs/activated carbon mass ratios were prepared in glass flasks to determine the adsorption capacity of the adsorbent material. These experiments were performed on solutions with PAHs individual concentrations of 5, 25, 50, 100, 150 and 200µg/l and a constant dose of activated carbon (0.5 g) at 2 hours contact time. The PAHs residues in the solutions were then extracted and analyzed using the same procedure as previously described.

**RESULTS AND DISCUSSIONS**

**Results of the Adsorbent Characterization Experiments**

**The X-ray Diffraction (XRD) Pattern of the Activated Carbon Prepared:** Figure 1 illustrates the X-ray diffraction profile of this activated carbon exhibits a sharp peak reveals hexagonal lattice structure at \( 2\theta = 40^\circ \) in spectrum. The peaks were matched using D8 Discover-Advanced X-ray Diffraction System.

**pH:** The adsorption of PAHs on corncob activated carbon studied at pH 1.5, 3, 4, 5 and 7 to specify the optimum value of pH for the adsorption of these PAHs. PAHs removed and calculated by comparing their different initial concentrations to their final concentrations in the solution after 2h.

Figure (2) shows that, the variation in pH has a different effect with each individual of the PAHs. Benz (a) pyrene, indo (1,2,3, c, d) pyrene and dibenz (a, h) anthracene were the least affected by this change. While the other PAHs (Naphthalene, Flourene, Pyrene, Anthracene and Benzo(a) anthracene) are moderately affected by change in pH values.

The limited effect of pH change is due to the properties of these chemical compounds, PAHs are chemically inert and their bond (\( \text{C=C} \)) give them the chemical stability. Furthermore, these compounds do not have ionized groups that can be influenced by the pH [22].

**Contact Time:** The optimum contact time was studied using 500 ml PAHs solution at different concentrations level of 100 µg/l with 0.5 g of activated carbon at pH=7 and applying different retention time range from 10 to 180 minutes.

The results presented in Figure (3) showed that the contact time improved the adsorption process of the studied PAHs until equilibrium state after two hours. This could be due to increases in PAHs loading. The force derived in mass transfer that occurred between solid-liquid phases led to high PAHs concentration on the surface of adsorbent. These results seem to be consistent with naphthalene adsorption on the activated carbon and the PAHs adsorption onto granular activated carbons [23].

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**Table 1: Characterization of the activated carbon**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of activation (°C )</td>
<td>400</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>700</td>
</tr>
<tr>
<td>Micro pore volume (cm³/g)</td>
<td>0.011</td>
</tr>
<tr>
<td>Iodine number (mg/g)</td>
<td>632</td>
</tr>
</tbody>
</table>

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Fig. 1: X-Ray Analysis of Corncob Activated Carbon
Fig. 2: Effect of pH on the removal of PAHs

Fig. 3: Effect of contact time on the removal of PAHs

Fig. 4: Effect of activated Carbon Dose on the removal of PAHs

**Activated Carbon Dose:** An improvement in amount of adsorbent should raise the certain number of active sites and could lead to increase in the adsorption rate. Figure (4) shows that, PAHs removal increase ascendingly with the increase of adsorbent dosage to reach 0.5g which is the optimum dose value of activated carbon. For doses higher than 0.5 g no significant effect on PAHs adsorption rate. Therefore, the optimum dose of adsorbent was around 0.5g/500 ml this also consistent with other studies [24].
Initial Concentrations of PAHs: Different initial concentrations of PAHs were tested to be adsorbed on the same amount of activated carbon at a constant contact time and pH. The results showed that, the increase in initial concentration of PAHs leads to decrease in the percentage binding as shown in Figure (5). These observations can be explained by the fact that at low PAHs concentrations, the ratio of adsorptive surface area is high and thus, there is a greater chance for PAHs removal. When PAHs concentration increase, the adsorptive sites become more quickly saturated since the amount of adsorbent remains constant so at low initial PAHs concentrations, the removal capacity is higher [5].

Adsorption Isotherm Models: The interactions between an organic adsorbate and the adsorbent can be assessed by Langmuir and Freundlich theory [25, 26]. Langmuir based on monolayer adsorption on active surface sites, while Freundlich depends on heterogeneous adsorption. However, to evaluate the linearity of the data the two isotherm models were applied. The Langmuir linear form equation;

\[
\frac{C_e}{q_e} = \frac{1}{bQ} + \frac{C_e}{Q}
\]  

where \( C_e \) (mg/l) is the equilibrium concentration of PAHs and \( q_e \) (mg/g) is the amount of PAHs adsorbed per unit weight of sorbent. \( Q \) and \( b \) are the Langmuir constants indicating adsorption capacity and energy of adsorption respectively. The values of various parameters obtained (Table 2). The favorability of adsorption process is confirmed by the value of separation factor \( R_L \) obtained which is given by equation;

\[
R_L = \frac{1}{1 + bC_o}
\]  

where \( C_o \) is the optimum initial PAHs concentrations (mg/l) and \( b \) is constant. The \( R_L \) values were found to be between 0 and 1 and indicated to adsorption favorability. The Freundlich sorption isotherm equation. Equation (4);

\[
\log q_e = \log K + \frac{1}{n} \log C_e
\]  

where \( q_e \) is the adsorbed solute amount (mg/g); \( C_e \) is the solute concentration (mg/l); \( K \) is the adsorption capacity and 1/n is the surface heterogeneity. After equilibrium the adsorption data for adsorption, Freundlich parameters (1/n and K) were obtained from straight lines by plotting \( \log q_e \) against \( \log C_e \)(Table 2). The adsorption of organic

Table 2: Values of Langmuir and Freundlich parameters

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Freundlich Statistical Parameter ( R^2 )</th>
<th>Langmuir Statistical Parameter ( R^2 )</th>
<th>( R_L ) (Separation Factor)</th>
<th>Langmuir Constants</th>
<th>Freundlich Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Q</td>
<td>B</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.985</td>
<td>0.972</td>
<td>0.004</td>
<td>27.4</td>
<td>5</td>
</tr>
<tr>
<td>Flourene</td>
<td>0.987</td>
<td>0.884</td>
<td>0.007</td>
<td>34.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.993</td>
<td>0.93</td>
<td>0.011</td>
<td>36.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.997</td>
<td>0.953</td>
<td>0.012</td>
<td>35</td>
<td>1.6</td>
</tr>
<tr>
<td>Benzo[a] anthracene</td>
<td>0.974</td>
<td>0.948</td>
<td>0.005</td>
<td>14.3</td>
<td>3.6</td>
</tr>
<tr>
<td>Benzo[a] pyrene</td>
<td>0.977</td>
<td>0.935</td>
<td>0.012</td>
<td>7.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Indo [1,2,3,c,d]pyrene</td>
<td>0.988</td>
<td>0.91</td>
<td>0.011</td>
<td>18.7</td>
<td>1.7</td>
</tr>
<tr>
<td>7,12Dimethylbenzo[a]anthracene</td>
<td>0.895</td>
<td>0.839</td>
<td>0.007</td>
<td>6.1</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Solutes are determined by various parameters that govern the relation between solute and adsorbent, such as Vander Waals, electrostatic forces, dipole-dipole interactions and weak intermolecular associations [27]. Since PAHs are nonpolar compounds, adsorption must be governed mainly by hydrophobic interactions [9].

Experimental results of adsorption equilibrium were obtained using Langmuir and Freundlich isotherm models. The linearity is shown in Figures 6 to 21. Linear regression analysis shows that PAHs adsorption followed by the Langmuir and then Freundlich isotherms. Freundlich with experimental data (R^2~0.90-0.99).

Several literatures were described the adsorption theories [28]. Langmuir and Freundlich models are most used models because of their simplicity and common uses [29, 30]. It is important to propose a suitable model that discuss the best isotherm models in the adsorption [23]. Based on the results, Freundlich isotherm models was the best with experimental data (R^2= 0.89 to 0.99). In Langmuir isotherm models, adsorption process and maximum adsorption have a constant slope  [31]. These results agreement with other studies for PAHs adsorption on activated carbon [15, 30].
Fig. 10: PAHs Langmuir adsorption model for Anthracene

Fig. 11: PAHs Freundlich adsorption model for Anthracene

Fig. 12: PAHs Langmuir adsorption model for Pyrene

Fig. 13: PAHs Freundlich adsorption model for Pyrene

Fig. 14: PAHs Langmuir adsorption model for Benzo(a)anthracene
Fig. 15: PAHs Freundlich adsorption model for Benzo(a) anthracene

Fig. 16: PAHs Langmuir adsorption model for Benzo(a) Pyrene

Fig. 17: PAHs Freundlich adsorption model for Benzo(a) Pyrene

Fig. 18: PAHs Langmuir adsorption model for Indo (1,2,3, c, d) pyrene

Fig. 19: PAHs Freundlich adsorption model for Indo (1,2,3, c, d) pyrene
Activated carbon, produced from agricultural wastes (corn cob), has succeeded in the removal of different concentrations of the eight individual PAHs (Naphthalene, Flourene, Anthracene, Pyrene, indeno (1,2,3, c, d) pyrene, Benzo(a) pyrene, dibenzo (a, h) anthracene and Benzo (a) anthracene) from aqueous solution. The experiment implemented in the lab scale to optimize factors affecting the adsorption processes.

Based on the results it was found that an increase in the contact time can improve the adsorption process till reaching equilibrium. The increases in initial concentration of PAHs decrease the percentage binding and the change in the solution acidity has a limited effect due to chemical stability of PAHs. It can be noted that, Freundlich isotherm models provided the best fit with experimental data ($R^2= 0.89$ to 0.99). This mean that adsorption process showed a strong correlation with Freundlich isotherm models. According to this study the optimum condition to achieve maximum adsorption efficiency is to use the ratio:(500ml / 0.5g) for PAHs solution to AC at neutral medium and shaking time for 2 hours.

REFERENCES


