Adsorption of Polycyclic Aromatic Hydrocarbons on Activated Carbons: Kinetic and Isotherm Curve Modeling

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Received October 16, 2013; Revised December 27, 2013; Accepted January 3, 2014

ABSTRACT

The modeling of kinetic and isotherm curves acquired in adsorption of polycyclic aromatic hydrocarbons (PAHs) as a model compound (phenanthrene) on activated carbons in the organic solvent. All the runs were carried out in a batch system at atmospheric pressure, process temperature of 24±2°C, and using the 100 ml phenanthrene in cyclohexane. This experimental work was mainly focused on the study of how the variables properties such as adsorbent dosage, the initial phenanthrene concentration, contact time and pH of cyclohexane solutions influence the kinetic and isotherm of the adsorption process. The results indicated that pH did not play a key role in the process of phenanthrene adsorption. The considerable adsorption (8.34 mg/g) was reached at pH 7, adsorbent dosage of 0.3 g/100 ml and agitation time of 11 h on activated carbons. The impact of adsorbent dose on phenanthrene concentration was not important after 0.3 g/100 ml. The results also showed that adsorption capacity became notably greater with an increase in contact time and initial phenanthrene concentration. Another important finding was that adsorption processes and equilibrium data well fitted by pseudo-second-order kinetic (R\(^2\)=0.99) and Freundlich adsorption models (R\(^2\)=0.99). It can be concluded that there was a significant positive correlation between adsorption processes and the Freundlich isotherm model but Langmuir theory showed only a weak association.

Keywords: Phenanthrene, Activated Carbons, Adsorption, Isotherm, Langmuir & Freundlich Theory, Kinetic Models

INTRODUCTION

Polycyclic aromatic hydrocarbon compounds (PAHs) can be defined as complex organic chemicals which are widely distributed in the ambient environment and are one of the first anthropogenic atmospheric pollutants. The coal, wood, and peat burning, cooking, mobile sources are the dominant source of PAHs in urban environment [1]. According to the semi-volatile nature of these chemical components, PAHs can be transferred over long distances in the air and water. Some PAHs can cause certain damages in DNA. These compounds have mutagenic and carcinogenic activities. Regarding to this concept, PAHs recorded in the US-EPA priority pollutant list [2]. Activated carbons are one of the most widely used adsorbent for adsorbing any organic compound in the waste incinerators [3]. Using activated carbons in the
solid waste incinerator ducts can increase PAHs removal efficiencies by adsorption processes [4]. The past decades has seen the rapid development in using of activated carbons as key adsorbents for air pollution control [5]. Activated carbons would adsorb PAHs from different media such as oil [6-7], gas phase [4, 8], and water [9-10]. Many studies have focused on the effects of adsorption properties of activated carbons with regard to adsorption of PAHs. Non-polar adsorbents (i.e., lower oxygen content) have proven to be adsorbed PAHs more efficiently (2). Most studies were carried out using activated carbons as an adsorbent for organic compounds especially in the environmental remediation and metal contaminants [3]. However, far too little attention has been paid to other benefits of activated carbons such as low energy consumption, recoverability, reusability, and widespread availability [3]. Recently, researchers have shown a dramatic change in porous structure and functional groups that improved the adsorption properties of the activated carbons [11].

Phenanthrene (Phe) was selected as a representative compound of PAHs in the present study because phenanthrene is one of the 16 US EPA priority PAHs and has high concentration in crude oil [2]. The objectives of this research were to investigate the kinetics and adsorption isotherms modeling of Phe at activated carbon beds in n-hexane solution. The research to date has tended to focus on treatment of phenanthrene in aqueous solutions but this study investigated the treatment of phenanthrene using activated carbons in organic solvents [12].

**Materials and Methods**

**Materials**

All chemicals used in the experiments obtained from Merck and Sigma Aldrich CO. Phenanthrene (Phe, \( \text{C}_{14}\text{H}_{10} \), purity > 98%, a three-ring PAH) has an average molecular weight of 178 g mol\(^{-1}\). Activated carbon (AC) was made from coconut shell chars (99.5% purity, particle size 6×70 mm and Darco granular 20/40 mesh).

**Chemicals and Experimental Procedure**

In all experiments, the volume of samples was 100 ml. All adsorption and kinetic models of phenanthrene was done in a batch system at 24±2°C using 500 ml Erlenmeyer flasks. Samples were mixed in magnetic stirrer with 150 rpm until equilibrium was reached. HCl or NaOH was added to adjust the pH of samples. Several variables were measured in the study including pH of n-hexane solutions (5, 7, 9, and 11), Phe concentrations (5, 10, 20, 30, and 40 ppm), contact time (2, 5, 8, 11, 14, and 17 h) and dosage of activated carbons (0.1, 0.2, 0.3, 0.4, and 0.5 g/100 ml). Samples were kept in the dark and adsorption studies were done within 20 minutes. In this study, initial and residual concentration of Phe was determined spectrophotometrically (Cam spec M501 Single Beam Scanning UV/Visible) at 270 nm wavelength of excitation light [13]. The amount of phenanthrene adsorbed on activated carbons was calculated using the following equation (1):

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

Where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of the Phe (mg/g) in organic solution, respectively; \( V \) is the volume of the solution (L), and \( M \) is the mass of the adsorbent (g) [14].
RESULTS

Effect of Agitation Time and Initial Concentration of Phe

The results of the effect of contact time and initial concentration of Phe on adsorption onto activated carbon (20/40 mesh) at pH 7 and adsorbent dose of 0.3 g per 100 ml have shown in Fig 1. The adsorption process was reached to equilibrium after 11 h. Furthermore, the adsorption of Phe rose when the initial Phe concentration increased.

Effect of Adsorbent Dosage

As shown in Fig 2, adsorbent dosage plays a key role in the adsorption rate. As expected, an increase in the adsorbent dose can improve the adsorption of Phe.

Effect of pH

It can be seen from Fig 3 that pH of n-hexane affected the adsorption capacity. The effect of pH on the adsorption rate of Phe onto activated carbons was determined. A series of experiments was conducted in the initial value of Phe 5, 10, 20, 30, and 40 µg/l, the adsorbent dosage of 0.3 g/100 ml and the pH range 3-11. All experiments were performed in constant time about 17 h [9, 15-17]. The maximum adsorption capacity was obtained at pH 7.

Adsorption Isotherm

To investigate the adsorption capacity of activated carbons, equilibrium data were obtained by adding a specified amount of adsorbent (0.3 g to 100 ml) to n-hexane solution in different initial Phe concentrations (5-40 ppm). To reach equilibrium, experiments were carried out at pH 7, 25°C, and magnetic stirrer with 150 rpm for 20 minutes. In this research, experimental results of adsorption equilibrium were obtained using Longmuir 1 & 2 and Freundlich isotherm models. The linear plots of isotherm models are shown in Fig 4. Linear regression analysis showed that Phe adsorption followed by the Langmuir and then Freundlich isotherm models. Freundlich isotherm models provided the best fit with experimental data ($R^2=0.99$). Table 1 shows isotherm constants for Phe adsorption onto activated carbon.
Effect of Agitation Time and Initial Concentration of Phe

Based on the results of the adsorption, an increase in contact time can improve the activated carbons adsorption. The adsorption rate was improved from 1.17 to 8.34 mg/g with an increase in concentration of Phe from 5 to 40 ppm. This could be due to increases in Phe surface loading. The driving force in mass transfer that occurred between solid-liquid phases can led to increases in amount of Phe concentration on the surface of the adsorbent. The first step in solution- solid diffusion model is to evaluate the intra-particle diffusion which is the last step of the PAHs extracting process. The particle resistance became less important and the solution film was controlled the mass transfer rates when the hydrophobicity of the compounds increased [9]. These results seems to be consistent with naphthalene adsorption on an activated carbons study [12] and the adsorption of poly aromatic hydrocarbons onto granular activated carbons and Macronet hyper-cross-linked polymers (MN200) [9]. This also accords with other studies which were done by other researchers [2-3, 14-17].

Effect of Adsorbent Dosage

An improvement in amount of adsorbent could raise the certain number of active sites and could lead to increase in the adsorption rate. Further increase in adsorbent dosage failed to have any significant effect on Phe adsorption rate onto activated carbons (Fig 3). Therefore, the optimum dose of adsorbent was around 0.3 g/100 ml. It is encouraging to compare this figure with that found by Rey-Salgueiro (2009) [15].

Effect of pH

A PH value of the aqueous solution is an important parameter in the adsorption rate of cautions and anions. Increased pH values of samples may lead to increases in the concentration of hydroxide ion in n-hexane solution.

### Table 1. Characteristics and isotherm constants for Phe adsorption on activated carbon

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Principle equation</th>
<th>Linear equation</th>
<th>Parameters</th>
<th>Ac</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>$q_e = K_f C_e^{1/n}$</td>
<td>$\log(q_e) = \log K_f + 1/n \log C_e$</td>
<td>$R^2$</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_f$</td>
<td>2.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n$</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>Langmuir 1</td>
<td>$q_e = \frac{q_m b C_e}{1 + b C_e}$</td>
<td>$\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b}$</td>
<td>$R^2$</td>
<td>0.977</td>
</tr>
<tr>
<td>Langmuir 2</td>
<td>$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b}$</td>
<td>$q_m$</td>
<td>21.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$</td>
<td>0.108</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.983</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$q_m$</td>
<td>16.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$</td>
<td>0.188</td>
<td></td>
</tr>
</tbody>
</table>

$q_e$: Adsorption capacity (mg/g AC); $C_e$: concentration in liquid phase (mg/l); $1/n$ and $k_f$: Freundlich equation constants; $q_m$: maximum saturation capacity at the isotherm temperature (mg/g); $b$: Langmuir constant [21]

### Phe Adsorption Kinetics

Adsorption kinetic studies were used to determine the adsorption efficiency and the type of adsorption mechanisms. In this research, Phe adsorption onto activated carbons in cyclohexane solution has been investigated using a simple mathematical expression containing pseudo-first and pseudo second order [12]. Specifications of the kinetic models are listed in Table 2. To evaluate the adsorption kinetic of Phe on activated carbons, experiments were performed in different initial Phe concentrations (5- 40 ppm), adsorbent dosage of 0.3 g/100 ml, pH 7, at 25°C and 2 and 17 h contact times. Based on results, pseudo-second order model represented the best fit with experimental data ($R^2 = 0.99$). The pseudo-second-order kinetic plots at various initial Phe concentrations are shown in Fig 5.

### DISCUSSION

#### Effect of Agitation Time and Initial Concentration of Phe

Based on the results of the adsorption, an increase in contact time can improve the activated carbons adsorption. The adsorption rate was improved from 1.17 to 8.34 mg/g with an increase in concentration of Phe from 5 to 40 ppm. This could be due to increases in Phe surface loading. The driving force in mass transfer that occurred between solid-liquid phases can led to increases in amount of Phe concentration on the surface of the adsorbent. The first step in solution-solid diffusion model is to evaluate the intra-particle diffusion which is the last step of the PAHs extracting process. The particle resistance became less important and the solution film was controlled the mass transfer rates when the hydrophobicity of the compounds increased [9]. These results seems to be consistent with naphthalene adsorption on an activated carbons study [12] and the adsorption of poly aromatic hydrocarbons onto granular activated carbons and Macronet hyper-cross-linked polymers (MN200) [9]. This also accords with other studies which were done by other researchers [2-3, 14-17].

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#### Effect of pH

A PH value of the aqueous solution is an important parameter in the adsorption rate of cautions and anions. Increased pH values of samples may lead to increases in the concentration of hydroxide ion in n-hexane solution.

### Table 2. Specifications of the kinetic models investigated in the study

<table>
<thead>
<tr>
<th>Kinetics model</th>
<th>Principle equation</th>
<th>Linear equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pseudo-first order model</td>
<td>$\frac{dq_1}{dt} = k_1 (q_e - q_1)$</td>
<td>$\log(1 - \frac{q_i}{q_e}) = -\frac{k_1}{2.303} t$</td>
</tr>
<tr>
<td>pseudo-second order model</td>
<td>$\frac{dq_2}{dt} = k_2 (q_e - q_1)^2$</td>
<td>$t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$</td>
</tr>
</tbody>
</table>

Parameters of pseudo-first-order, pseudo-second-order, Phe adsorption from cyclohexane solvent: under conditions $q_t = 0$ at $t = 0$, $q_t$ at $t = t$ gives, where $q_1$ and $q_t$ are the amount of solute adsorbed at equilibrium and time $t$ respectively, and $K_1$ is the pseudo-first order rate constant that could be obtained from lineal regression analysis $\log( q_e - q_t) = F(t)$. Where $K_2$ is the pseudo-second-order rate constant (kg g\(^{-1}\) min\(^{-1}\)). Note that $K_2$ and $q_e$ could be obtained from linear regression analysis $t/q_t = F(t)$ [30].

Published online: January 14, 2014
Compounds are greater in their ionized form. Thus, maximum adsorption occurred at pH 8 of organic solution and in the lowest presence of ionized forms [16]. This finding is in agreement with previous studies [18-19]. Reducing the pH values of samples can increase the adsorption rate of activated carbons because of the release of hydrogen ions. Hydrogen ions may improve the adsorption process by activating the carboxyl groups which presented on the surface of activated carbon. The amount of hydrogen ion that adsorbed onto activated carbons could reduce the free space of adsorbent [16].

**Adsorption Isotherm**

Several models in the literature were described the adsorption isotherms [20]. These models are preferred because of their simplicity and common uses. There are two and three parameter isothermal models. Langmiur and Freundlich models are most commonly used models [21]. When a perfectly homogeneous adsorption occurred in the adsorption process, correct Langmuir adsorption data can be yield. Freundlich isotherm model was used in the adsorption on heterogeneous surfaces. The Freundlich model in high and low concentration of samples is in agreement with Langmuir model. Langmuir and Freundlich isotherms can be graphically determined. It is necessary to propose a suitable model that describes the best isotherm models in the activated carbons adsorption [22]. Data were obtained from the isotherm studies applied for explaining the reaction between adsorbent and adsorbed Phe and optimizing the amount of adsorbent [23]. Based on the results, Freundlich isotherm models provided the best fit with experimental data ($R^2 = 0.99$). In Langmuir isotherm models, adsorption process and maximum adsorption capacity have a constant slope [24]. These results are in a good agreement with other studies carried out in Phe adsorption on activated carbons [2, 15, 17, 24-25].
Table 3. Parameters of the pseudo-second-order kinetic model at various initial Phe concentrations

<table>
<thead>
<tr>
<th>Phe Conc. (ppm)</th>
<th>R²</th>
<th>qₑ (exp)</th>
<th>qₑ (calc)</th>
<th>k₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.997</td>
<td>2.51</td>
<td>1.53</td>
<td>0.63</td>
</tr>
<tr>
<td>10</td>
<td>0.997</td>
<td>3.943</td>
<td>3.06</td>
<td>0.316</td>
</tr>
<tr>
<td>20</td>
<td>0.995</td>
<td>6.99</td>
<td>6.06</td>
<td>0.142</td>
</tr>
<tr>
<td>30</td>
<td>0.994</td>
<td>9.98</td>
<td>9.14</td>
<td>0.077</td>
</tr>
<tr>
<td>40</td>
<td>0.996</td>
<td>12.48</td>
<td>12.01</td>
<td>0.0715</td>
</tr>
</tbody>
</table>

**Phe Adsorption Kinetics**

The pseudo-first order equation and pseudo-second-order kinetic model are said to use for expressing chemical reactions in the adsorption process. The most widely used equation in activated carbons adsorption is pseudo-second-order [11]. In all various initial concentrations of Phe on activated carbons, pseudo-second order kinetic model showed better fitting. Therefore, Phe adsorption mechanism is predominantly managed by chemical bonding or chemisorptions. Plots of the pseudo-second-order kinetic model at different initial Phe concentrations are illustrated in Fig 5 and parameters of the model are presented in Table 3. These results are in a good agreement with other studies carried out in naphthalene adsorption on an activated carbon [12], sorption of poly aromatic hydrocarbons onto granular activated carbons [9], desorption studies of 2,4,6-trichlorophenol on oil palm [26], phenols on activated carbon fibers [14], modified coir pith [27], dolomite [28], and ZnCl₂ activated coir pith carbon [29].

**CONCLUSION**

In this study, Phe adsorptions on activated carbons in cyclohexane solution were examined. The effect of operating parameters such as initial Phe concentration, contact time, adsorbent dosage, and pH on Phe adsorption process were investigated. An increase in contact time and initial Phe concentration improved the adsorption capacity. Adsorption process reached to equilibrium after 17 h. pH did not play an important role in adsorption process of Phe but the maximum of Phe adsorption (8.34 mg/g) was obtained at pH 7, activated carbon dosage of 0.3 g/100 ml and agitation time of 11 h. The experimental results also showed that the adsorption process and equilibrium data well fitted by pseudo second-order kinetic models (R²=0.99) and Freundlich isotherm (R²=0.99). This means that adsorption process showed a strong correlation with Freundlich isotherm models. Langmuir theory showed a weak correlation with adsorption data. Langmuir equation supported the adsorption process in aqueous media as well as saturation isotherms. In organic media, activated carbons have high saturation capacity. So the Langmuir model could not explain the observed trends. Therefore, the Freundlich isotherm model is an empirical equation developed to overcome some limitations of the Langmuir theory. The heterogeneity of the adsorbent surface and intermolecular interactions led to better justifications with Freundlich isotherm model.

![Fig 5. Plots of the pseudo-second-order kinetics at various initial Phe concentrations: adsorbent dose 0.3 g/100 ml, pH 7, temperature 25 °C](image-url)
ACKNOWLEDGEMENTS

This project was financially supported by Tehran University of Medical Sciences. The authors gratefully appreciate them for this support. The authors announced no conflict of interest.

REFERENCES


