Research Article

Benzene Removal by Iron Oxide Nanoparticles Decorated Carbon Nanotubes

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Received 17 July 2015; Revised 22 November 2015; Accepted 24 November 2015

Academic Editor: Xie Quan

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In this paper, carbon nanotubes (CNTs) impregnated with iron oxide nanoparticles were employed for the removal of benzene from water. The adsorbents were characterized using scanning electron microscope, X-ray diffraction, BET surface area, and thermogravimetric analysis. Batch adsorption experiments were carried out to study the adsorptive removal of benzene and the effect of parameters such as pH, contact time, and adsorbent dosage. The maximum removal of benzene was 61% with iron oxide impregnated CNTs at an adsorbent dosage 100mg, shaking speed 200rpm, contact time 2 hours, initial concentration 1 ppm, and pH 6. However, raw CNTs showed only 53% removal under same experimental conditions. Pseudo-first-order kinetic model was found well to describe the obtained data on benzene removal from water. Initial concentration was varied from 1 to 200mg/L for isotherms study. Langmuir isotherm model was observed to best describe the adsorption data. The maximum adsorption capacities were 987.58mg/g and 517.27mg/g for iron oxide impregnated CNTs and raw CNTs, respectively. Experimental results revealed that impregnation with iron oxide nanoparticles significantly increased the removal efficiency of CNTs.

1. Introduction

Benzene is an aromatic compound which is natural part of petroleum fractions. It is widely used for many applications which include application as raw material for polymer and plastic industries and also as a solvent in paints industries [1–3]. Benzene is highly toxic and causes different diseases in humans such as cancer, central nervous system damage, and skin and eyes diseases [4]. Various methods have been reported for removal of this pollutant from water. Those methods include wet air oxidation [5], advanced oxidation process, photocatalytic degradation [6], and adsorption, which is considered as cheap and best practiced technique for removal of benzene [7].

Carbon nanotubes, since their discovery, by Iijima in 1991 [8], have shown a great potential in many areas especially in water treatment. CNTs attained great attention due to better electrical, chemical, and mechanical properties as compared to other adsorbents such as fly ash and activated carbon [9,10]. Carbon nanotubes are sp² hybridized graphitic carbon sheets, folded in the form of hollow cylinders. These materials contain localized π-electrons on their surface which make them better adsorbents for removal of contaminants as compared to conventional adsorbent, activated carbon [11,12].

Different adsorbents have been used for the removal of benzene, toluene, ethylbenzene, and xylene isomers (BTEX) from water. The most common materials reported are activated carbon [4], raw carbon nanotubes [13], and modified carbon nanotubes [14–16] for removal of BTEX. Recently, metal oxide impregnated CNTs have shown better adsorption capacity and removal efficiency as compared to raw CNTs and other adsorbents for different pollutants [17–22]. Novel carbon nanotube membranes are also appealing candidates for a number of applications in water treatment [23,24].

According to our knowledge, not even a single publication was found to study the removal of benzene using metal oxide impregnated CNTs. Based on this, objective
of this study was to prepare and characterize iron oxide nanoparticles impregnated multiwall carbon nanotubes and to demonstrate the utilization for adsorption of benzene from water.

2. Materials and Experimental Setup

2.1. Materials. Commercial multiwall carbon nanotubes were purchased from Chengdu Organic Chemicals Co. Ltd. (China) with purity of greater than 95%. Other chemicals which include iron nitrate, ethanol, benzene (99.7% purity), nitric acid (>69% purity), and sodium hydroxide were purchased from Sigma Aldrich.

2.1.1. CNTs Impregnation with Iron Oxide Nanoparticles. The carbon nanotubes purchased were 10–30 micrometers in length, 10–20 nanometers in outer diameters, and having specific surface area of >200 m$^2$/g. For impregnation of iron oxide nanoparticles on CNTs, 20 g of CNTs (90% of total weight of CNTs and metallic salt) was weighed and dissolved in sufficient amount of ethanol. CNTs dissolved in ethanol were ultrasonicated for 30 minutes, to deagglomerate and disperse CNTs in the solvent. 2 g of iron nitrate salt (10% of total weight of CNTs and metallic salt) was dissolved in sufficient amount of ethanol, mixed with CNTs, and sonicated further for 30 minutes. Sample was dried in oven at 80°C. After complete drying of ethanol, the sample was calcined in a furnace at 350°C for 4 hours.

2.2. Characterization of Adsorbents. The adsorbents were analyzed using various characterization techniques. Physical morphology and structure analysis was carried out using scanning electron microscope (SEM Model, TESCAN MIRA 3 FEG-SEM). Energy dispersive X-ray (TESCAN MIRA 3 FEG-SEM) was also performed to verify the presence of different elements in prepared adsorbents. The samples were coated with a Platinum layer of 5 nm thickness (Quorum sputter coater model: Q150R S). X-ray dispersive X-ray (XRD) spectroscopy was performed to confirm the presence of different elements in prepared adsorbents. The samples were dissolved in ethanol. CNTs dissolved in ethanol were ultrasonicated for 30 minutes, to deagglomerate and disperse CNTs in the solvent. 2 g of iron nitrate salt (10% of total weight of CNTs and metallic salt) was dissolved in sufficient amount of ethanol, mixed with CNTs, and sonicated further for 30 minutes. Sample was dried in oven at 80°C. After complete drying of ethanol, the sample was calcined in a furnace at 350°C for 4 hours.

2.3. Batch Adsorption. For batch adsorption experiments, stock solution of benzene with the concentration of 100 ppm was prepared and diluted to get 1 ppm concentration. Glass flasks containing adsorbents were filled completely with benzene solution and were mounted on mechanical shaker (Lab Companion Model: SK-600) for specific time at room temperature. After completion of provided contact time, samples were removed from shaker and filtered using Whatman Filter Paper number 1 of 11 μm pore size to collect sample for analysis of benzene concentration. To study the effect of pH on the adsorption of benzene, pH of the solution was varied from 5 to 8 by using 1 M solution of nitric acid and 1 M solution of sodium hydroxide.

The adsorption capacity of benzene on CNTs surface was calculated using

$$q = \frac{(C_0 - C)}{m} \times V,$$

where $q$ is adsorption capacity (mg/g), $C_0$ is initial concentration of benzene in sample (mg/L), $C$ is final concentration of benzene in sample at time $t$ (mg/L), $V$ is volume of sample (mL), and $m$ is amount of adsorbent (g).

Percentage removal was found using the following equation:

$$\text{Removal} (\%) = \frac{C_0 - C}{C_0} \times 100.$$  \hspace{1cm} (2)

In order to avoid any losses due to volatilization during experimentation, benzene solution was filled completely in flasks and no headspace was left. Control experiments were conducted without adding any adsorbent to check the adsorption of benzene on surface of glass flasks and loss due to volatilization.

Most widely used kinetics models for adsorption are pseudo-first-order model and pseudo-second-order model [25]. Pseudo-first-order model of Lagergren is provided by

$$\log (q_e - q) = \log (q_e) - \frac{k_1 t}{2.303},$$

where $q_e$ and $q$ indicate the amount of benzene (mg/g) adsorbed at equilibrium and various time “$t$,” respectively, and $k_1$ (min$^{-1}$) is the rate constant of this model. In order to determine the values of $k_1$ and $q_e$, linear plot of log$(q_e - q)$ and “$t$” was used [25, 26].

The linear form of pseudo second order is given as

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$

where $q_e$ and $q$ are the amount of benzene adsorbed (mg/g) on the surface of CNTs at equilibrium and various time “$t$,” respectively, $k_2$ (g/(mg min)) is the rate constant for pseudo-second-order kinetic model. The values of $q_e$ and $k_2$ can be determined from slope and intercept of linear plot of $t/q$ versus $t$ [16, 27].

In order to get more information for internal diffusion inside adsorbent, intraparticle diffusion model was also used. Linear form of intraparticle diffusion model is provided in

$$q_t = k_{id} t^{0.5} + C,$$

where $k_{id}$ is intraparticle diffusion rate constant with units as mg/g min$^{-0.5}$ and $C$ (mg/g) is intercept which can be calculated by plotting $q_t$ versus $t^{0.5}$.

Adsorption isotherms are most important in order to understand the adsorption mechanism and also to determine the amount of adsorbent needed to adsorb a specific
amount of adsorbate. For this purpose Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models were employed to fit the experimental data [28–30]. Representative equations of Langmuir and Freundlich models are provided as

\[ q_e = \frac{K_L q_m C_e}{1 + K_L C_e}, \]  
\[ q_e = K_F C_e^{1/n}, \]  

where \( q_e \) represents the concentration of adsorbate on the surface of adsorbent and \( C_e \) indicates the concentration of adsorbate in water when equilibrium was reached. \( q_m \) is the maximum adsorption capacity and \( K_L \) is the Langmuir adsorption equilibrium constant (L/mg). \( K_F \) is Freundlich constant related to adsorption capacity with units (mg/g) (L/mg)\(^{1/n}\) and "\( n \)" is Freundlich constant related to adsorption intensity of the adsorbents; it is dimensionless.

D-R model was used to have an idea about physical or chemical adsorption of benzene molecules with CNTs surface. Equation of D-R model is as follows:

\[ q_e = q_m e^{-B\varepsilon}. \]  

Here, \( B \) (moles\(^2\)/kJ\(^2\)) is related to mean free energy of adsorption and \( q_m \) (mg/g) is saturation capacity. \( \varepsilon \) is Polanyi potential and is calculated as

\[ \varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right), \]  

where \( R \) (kJ/mole/K) is the gas constant and \( T \) (K) is absolute temperature. Mean free energy of adsorption (\( E_a \)) for one mole of adsorbate, by moving from infinity to adsorption site, is calculated as follows:

\[ E_a = (2B)^{0.5}. \]  

In order to avoid the error occurring due to use of linearized form of models, nonlinear regression analysis was performed for all models using Mathematica 9.0.

2.4. Benzene Concentration Analysis. The concentration of benzene solution was determined using gas chromatograph mass spectrometer (GC 7890A and MS 5975C, Agilent Inc., USA). GC-MS headspace auto-multisampler was used for sample injection.

The capillary column (DB-1) was used with specification of 30 m length, 320 \( \mu \)m inner diameter (ID), and 1 \( \mu \)m column width. Split mode was used for sample injection with 50:1 and volume of sample injected was 1000 \( \mu \)L. The temperature of oven was 40°C and later raised to 180°C with the rate of 35°C per minute, injection inlet temperature was 200°C, and auxiliary temperature was 280°C, while syringe temperature used was 100°C.

3. Characterization of Raw and Impregnated CNTs

Figures 1(a) and 1(b) display the SEM images of low and high magnifications of raw carbon nanotubes. The diameters of the CNTs were varying from 10 to 20 nm with an average diameter of 14 nm, while the length of these carbon nanotubes was varying from 10 to 30 \( \mu \)m. This study was also supported by the characterization of doped CNTs with iron oxide nanoparticles using backscattering SEM in order to verify the presence of nanoparticles on the surfaces of the CNTs as shown in Figures 2(a) and 2(b). The backscattering images were taken for two different samples at 1 and 10 wt.% of \( \text{Fe}_2\text{O}_3 \) nanoparticles doped on CNTs. It was observed that there are many formations of white crystal structures of \( \text{Fe}_2\text{O}_3 \) nanoparticles with small sizes and irregular shapes. The distribution and agglomeration of \( \text{Fe}_2\text{O}_3 \) nanoparticles were also observed. At low concentration of \( \text{Fe}_2\text{O}_3 \) nanoparticles (1 wt.%), the particles spread widely on the surfaces of carbon nanotubes forming very small crystals particles with diameters varying from 1 to 5 nm, while at high concentration of \( \text{Fe}_2\text{O}_3 \) nanoparticles (10 wt.%) the particles were agglomerating forming big crystals nanoparticles with diameters varying from 1 to 15 nm.
Figure 2: Backscattering SEM images for (a) 1 wt.% and 10 wt.% of iron oxide nanoparticles impregnated on the surface of CNTs.

Figure 3: TGA curves for raw CNTs and iron oxide nanoparticles impregnated CNTs. Figure 3 demonstrates the thermogravimetric behavior of both raw and iron oxide nanoparticles impregnated CNTs. It can be observed that the raw CNTs are more stable and thermal degradation takes place at around 530°C. Impregnation of CNTs with iron oxide nanoparticles increased the destabilization in CNTs and degradation started at lower temperature, 450°C [31]. The reason behind this phenomenon may be due to high thermal conductivity of iron oxide nanoparticle heating rate in sample enhanced, hence leading to fast degradation of CNTs. The mass left over the pan after burning of raw CNTs represents the catalyst particles, which was found to be nickel as confirmed from EDX analysis. It is also observed that the residual mass was high (about 7%) for iron oxide impregnated CNTs and it represented the metal oxide nanoparticle impregnated on CNTs.

Figures 4 and 5 demonstrate the nitrogen adsorption desorption isotherms for both raw CNTs and iron oxide impregnated CNTs, respectively. Isotherm was found to be of type V, according to International Union of Pure

Figure 4: Nitrogen adsorption desorption isotherms for raw CNTs.

Figure 5: Nitrogen adsorption desorption isotherms for iron oxide impregnated CNTs.
4. Adsorption Experiments

Batch adsorption experiments were carried out to study the effect of contact time, sorbent dosage, and pH of the solution on the benzene sorption.

4.1. Effect of Contact Time. The effect of contact time on benzene adsorption was carried out by varying the time from 60 minutes to 240 minutes. Figure 7 reveals the effect of contact time on removal efficiency and adsorption capacity of raw CNTs and iron oxide nanoparticles impregnated CNTs. Maximum removal achieved was 51%, while maximum adsorption capacity was 1.14 mg/g with raw CNTs. By impregnating CNTs with iron oxide nanoparticles, removal efficiency and adsorption capacity both increased, maximum removal was 70%, and adsorption capacity enhanced to 1.54 mg/g. The enhancement in removal efficiency of impregnated CNTs was due to the increase in the surface area from 155 m²/g to 210 m²/g. The increase in surface area resulted in increase in the number of sorption sites on the surfaces of CNTs. It can also be observed that, by increasing the time, the adsorption capacity and percentage removal were increased for both raw and impregnated CNTs. This might be due to the attachment of more molecules on the available active π-π sorption sites after long contact time.

4.2. Effect of Adsorbent Dosage. The impact of adsorbent dosage on adsorption capacity and percentage removal was analyzed using different amount of adsorbents (25 to 100 mg). Figure 8 represents the effect of adsorbent dosage on removal efficiency and adsorption capacity of raw CNTs and CNTs impregnated with iron oxide nanoparticles, respectively. It was observed that, with increase in the adsorbent dosage, the adsorption efficiency has increased. This can be justified due to the availability of more active adsorption sites at higher adsorbent dosage [17, 26].
4.3. Effect of Solution pH. Figure 9 represents the pH effect on removal efficiency and adsorption capacity of iron oxide nanoparticles impregnated CNTs. pH of the solution was varied in the range of 5 to 8, which is a typical pH range for mostly industrial water. It was observed that the removal efficiency was almost constant in this pH range. Since benzene exists in the molecular form at whole range of pH, in this case dispersive interactions due to π-π bond interaction were dominant in the removal of benzene from water. This is also in agreement with the existing literature [4].

5. Adsorption Kinetics Analysis

Figure 10 represents the adsorption capacity of the adsorbent versus time, for the removal of benzene. It was observed that the adsorption capacity increases almost linearly with increase in time. This might be due to the attachment of more molecules on the available active π-π sorption sites after long contact time.

In order to further investigate the adsorption phenomena, kinetics studies with pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model were conducted. As shown in Figures 11, 12, and 13, three kinetics models were employed to fit the experimental data of benzene adsorption from water. Kinetics parameters and determination coefficients ($R^2$) of these models are provided in Table 1. It is evident from the values of determination coefficient ($R^2$) that all models have good fit with experimental data. Pseudo-first-order model was found to best describe the adsorption of benzene on both raw and impregnated CNTs [16]. Besides, intraparticle diffusion model was also the best to describe the adsorption kinetics but plot of $q_t$ versus $t^{0.5}$ does not pass through the origin so it is not rate limiting step. Generally adsorption phenomenon occurs in three steps. In the first step, external diffusion occurs in which adsorbate molecule moves from bulk solution to the external surface of the adsorbent; in the second step, internal diffusion occurs in which adsorbate molecules move deep inside adsorbent.
Table 1: Kinetic parameters for benzene adsorbed on iron oxide nanoparticles impregnated CNTs.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw CNTs</td>
<td>CNTs – iron oxide</td>
</tr>
<tr>
<td>Experimental</td>
<td>$C_0$ (mg/L)</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>$q_{e, experimental}$</td>
<td>1.14</td>
</tr>
<tr>
<td>Pseudo first order</td>
<td>$k_1$ (min$^{-1}$)</td>
<td>0.0048</td>
</tr>
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<td></td>
<td>$q_{e, calculated}$</td>
<td>2.1732</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9107</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td>$k_2$ (g mg$^{-1}$ min$^{-1}$)</td>
<td>2.854E–07</td>
</tr>
<tr>
<td></td>
<td>$q_{e, calculated}$</td>
<td>90.90</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.8635</td>
</tr>
<tr>
<td>Intraparticle diffusion model</td>
<td>$k_{id}$ (g mg$^{-1}$ min$^{-0.5}$)</td>
<td>0.132</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>−0.9212</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9725</td>
</tr>
</tbody>
</table>

Figure 12: Adsorption kinetics pseudo-second-order model fitting with experimental data.

Figure 13: Adsorption kinetics intraparticle diffusion model fitting with experimental data.

to active adsorption site; and in the last step, adsorbate is adsorbed on adsorption site, which is fast and negligible step [16].

6. Adsorption Isotherms

Figures 14, 15, and 16 represent the fitting of adsorption data with adsorption isotherm models for both raw and impregnated CNTs. Theoretical results of parameters and determination coefficient values are provided in Table 2. It can be seen from values of $R^2$ in Table 2 that all models fitted well with adsorption data but Langmuir model was best to represent the data. Values of dimensionless equilibrium parameter for Langmuir isotherm ($R^L$) were found to be as 0.969 and 0.986 for raw CNTs and iron oxide impregnated CNTs, which indicates the favorable adsorption of benzene on these adsorbents. Adsorption capacity was higher for impregnated CNTs as compared to raw CNTs which may be due to more dispersion and surface area available for adsorption of benzene molecules.

D-R model was used to predict the energy of adsorption. Value of $E_a$ can provide information about adsorption mechanism. When 1 mole of a material is transferred to adsorption site, value between 1 and 8 kJ/mole indicates physical adsorption, value between 8 and 16 kJ/mole shows adsorption due to ion exchange, and the value between 20 and 40 kJ/mole provides indication of chemisorption [29, 30]. From Table 2, values of adsorption energy are 0.027 kJ/mole for raw CNTs and 0.021 kJ/mole for iron oxide impregnated CNTs, indicating physical adsorption of benzene.

Main forces mainly involved in adsorption of organics on CNTs surface are hydrophobic effects, $\pi-\pi$ stacking, hydrogen covalent interactions, and Vander Waals forces [37,
Table 2: Isotherm models parameters for benzene adsorbed on raw and iron oxide nanoparticles impregnated CNTs (pH: 6, temperature: 298 K, and initial concentration: 1–200 mg/L).

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Raw CNTs</th>
<th>Adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K (L/mg)</td>
<td>0.0031</td>
</tr>
<tr>
<td>Langmuir</td>
<td>q (mg/g)</td>
<td>517.27</td>
<td>987.58</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.992</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>R L</td>
<td>0.969</td>
<td>0.986</td>
</tr>
<tr>
<td>Freundlich</td>
<td>K (L/mg)</td>
<td>3.027</td>
<td>1.926</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>1.264</td>
<td>1.119</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.989</td>
<td>0.993</td>
</tr>
<tr>
<td>Dubinin-Radushkevich (D-R)</td>
<td>q (mg/g)</td>
<td>207.21</td>
<td>248.45</td>
</tr>
<tr>
<td></td>
<td>B (mole²/kJ²)</td>
<td>671.45</td>
<td>1136.23</td>
</tr>
<tr>
<td></td>
<td>E a (kJ/mole)</td>
<td>0.027</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.993</td>
<td>0.994</td>
</tr>
</tbody>
</table>

Figure 14: Langmuir adsorption isotherm model fitting with benzene adsorption on raw CNTs and iron oxide impregnated CNTs.

Figure 15: Freundlich adsorption isotherm model fitting with benzene adsorption on raw CNTs and iron oxide impregnated CNTs.

Figure 16: Dubinin-Radushkevich adsorption isotherm model fitting with benzene adsorption on raw CNTs and iron oxide impregnated CNTs.

So, here, two main effects are Vander Waals forces and π-π interaction between π-electrons of CNTs and benzene ring.

7. Conclusion

Raw and iron oxide nanoparticles impregnated CNTs were used for the adsorptive removal of benzene from water. The maximum removal by raw and iron oxide impregnated CNTs under these experimental conditions was 53 and 61%, respectively. From kinetic study, it was found that pseudo-first-order model best fits the experimental data for adsorption of benzene from water. Initial concentration of benzene was varied from 1 to 200 mg/L. Langmuir isotherm model was found to give better fit with adsorption data. Iron oxide impregnated CNTs showed higher adsorption capacity of 987.58 mg/g than raw CNTs, which showed adsorption capacity of 517.27 mg/g, under the same experimental conditions. D-R model provided information about physical adsorption
of benzene on CNTs. Values of adsorption energy calculated using D-R model were 0.027 kJ/mole for raw CNTs and 0.021 kJ/mole for iron oxide impregnated CNTs, indicating physical adsorption of benzene.

Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment
The authors would like to acknowledge the support provided by the Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Saudi Arabia.

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