Removal of Phenol from Water Different Types of Carbon – A Comparative Analysis

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Abstract

Toxic organic substances are considered among the pollutants that have direct effect on humans and animals. Industrial wastewaters containing dissolved phenol can contaminate groundwater resources and thus lead to a serious groundwater pollution problem. In the present research, the adsorption technique for the efficient removal of phenol pollutants at trace level in water was employed. Four type of micro and nanocarbon materials including carbon nanotubes (CNTs) and carbon nanofibers (CNFs) as nano carbon adsorbents, activated carbon (AC) and industrial carbon fly ash (CFA) as micro carbon adsorbents were used to remove phenol from water. Characterization of these adsorbents was performed by Field Emission Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscopy(TEM), Thermogravimetric Analysis (TGA), BET specific surface area while the concentration of phenol in water before and after treatment was analyzed using UV-Spectroscopy. The pH (3-9) of the solution, was varied in order to determine their effect on the removal of phenol from water and hence on the adsorption rate.

1. Introduction

Environmental pollution is currently one of the most important issues facing humanity. It has increased exponentially in the past few years and reached alarming level in terms of its effects on living creatures. Toxic organic substances are considered among the pollutants that have direct effect on human and animals.
Industrial wastewaters containing dissolved polycyclic aromatic hydrocarbons (PAHs) and phenols can contaminate groundwater resources and thus lead to a serious groundwater pollution problem. Exposure to such chemicals can damage the central nervous system, respiratory system, kidney, and blood system if entered into human body [1]. Agency for Toxic Substances and Disease Registry, USA, has classified phenols as the top 45th priority hazardous substances that need urgent treatment before entering into the environment [2]. Therefore, removing these organics or decreasing their concentrations to the permitted levels before discharging becomes a challenging issue. Several ways have been developed to remove phenol compounds from wastewaters, including electrochemical oxidation [3], chemical coagulation [4], solvent extraction [5], membrane separation [6], bioremediation [7] and photo catalytic degradation [8]. Several technological processes can be performed to remediate organic compounds from water. Bioremediation of phenols and low molecular weight PAH is a preferred technique because of its ease of implementation but tends to be timely and often incomplete especially at high-molecular weight PAHs (with five or six aromatic rings), which are proven to be more recalcitrant to biological degradation [7]. Among the potential adsorbent materials are carbon-based compounds which are hydrophobic and non-polar, including materials such as activated carbon (AC) [1]-[17], carbon nanotubes (CNTs) [15], carbon nanofibers (CNFs) [16] and industrial fly ash (FA) [17]. Carbonaceous materials such as AC are characterized by a large surface area, well-developed porosity and tunable surface-containing functional groups. It is extensively used for removal of both organic and inorganic compounds from aqueous solution [12]-[20]. In the present work, the effect of four types of micro and nano carbon materials on the removal of phenol from water was investigated.

2. Experimental Procedure and Materials

2.1. Carbon nanotubes and carbon nanofibers, Activated Carbon and Carbon Fly ash

Carbon nanotubes and carbon nanofibers were purchased from Nanostructured & Amorphous Materials, Inc. USA. The Purity of CNTs and CNFs are >95%, their outside diameters are 10-20 nm and 200-500 nm; respectively while their length ranges from 1-10 μm and 10-40 μm respectively. The activated carbon (AC) used in this study was purchased from Calgon, and it was supplied in 10–30 mesh (0.60 –1.0 mm) size. The granular-activated carbon was milled in a hammer-cutter mill to a powder (<0.18 mm in particle diameter). The surface area of AC was measured by nitrogen adsorption at 77 oK using Micromeritics Gemini 2375 surface area analyzer (Micromeritics, Norcross, GA) using a 15-point BET. Fly ash (FA) is one of the residues generated in the combustion process of coal and liquid fuels and represents the fine particles that rise with the flue gases. The fly ash used for this study was produced by burning heavy fuel oils in one of Saudi Aramco company main power plants and the produced ash contains high percentage of unburned carbon and some other metals. Saudi Aramco produces hundreds of thousands of tons of FA per year [20]. FA was analyzed by Energy Dispersive X-ray (EDX) analysis to identify the elemental composition. The EDX analysis indicated that FA contains 67.56% weight carbon beside many other different metals as shown in the EDX spectrum (Table 1).

Table 1. The Energy Dispersive X-ray analysis of FA

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>S</th>
<th>V</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>67.56</td>
<td>23.73</td>
<td>0.12</td>
<td>2.04</td>
<td>4.98</td>
<td>0.76</td>
<td>0.12</td>
<td>0.25</td>
<td>0.25</td>
<td>0.19</td>
<td>100.0</td>
</tr>
</tbody>
</table>

2.2. Batch mode adsorption experiment

Experiments of batch mode adsorption were conducted at room temperature to study the effect of the initial pH of the solution, the carbon dosage, the contact time and the agitation speed on the adsorption of phenol
ions. Each experiment was conducted in a volumetric flask and the initial and final concentrations of phenol were analyzed using UV-Vis spectrophotometer. The adsorption capacity \((q)\) was calculated using the following formula:

\[
\text{%removal} = \frac{C_i - C_e}{C_i} \times 100
\]

Where \(C_i\) is the initial concentration of metal ion in the solution (mg/L), \(C_e\) is the concentration of metal ion in solution (mg/L), \(V\) is the total volume of solution (L), and \(MS\) is the carbon dosage (g).

### 2.3. Characterization

BET surface analysis was performed using Micromeritics ASAP 2020 where fixed mass of carbon of ~0.35 g was degassed initially at 90oC for 1 h, followed by ramping the temperature at 10oC/min to reach 250oC. The sample left at this condition for 5 hours to remove all adsorbed water and air molecules. The mass of the sample was measured again and used for the isotherms. The analysis conditions were performed in the absence of glass rode in order to determine the micropores surface area. The microstructure of the utilized carbon based materials, namely CNTs; CNFs; AC; and FA, were characterized using field emission scanning electron microscope (FE-SEM)

![Fig. 1. Images of (a) carbon nanotubes, (b) carbon nanofibers (c) activated carbon and (d) fly ash.](image)

### 3. Results and Discussion
3.1. Characterization of the absorbents

Fig. 1 displays SEM images of CNTs, CNFs, AC and FA respectively. The diameter of the produced CNTs varies from 20 nm to 40 nm with an average diameter of 24 nm while for CNFs it varies from 100-250 nm. The size of AC is from 600 – 1000 micron, and from 500 -1500 micron for FA. The SEM image of FA compared to the AC demonstrates the high surface area of the FA and its potential for use as adsorbent. One important feature of FA over other carbon based adsorbents is its high content of metals which can contribute greatly in enhancing the adsorption.

3.2. BET analysis

Fig. 2 illustrates the adsorption-desorption curves of N2 at 77 K for CNTs, AC, FA and CNFs, respectively. The obtained BET surface area for these carbon materials is as follows: CNTs (155.5 m²/g); CNFs (40.7 m²/g); AC (1126.6 m²/g); and FA (7.1 m²/g).

3.3. Adsorption of phenol

![Graphs showing adsorption-desorption curves of N2 at 77 K for CNTs, AC, FA, and CNFs.](image-url)
Since the surface charge of an adsorbent could be modified by changing the pH of the solution, pH plays an important role in the removal of phenols by adsorption process. The extent of dephenolation by all types of considered carbon materials was studied at various pH values ranging from pH 2 to pH 9 while keeping the other parameters constant including contact time for 2 hr, dosage of adsorbent at 50 mg, and shaking/agitation speed at 100 rpm. The results of the effect of pH on phenol adsorption are represented in Fig. 3. The figure revealed that the highest removal efficiency was observed at pH 7.0 with maximum percentage removal of phenol by AC, CNTs, CNFs and FA, being approximately 65%, 47%, 31%, and 43%, respectively. However, at higher pH values, the percentage removal of phenol decreased significantly. This behavior can be explained in the light of the types and ionic state of the functional groups on the surface of the adsorbent as well as ionic chemistry of the solution. As a result, phenol, which is a weak acid (pKa = 10), will be adsorbed to a lesser extent at higher pH values due to the repulsive force prevailing at higher pH values. Adsorption of phenol up to pH 7.0 suggests that the negatively charged phenolate ions bind through electrostatic attraction to positively charged functional groups on the surface of carbon materials, because in this pH range more functional groups carrying positive charge would be exposed. However, at pH above 7.0, it seems that carbon materials possess more functional groups carrying a net negative charge, which tends to repulse the anions. Moreover, in the high pH range, phenols form salts, which readily ionize leaving negative charge on the phenolic groups and precipitate. It is worth mentioning here that above pH 7.0 other mechanisms like physical adsorption may play an important role in the adsorption of phenol and the exchange mechanism might be affected. The results agree well with those obtained by Banat et al. [21], and Halouliet al. [22], for the adsorption of phenols onto activated charcoal and bentonite clay respectively. It is worthwhile to mention that the pH of the solution was monitored before and after the adsorption and no noticeable change in pH was observed.

In the present study, the influence of four parameters namely pH of the solution, agitation speed, contact time, and adsorbent dosage (CNTs, CNFs, AC and FA) were investigated to determine their influence on the removal of phenol from water. It was noticed that with increasing pH from 3 to 7 the removal of phenol in the solution increased continuously and then decreased within the pH range of 7-9. The values of the correlation coefficients show favorable adsorption by most adsorbents. Finally, for the macro carbonaceous materials, AC showed excellent performance on the removal of phenol compared to FA, while for the nano carbonaceous materials, CNTs exhibited better performance compared to CNFs.

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References


