Regeneration of Carbon Nanotubes Exhausted with Humic Acid Using Electro-Fenton Technology

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Abstract Among the adsorbents, carbon nanotubes (CNTs) are relatively new nanomaterials which are frequently used for water purification. In this work, experiments were carried out to study the feasibility of regeneration of humic acid-exhausted CNTs using electro-Fenton process. The results showed that electro-Fenton process has high efficiency at pH equal to 3. The results also clearly indicated that the regeneration efficiency at lower molarities of H₂O₂ such as 0.05 is higher than at higher molarities. The results also implied that the regeneration efficiency at current density equal to 0.1 mA was 98.32% and with increasing current density, the regeneration efficiency decreased. The regeneration efficiency at molar ratios of Fe²⁺:H₂O₂ as 0.03:10 was higher than other examined molar ratios and after five cycles of regeneration decreased to 87%. The results of the present study indicated that electro-Fenton process has high efficiency for the regeneration of CNTs exhausted with humic acid.

Keywords CNTs · Humid acid · Regeneration · Electro-Fenton

1 Introduction

Carbon nanotubes (CNTs), as new nanomaterials, have shown a considerable potential in environmental applications such as efficient adsorbents for the removal of toxic materials including organic chemicals and metals [1–3]. Recently, considerable attention has been centered upon the CNTs. Humic compounds can interfere with disinfection process in surface drinking water treatment, which leads to generation of disinfection by-products. Therefore, their presence in water should be considered. CNTs are considered as efficient adsorbents for the removal of humic acids from water [4]. CNTs have a specified adsorption capacity: they become exhausted after a period of usage. Furthermore, there are serious concerns regarding the release of toxic substances into environment from discarded CNTs [5, 6]. Adsorption of toxic substances can increase the toxicity of nanotubes and finally affects the behavior of these substances in the environment [7]. Therefore, exhausted CNTs must be regenerated for further use.

Common regeneration procedures of CNTs include thermal treatment [8], chemical extraction [9], bio-regeneration [10], supercritical regeneration [11], ultrasonic regeneration [12, 13] and Fenton and electro-Fenton regeneration [14]. Thermal regeneration techniques are extensively used for the regeneration, but they have restrictions and result in 5–10% carbon loss due to oxidation and attrition, and high energy consumption to keep the temperature in the range of 800–850°C [8].

Furthermore, chemical extraction techniques require separation and extraction methods and they are not suitable [9]. The drawback of bio-regeneration is that large time is required for reaction and large reactors for regeneration. Furthermore, accumulations of biological sludge on the pores result in blockage and decrease in surface adsorption capacity [10]. Supercritical regeneration of exhausted CNTs by the use of supercritical fluids like carbon dioxide is expensive [11]. As noted, most of the techniques have restrictions; therefore, other techniques such as Fenton and electro-Fenton have attracted most attention.

Fenton process is a method in which reaction between divalent iron (Fe²⁺) and H₂O₂ generates hydroxyl radicals
which rapidly attack organic pollutants in aqueous solutions and degrade them. If, in Fenton process instead of Fe$^{2+}$, electric current and iron electrode are used to generate Fe$^{2+}$, this process is known as electro-Fenton [15].

Electro-Fenton method is an advanced oxidation process in which two radicals including OH$^o$ and HO$_2$ are formed [16,17]. Advanced oxidation processes are based on the generation of powerful oxidants, like OH$^o$ radicals. Hydroxyl radicals are extraordinarily reactive species with oxidation power of 2.78 V. Hydroxyl radicals cause nonselective degradation of organic compounds where conventional treatment processes are ineffective. Hydroxyl radicals react with organic pollutants leading to their mineralization, i.e., their conversion into CO$_2$, H$_2$O and inorganic matters [18]. Hydroxyl radicals can be generated via two main processes: direct and indirect electro-oxidation. In direct electro-oxidation process, OH$^o$ radicals are produced by the reactions at the electrode (anode) surface by hydrolysis of water as Eq. 1:

\[
H_2O \rightarrow OH^o + H^+ + e^- 
\]  (1)

In the second process (indirect process), hydroxyl radicals are generated electrochemically via Fenton’s reagent reaction in homogeneous solution via electro-generated H$_2$O$_2$ in the presence of ferrous ions. In this process, Fe$^{2+}$ and H$_2$O$_2$ react with each other in order to generate hydroxyl radicals [18].

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^o 
\]  (2)

Hydroxyl radicals, in addition to oxidation of refractory organic compounds, accelerate the rate of electro-Fenton reaction [18].

Main advantages of electro-Fenton process in comparison with other oxidation methods are [19–23]:

1. Environmentally friendly due to the use of electricity as a clean energy source in the process.
2. Flexibility, energy efficiency, electronically controlled and safety because of controlled operation.
3. Control of the kinetics of degradation to allow more mechanistic studies.
4. Higher degradation rate of organic pollutants due to continuous regeneration of Fe$^{2+}$ at the cathode, thus minimizing the sludge production.
5. If properly operated, it can mineralize organic compounds completely at a relatively low cost.
6. In the process, soluble Fe$^{3+}$ can be reduced to Fe$^{2+}$ at the cathode, which is known as electrochemical catalysis.

In electro-Fenton process, both Fe$^{2+}$ and Fe$^{3+}$ are present in the solution due to the continuous reaction of H$_2$O$_2$. Oxidation of Fe$^{2+}$ generates OH$^o$ radicals which can efficiently remove organic pollutants [24,25]. Fenton and electro-Fenton processes have been studied by many researchers, and both have shown high efficiency in destroying most of the organic matters, even organochlorine compounds in aqueous solutions [26].

Methatham et al. [27] studied electro-Fenton ferrous regeneration (EFFR) process for kinetic determination under various reaction conditions, and a degradation pathway for chlorinated organic compound oxidation by EFFR process was proposed on the basis of the intermediate compounds detected.

As there is no literature related to the degradation of adsorbed organic molecules onto CNTs and to their regeneration by the use of electro-Fenton, the present study aimed to evaluate the regeneration capability of CNTs exhausted with humic acid using electro-Fenton process.

### 2 Materials and Methods

#### 2.1 Synthesis of CNTs

The CNTs utilized herein have been prepared by chemical vapor deposition (CVD) technique in Research Institute of Petroleum Industry (RIPI), Iran.

Synthesis of CNTs was done by the use of CO-MO/MgO (cobalt–molybdenum/magnesium oxide) as catalyst in a horizontal furnace where a quartz sleeve is suitably placed in it. Catalyzer was placed in a quartz reservoir, and then, both were placed in a quartz sleeve. Then, hydrogen gas was blown through the catalyzer to clean and regenerate it. The reaction was done by the use of methane gas as precursors and hydrogen as carrier gas at a sufficiently high temperature range (900–1200 °C). Then, furnace was cooled at the room temperature. Generated nanotubes have impurities such as metal particles as well as amorphous carbon which contaminates the resulting CNTs. Removal of the impurities is necessary to increases the adsorption capacity of the synthesized CNTs. To remove metal nanocatalysts, CNTs were impregnated with HCl (30 min) and placed at room temperature. Then, samples were washed several times with distilled water to adjust pH near neutral. All the steps were carried out in duplicate to synthesize high-quality CNTs [4].

#### 2.2 Textural Characteristics of CNTs

To characterize the structure of CNTs, images of scanning electron microscope (SEM, Cam ScanMV2300) were used. Transmission electron microscopy (TEM, JEOL 2010F) was used to characterize the microstructure of materials with very high spatial resolution. Also, Porosimeter (ASPA 2010) was used for the determination of reliable information on the surface area, pore volume and pore size distribution (PSD).
X-ray diffraction of CNTs was taken using a Philips X’Pert Pro diffractometer in a range from 5 to 75°.

2.3 Electrolyte Solution

Prior to the commencement of the study, it was necessary to prepare feed solution. Humic acid (humic acid sodium salt) was prepared as a 500 mg/l stock solution by mixing 926 mg of humic acid (0.54 % purity). Due to hydrophobic nature of humic substances, humic acid sodium salt purchased from Acros Organics Company, New Jersey, USA, was used for the experiments. The test solution was prepared by diluting this stock solution. For preparation of electrolyte solution, 30 % H2O2 was used.

2.4 Analysis Procedures of Humic Acid Samples

Natural organic matters in water cannot be analyzed using common analytical methods due to their heterogeneous chemical structure. Therefore, to determine natural organic matter in water, alternative and index parameters were used. Humic acids are natural organic matters present in surface waters.

In most of the studies, humic acids are quantified by two main methods: absorbance of ultraviolet light at 254 nm (UV254) and TOC analysis. To investigate the relationships between these two, some specified samples of humic acids were prepared and concentration of humic acid was read as mg/l by absorbance of ultraviolet light at 254 nm. Also, the samples were analyzed using TOC analyzer. Consequently, by considering value of regression coefficient, our samples were tested using UV254.

2.5 Adsorption Experiments

In order to determine the optimum time, humic acid of initially specified concentrations was prepared by the use of deionized water. Reactors should be sealed sufficiently to prevent leakage of test solution. At the beginning, powdered CNTs were used to study kinetics of CNTs. Then, a weighed amount of CNTs was added into the reactor and mixed thoroughly, and contact time was measured by a timer.

Consequently, equilibrium time, the time no more adsorption takes place, was obtained. This time was used for the regeneration process, in other words, by reaching the CNTs to equilibrium, experiments were stopped and adsorbent samples were prepared for regeneration. Humic acid of concentrations 3, 5 and 10 mg/l were used, and range of adsorbent (CNTs) concentration was determined by pretest.

In all the cases, the adsorption capacity, q (mg/g), was calculated as Eq. 3:

$$q = \frac{(C_0 - C_e) V}{m}$$

where $C_0$ is the initial concentration of humic acid (mg/L), $C_e$ is the equilibrium concentration of humic acid (mg/L), $V$ is the initial volume solution (L) and $m$ is the mass of the adsorbent (g).

2.6 Regeneration Experiments by Electro-Fenton

The aim of the study was to regenerate humic acid-exhausted multi-walled CNTs (MWCNTs) by the use of electro-Fenton process. An electrochemical cell containing anode, cathode and power supply was used. The schematic of electro-Fenton reactor is shown in Fig. 1. In order to evaluate the regeneration efficiency of CNTs, H2O2 and Fe electrode were used as electrolyte solution and as a source of Fe2+ supply, respectively. The generation of ferrous ions is a combined process that has advantages of both electro-chemical (electro-coagulation) process and Fenton oxidation.

In the present study, chemical oxidation method (electro-Fenton) was used to regenerate CNTs after exhaustion with humic acid. After each period of regeneration, CNTs were separated from solution, dried and stored for further use. Five regeneration cycles were considered in this study. Regeneration efficiency (RE) was calculated using Eq. 4:

$$RE (%) = \frac{(H_{A_{total}}) - (H_{A_{residual}})}{H_{A_{total}}} \times 100 \quad (4)$$

where $H_{A_{total}}$ is total amount of adsorbed humic acid onto CNTs before regeneration (mg) and $H_{A_{residual}}$ is the amount of residual humic acid onto CNTs after regeneration (mg).
In these experiments in order to regenerate exhausted CNTs by electro-Fenton, H$_2$O$_2$ was used as electrolyte solution and iron electrode was used for the continuous supply of Fe$^{2+}$.

3 Results and Discussion

3.1 Characterizations of CNTs

Figure 2 shows SEM and TEM images of CNTs. The outer diameters and lengths of CNTs ranged from 10 to 50 nm.

XRD spectra of CNTs are shown in Fig. 3. It can be concluded that the peaks at 24 and 43 relate to graphene structure of carbon nanotubes.

In Table 1, the properties of CNTs including surface area measured by BET (Brunauer, Emmet and Teller) and BJH (Barrett-Joyner-Halenda) methods, average pore size diameter and pore volumes are presented.

3.2 Determination of Optimum pH

Figure 3 shows the effect of different pH on the regeneration of MWCNTs exhausted with humic acid. When the pH increases, the regeneration efficiency decreases. Considering the decrement in efficiency, experiments have been carried out at pH 3.

It can be noticed from the figure that the adsorption efficiency decreases by increasing the pH from 2 to 12 at a constant amount of humic acid. The results of the present study agree with the findings of the other studies which have used activated carbon for adsorption of humic acids [30,31]. When the pH increases, there exists lower complexation of humic acid molecules which results in decrease in overall desorption capacity. Also, by increasing pH value, charge of
Table 1  Surface properties of CNTs

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>Average pore diameter by BET (nm)</th>
<th>( S_{\text{BJH}} ) (m(^2)/g)</th>
<th>Average pore diameter by BJH (nm)</th>
<th>( V_{\text{meso}} ) (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>138.31</td>
<td>12.79</td>
<td>171.74</td>
<td>12.52</td>
<td>0.54</td>
</tr>
</tbody>
</table>

\( S_{\text{BET}} \) surface area calculated by BET method, 
\( S_{\text{BJH}} \) surface area calculated by BJH method, 
\( V_{\text{meso}} \) mesopore volume calculated by BJH method

Humic acid with carboxylic and phenolic functional groups would be increased [32]. Therefore, at higher pH, repulsion force between humic acid and CNTs increases which results in decrease in amount of humic acid adsorption on CNTs. When the pH increases, the regeneration efficiency decreases. Considering the decrement in efficiency, experiments have been carried out at pH 3.

### 3.3 Effect of H\(_2\)O\(_2\) Concentration on Regeneration of CNTs by Electro-Fenton

Figure 4 shows the effect of various moralities of H\(_2\)O\(_2\) on the regeneration of MWCNTs using electro-Fenton process. As can be seen in the figure, molarity of 0.05 showed the highest regeneration efficiency (98.32%).

It can be ascertained from the figure that the highest regeneration percent (98.32%) was obtained in the molarity of 0.05 for these CNTs. The results also showed that electro-Fenton process can regenerate MWCNTs well even in low molarities of H\(_2\)O\(_2\). Increase in H\(_2\)O\(_2\) molarity had a slight change in the efficiency. However, it has advantage from the economic consideration due to the lower consumption of H\(_2\)O\(_2\) needed for CNTs regeneration that causes a decrease in the overall costs. These results concurred with the finding of Banuelos and colleagues who found that after 10 regeneration cycles by the use of electro-Fenton process, only 10 percent of adsorption capacity of CNTs was reduced in comparison with the virgin ones [33].

### 3.4 Effect of Applied Current on Regeneration of Exhausted MWCNTs

Effect of applied current on regeneration of exhausted MWCNTs is shown in Fig. 5. As can be seen in the figure, the optimum current for the regeneration of MWCNTs by the use of electro-Fenton was 0.1 mA (miliampere) with efficiency of 98.32%.

It can be noticed from the figure that a current density of 0.1 mA was assumed ideal for the process and showed 98.32% efficiency. Therefore, the efficiency increased with increasing current up to 0.1 mA. After that, efficiency decreased slightly with an increase in the current density. It can be attributed to the deposition of Fe particles and aggregates on the nanotubes porosity at high current which results in efficiency decrease. Therefore, the optimum current for the regeneration of MWCNTs was 0.1 mA. The results of the study showed that regeneration efficiency is higher at low current. At lower current, amount of electricity consumption is low. However, it has advantage from the economic consideration due to the lower consumption of energy.

### 3.5 Efficiency of CNTs Regeneration in Different Cycles of Regeneration

Regeneration efficiency of CNTs in different regeneration cycles, at optimum molar ratios of H\(_2\)O\(_2\) and current densi-
Adsorption capacity of humic acid on MWCNTs after five cycles of regeneration for different ratios of Fe$^{2+}$:H$_2$O$_2$ ($C_0 = 100$ mg/L, $M = 200$ mg, pH = 3)

Regeneration capacity of MWCNTs was decreased from 53.5 to 45.8 mg/g after five cycles of regeneration.

Table 2 summarizes amount of specific surface area ($S_{BET}$) in different regeneration cycles. It can be seen in the table that surface area of MWCNTs decreased from 138.33 to 119.93 m$^2$/g after five cycles of regeneration.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Regeneration cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original CNTs</td>
</tr>
<tr>
<td>$S_{BET}$ (m$^2$/g)</td>
<td>138.31</td>
</tr>
</tbody>
</table>

The results showed that $S_{BET}$ of MWCNTs decreased from 138.31 to 119.93 m$^2$/g for 0.03:10 molar ratio of Fe$^{2+}$:H$_2$O$_2$ after five cycles of regeneration. In other words, $S_{BET}$ of MWCNTs was deceased nearly 13 % after five cycles of regeneration. This reduction can be attributed to the deposition of Fe particles and other materials on the surface of CNTs, which results in blockage of adsorbent pores and finally in decrease in adsorption capacity. Huling et al. studied regeneration of GAC exhausted with MTBE by the use of Fenton and reported that amount of surface area and adsorption capacity decreased 10 and 9 %, respectively, after two cycles of regeneration [35].

4 Conclusion

In this work, experiments were carried out to study the feasibility of regeneration of humic acid-exhausted CNTs using electro-Fenton process. The 0.03:10 molar ratio of Fe$^{2+}$:H$_2$O$_2$ in electro-Fenton process was found to be more effective for regeneration of CNTs exhausted with humic acid. The regeneration efficiency in optimum Fe$^{2+}$:H$_2$O$_2$ molar ratio decreased to 87 % after five cycles of regeneration.

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References