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Fenton regeneration of humic acid-spent carbon nanotubes

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ABSTRACT

Carbon nanotubes (CNTs) are known as efficient sorbents for removal of organic compounds from aquatic solutions. In the present study, the efficiency of Fenton solution for regeneration of CNTs exhausted with humic acid was studied. CNTs were produced using chemical vapor deposition method. The molar ratios of Fe^{2+} to H_2O_2 as 0.5:10, 1:10, and 2:10 were used. The saturation cycles were continued up to five stages. Results of Fenton regeneration showed higher regeneration efficiency (65.4%) for 2:10 M ratio comparing to other molar ratios after five cycles of regeneration. Slight decrease in adsorption capacity after each regeneration cycle was observed which may be due to the deposition of decomposed residues in CNT pores, which blocked the carbon porosity and decreased the specific surface area. In conclusion, the Fenton regeneration especially at higher Fe^{2+}:H_2O_2 molar ratios showed a possibility as an alternative to chemical and thermal regenerations of CNTs.

Keywords: Carbon nanotubes; Fenton; Regeneration; Humic acid; Hydrogen peroxide

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1. Introduction

Carbon nanotubes (CNTs) have been widely studied as new nanomaterials in terms of their potential in environmental applications as superior sorbents for removal of toxic substances such as organic chemicals [1,2] and metals [3]. Humic acid as a major constituent of natural organic matters in water resources should be highly considered because of its potential as precursors for disinfection by-products production in conventional water treatment plants. Removal of humic acid by adsorption on CNTs has been recognized as an effective means for water purification [4]. Depending on its adsorption capacity, however, CNTs saturate after some service time. Moreover, there are serious concerns over their health and environmental issues once released to the environment [6,7]. Adsorption of toxic substances by CNTs may enhance the toxicity of CNTs and further affect the fate and transfer of toxic substances in the environment [8]. Therefore,

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the spent CNTs should be regenerated for wider application of CNT adsorption processes.

The common techniques for regeneration are thermal treatment [9], chemical extraction [10], bio-regeneration [11], supercritical regeneration [12], ultrasonic regeneration [13], and Fenton regeneration.

Thermal regeneration techniques are widely used but have several disadvantages such as loss of 5–10% carbon due to oxidation and attrition and also require high energy consumption to keep the temperature between 800 and 850°C. On the other hand, chemical regeneration may not be suitable because of the necessity for additional separation or decomposition steps [9]. The bio-regeneration process requires long reaction time for regeneration and greater volume for treatment reactors. Further, loss of adsorbents capacity due to the accumulation of biosolids can block pore throats and sorption sites [11]. Supercritical regeneration of carbon through extraction of the adsorbate into a supercritical fluid such as CO_2 is also considered to be very expensive. Hence, these techniques are presenting drawbacks; it is of interest to explore other methods of regeneration.

In this research, the feasibility of using Fenton's reaction for regeneration of spent nanotubes which had been used to collect and concentrate humic acid was studied. Fenton's reaction is an advanced oxidation process, in which reaction of hydrogen peroxide (H_2O_2) with iron generates two radical species ($\bullet OH$ and $HO_{2\bullet}/O^-_{2\bullet}$) [14]. The mechanism of heterogeneous Fenton reaction is presented as:

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+ \tag{1}$$

$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + HO^{2\bullet} \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet \tag{3}$$

$$Fe^{3+} + HO_{2\bullet} \rightarrow Fe^{2+} + H^+ + H^+ + O_2 \tag{4}$$

In Fenton's mechanism, iron cycles between Fe^{2+} and Fe^{3+} oxidation states, due to reaction with H_2O_2. The oxidation of Fe^{2+} produces a highly aggressive hydroxyl radical ($\bullet OH$), which can efficiency attack organic environmental contaminants [15,16]. Fenton's reaction has been extensively studied and has shown high efficiency to destroy most classes of organics, even the more refractory organochlorinated compounds, in aqueous solutions [17]. But based on the literature, no work has been carried out for the oxidation of adsorbed organic molecules and regeneration of CNTs.

The objectives of this study were to evaluate the feasibility of Fenton regeneration of CNTs saturated with humic acid, which is widely known as an important contaminant of surface water resources, and to suggest the possible mechanism of Fenton regeneration.

2. Materials and methods

2.1. Synthesis of CNTs

CNTs were produced using chemical vapor deposition (CVD) method [4] in the research institute of petroleum industry in Tehran, Iran. For synthesis of CNTs, the catalytic reactions were accomplished in presence of Co-Mo/MgO as the catalyst. The CVD method was carried out in a horizontal furnace consisting of a quartz tube. The catalyst was set in a quartz boat that was placed into a quartz tube followed by being purged in the hydrogen stream in order to reduce the catalyst. The reaction was carried out using methane as the carbon source and hydrogen as the carrier gas at 900–1,000°C. The furnace was then cooled to room temperature under a nitrogen atmosphere.

The black product was not pure and contained many impurities including various types of carbon (graphitic nanoparticles, amorphous carbon, fullerenes, and polyaromatic hydrocarbons) and catalyst material (particles containing metals and catalyst support). In order to purify and remove the metal nanocatalysts from CNTs, the product was dissolved in 37% hydrochloric acid solution for about 16 h at room temperature and then washed several times with distilled water until the solution pH was adjusted at approximately neutral. Treated CNTs were dried in vacuum at 40°C overnight. For eliminating the amorphous carbons, the purified CNTs were placed in the furnace at 400°C for 30 min.

2.2. Characterization of CNTs

In order to verify the desired structure of the synthesized nanotubes, specific surface area (S_{BET}) and mesopore volume (V_{meso}) were determined according to the N_2 adsorption isotherms using an ASAP-2010 porosimeter from the Micromeritics Corporation GA [4].

2.3. Preparation of stock solutions

Humic acid stock solution (500 mg/L) was prepared by mixing 926 mg of humic acid (0.54% purity)

(Acros Organics Company; New Jersey, US) with deionized water.

$FeSO_4{\cdot}7H_2O$ as the source of Fe^{2+} and H_2O_2 30% were used for Fenton solution preparation. In this solution, the molar ratios of Fe^{2+} to hydrogen peroxide were changed as 0.5:10, 1:10, and 2:10. For preparation of Fenton solution with above mentioned molar ratios, 1.5, 3, and 6 mL of 1 g/L $FeSO_4{\cdot}7H_2O$ solution were added to 100 mL of 30% (*w*/*w*) H_2O_2 solution, respectively.

The calculation method for computing the required volume of Fe and H_2O_2 for preparing the mentioned molar ratios as follows:

For preparation of 0.5:10 M ratio (Fe:H_2O_2), 0.5 mL of 1,000 mg/L $FeSO_4{\cdot}7H_2O$ should be added to 10 mL of 1,000 mg/L pure H_2O_2 (H_2O_2 solution density was 1,000 mg/L according to manufacturing data recommendations). But considering the low volume of this solution, both volumes (0.5 and 10 mL) have tripled and resulted 1.5 and 30 mL. Regarding to purity percent of H_2O_2 (30%), the volume of H_2O_2 required for preparing the 0.5:10 M ratio was 100 mL [30 mL/(30/100)) = 100 mL]. Other molar ratios were produced according to this calculation method.

Remaining H_2O_2 was measured using a modified peroxytitanic acid colorimetric procedure [5].

2.4. Batch adsorption experiments

Batch adsorption experiments were carried out with CNTs at 25 ± 1˚C. At equilibrium, humic acid concentration remaining in the solution was determined at UV absorbance wavelength of 254 nm by a Lambda UV/VIS-spectrophotometer (PerkinElmer, USA) with cuvettes of 1 cm length. The amount of the adsorbed humic acid on CNTs was calculated from the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \tag{5}$$

where q is the amount of humic acid adsorbed by multiwall carbon nanotubes (MWCNTs) (mg/g); C_0 is the initial humic acid concentration (mg/L); C_e is the equilibrium concentration of humic acid (mg/L); V is the initial solution volume (L); and m is the CNTs dosage (g).

2.5. Adsorption–regeneration experiments

About one gram of CNTs as the adsorbent was placed in the bottles, and 1 L of solution containing 100 mg/L of humic acid was added to the adsorbent. Then, the bottles were sealed with aluminum foil-lined caps and placed on a rotary shaker (IKA RCT basic model) and shaken at 180 rpm for 2 h to ensure that the adsorption process reached equilibrium. Our previous study has shown that under such conditions, CNTs are saturated (4). CNTs were separated from water by filtration, dried at 60˚C for 2 h, and milled (particle size < 0.15 mm). The pore size of filter was 0.2 μm. The milling process was used for grinding the agglomerated nanotubes that formed in purification and functionalization processes.

For determination of optimum regeneration times, exhausted CNTs were regenerated with different Fe: H_2O_2 molar ratios (2:10, 1:10, and 0.5:10) and at different contact times. The number of contact times sampled was 11 and selected between 0 and 90 min.

The optimal regeneration time was the time that after this time no amounts of humic acid introduced to the Fenton solution. In other words, in regeneration experiments after optimal regeneration times, no values of humic acid desorbed from the nanotubes.

The regeneration experiments were performed as below:

About one gram of saturated CNTs was loaded in a new bottle with 100 mL ultra-pure water and then placed in Erlenmeyer and regenerated with Fenton solution.

After each Fenton regeneration cycle, the CNTs were separated and dried. The saturation–regeneration process was carried out in five cycles and after each cycle; the adsorption capacity of the regenerated CNTs was evaluated.

Regeneration efficiency (RE) of humic acid was calculated using Eq. (6):

$$\text{RE }(\%) = (\text{HA})_{\text{total}} - (\text{HA})_{\text{residual}}/\text{HA}_{\text{total}} \times 100 \tag{6}$$

where HA_{total} is the total amount of humic acid adsorbed on CNTs before Fenton regeneration (mg) and $\text{HA}_{\text{residual}}$ is the residual amount of humic acid within CNTs after Fenton regeneration (mg).

The residual amount of humic acid on the CNTs was determined by subtraction of adsorption capacity of original CNTs (q_e) and adsorption capacity of CNTs after each cycle of regeneration.

3. Results and discussion

Our previous studies indicated that the adsorption capacity of CNTs for humic acid was 53.50 mg/g [4]. In order to evaluate the efficiency of Fenton solution for humic acid desorption, 1 g CNTs which had adsorbed 53.50 mg humic acid was regenerated in 100 mL of Fenton solution.

In order to determine the proper regeneration time, with the highest efficiency, exhausted CNTs were contacted with different Fe^{2+}:H_2O_2 ratios at different contact times. Then, adsorption experiments were repeated for regenerated CNTs. The related results are shown in Fig. 1.

As shown in Fig. 1, optimum regeneration time was 15 min for 2:10 M ratio, for which the RE was obtained as 87.51%. The optimum regeneration times were 30 and 45 min for 1:10 and 0.5:10 (mole:mole) ratios, respectively, for which the obtained regeneration efficiencies were 84.09 and 74.78%, respectively.

Table 1 shows initial and final concentration of humic acid in first regeneration cycle. According to the table, percent regeneration of CNTs after first regeneration cycle in mentioned molar ratios was 87.51, 84.04, and 74%, respectively. The supplemental information about different alternative methods about determining the percentage regeneration can be found in previous literature [18].

Adsorption capacities of CNTs after five cycles of Fenton regeneration with different molar ratios of Fe^{2+}:H_2O_2 are shown in Fig. 2. It was concluded that after five cycles of Fenton regeneration with 2:10 M ratio of Fe^{2+}:H_2O_2, the adsorption capacity of CNTs decreased from 53.50 to 35.12 mg/g. In other words, the adsorption efficiency after five cycles reached 65.4% of its initial amount. Also, in 1:10 and 0.5:10 M ratios of Fe^{2+}:H_2O_2, the adsorption capacities of CNTs after five cycles of regeneration reached 30.34 and 20.95 mg/g, respectively. Based on these results, it was indicated that Fenton solution especially in higher ratios of Fe^{2+} to H_2O_2 can be a good choice for regenerating CNTs exhausted with humic acid.

According to previous studies, if H_2O_2 concentration in Fenton solution is low, the Fenton's mechanism slows down, which limits the rate of production of radicals. If, on the other hand, excess H_2O_2 is present, it acts as both a source of radicals and a scavenger for •OH [19].

Thus, in lower ratios of Fe to H_2O_2, which the amount of available hydrogen peroxide is higher, the RE is lower due to higher consumption of •OH radical by H_2O_2. But in higher ratios of Fe^{2+} to H_2O_2, since there exists fewer extra H_2O_2 to consume •OH radicals, thus higher amounts of these radicals remain in the solution and attack humic acid adsorbed on the CNTs and destroys them [20]. Therefore, humic acid is more oxidized and the RE increases accordingly. These results have also shown in a study carried out by Delmas et al. who tested regeneration of different kinds of activated carbon with different Fenton molar ratios [21]. In that study, researchers concluded that higher concentrations of Fe^{2+} and lower concentrations of H_2O_2 cause better regeneration of activated carbon.

Another reason for higher RE in 2:10 M ratio is that whenever the higher amounts of Fe^{2+} exist in the solution, it is adsorbed by CNTs, and considering the

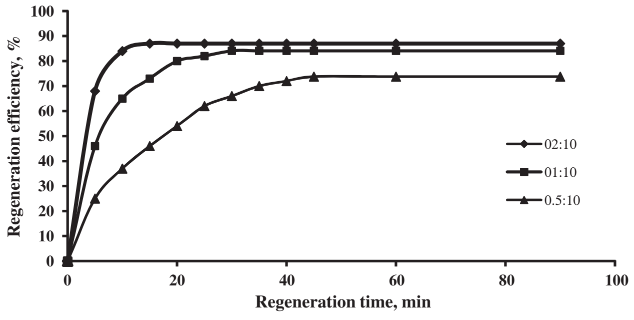

Fig. 1. Determination of optimum Fenton regeneration time for MWCNTs in the first regeneration cycle.

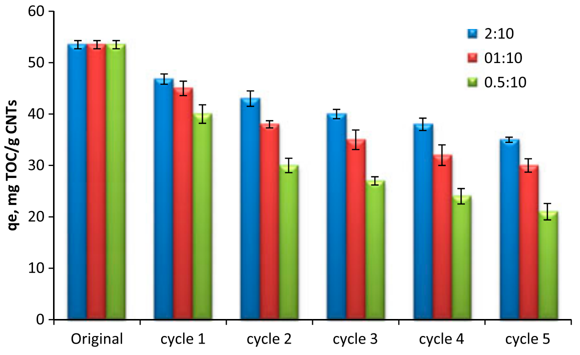

Fig. 2. Adsorption capacities of CNTs after five cycles of regeneration for different ratios of Fe^{2+}:H_2O_2.

Table 1
Initial and final HA concentration in the first regeneration cycle

Fe^{2+}:H_2O_2 molar ratio	Initial HA concentration, mg/L	Final HA concentration, mg/L	Percent regeneration, %	Adsorption capacity, mg/g
2:10	30	3.75	87.51	47
1:10	30	4.8	84.09	45
0.5:10	30	7.8	74	40

Table 2
Surface area and mesopore volume of original and regenerated CNTs with different Fe^{2+}:H_2O_2 molar ratios and for different regeneration cycles

Fe^{2+}:H_2O_2 molar ratio	Parameters	Original CNTs	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
2:10	S_{BET} (m^2/g)	130.52	125.93	122.03	118.77	113.57	110.94
	V_{meso} (cm^3/g)	0.56	0.52	0.49	0.48	0.45	0.41
1:10	S_{BET} (m^2/g)	130.52	119.13	114.16	106.32	97.11	95.23
	V_{meso} (cm^3/g)	0.56	0.49	0.45	0.40	0.37	0.31
0.5:10	S_{BET} (m^2/g)	130.52	102.41	93.72	88.54	80.35	71.19
	V_{meso} (cm^3/g)	0.56	0.35	0.33	0.29	0.26	0.22

Notes: S_{BET}: Surface area calculated by BET method.
V_{meso}: Mesopore volume calculated by BJH method.

positive charge of Fe^{2+} and negative charge of humic acid, more humic acid would be adsorbed on the surface of CNTs. In fact, in these cases, Fe^{2+} ions are placed on the surface of CNTs and increase the adsorption of humic acid as well as better efficiency for hydrogen peroxide. The latter happens because homogenous cover of Fe cations locates on the surface of CNTs, and while reacting with hydrogen peroxide, produced OH radicals in overall surfaces of CNTs cause better deterioration of humic acid. Other studies have also reached to the same results [22].

The amounts of S_{BET} and V_{meso} in five cycle regeneration with different ratios of Fe:H_2O_2 are presented in Table 1, in which it is shown that S_{BET} and V_{meso} decreased as regeneration cycles increased, in a way that these parameter reduced (for 2:10 M ratio), from 130.52 to 110.94 m^2/g and 0.56 to 0.41 cm^3/g, respectively.

Based on the results presented in Table 2, it can be concluded that after five regeneration cycles with 2:10, 1:10, and 0.5:10 M ratios of Fe^{2+}:H_2O_2, CNT surface area was reduced about 15, 27, and 45%, respectively.

As shown in Table 2, higher molar ratio of Fe: H_2O_2 increased the relative amount of Fe^{+2} and oxidized more HA. The immediate reaction of Fe^{+2} and H_2O_2 yields a burst of hydroxyl radicals that oxidizes HA. Consequently, there is more unoccupied surface area and pore volume remaining. The surface area reduction can be attributed to accumulation of other byproducts that leads to fouling of adsorption pores and, resulting in decrease of the adsorption capacity. To support this finding, in a study conducted by Hulling et al. on regeneration of activated carbon exhausted with MTBE, they pointed out that regenerating granular-activated carbon with Fenton resulted in about 10% reduction of surface area and nearly 9% reduction in adsorption capacity after two regeneration cycles [22]. Generally, decrease in adsorption capacity in each ratio occurred after successive cycles of regeneration which may be due to the deposition of decomposed residues within CNTs pores, which blocked the carbon porosity and decreased the S_{BET} [23].

4. Conclusion

In this study, the feasibility of Fenton regeneration of CNTs loaded with humic acid was investigated. The 2:10 M ratio of Fe^{2+}:H_2O_2 in Fenton solution was found to be more effective for regeneration of CNTs exhausted with humic acid. The RE reached 65.4% after five cycles of regeneration.

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