

Research Article

Removal of Natural Organic Matter (NOM) from Aqueous Solutions by Multi-Walled Carbon Nanotube Modification with Magnetic Fe₃O₄ Nanoparticles

Abbas Khodabakhshi ¹, Ayoub Riahi Farssani ², Morteza Sedehi ³
and Mehraban Sadeghi ¹

¹Department of Environmental Health Engineering, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran

²Environmental Health, Department of Environmental Health Engineering, Chaharmahal and Bakhtiari Province Water and Wastewater Company, Isfahan, Iran

³Statistics and Epidemiology Department, Shahrekord University of Medical Sciences, Shahrekord, Iran

Correspondence should be addressed to Ayoub Riahi Farssani; ayoubriahifarssani@yahoo.com

Received 28 December 2022; Revised 2 March 2023; Accepted 21 March 2023; Published 4 April 2023

Academic Editor: Sébastien Déon

Copyright © 2023 Abbas Khodabakhshi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Background and Aim. Natural organic matter (NOM) has become one of the most serious environmental problems due to its persistence in aqueous solutions and the risk of carcinogenesis. In this study, the removal efficiencies of real and synthetic humic acid (HA) by multi-walled carbon nanotubes (MWCNTs) coated with iron oxide were evaluated. **Materials and Methods.** The MWCNTs were synthesized and coated with iron oxide. In addition, the effects of pH, contact time, mixing speed, and adsorbent dose on the removal efficiency of NOM by MWCNTs-Fe₃O₄ were studied. Then, the removal efficiency of NOM from real samples was investigated at optimal conditions. The MWCNT-Fe₃O₄ was characterized by scanning electron microscopy (SEM) test and X-ray diffraction (XRD), respectively. Data analysis was performed using Minitab software based on the Taguchi method. **Results.** The results showed that MWCNTs were coated with Fe₃O₄. The SEM test shows particle (MWCNTs-Fe₃O₄) size in the range of 48–143 nm, and the particles have uniform spherical shapes. Enix software was used to identify the phase in this sample. The conditions including pH = 3, mixing speed = 120 rpm, adsorbent dosage = 1.5 g·L⁻¹, and contact time = 90 minutes were selected as optimal for NOM adsorption. The mean removal efficiencies of NOM in synthetic samples at 5, 10, and 20 mg·L⁻¹ concentrations were 86.6%, 84.87%, and 95.41%, respectively. In addition, the mean removal efficiency of NOM in Choghakhor Wetland was 77%. **Conclusion.** Our findings demonstrated that the MWCNTs-Fe₃O₄ can be potentially used as an adsorbent for removing natural organic matter (HA) from aqueous solutions.

1. Introduction

The general term for the combination of organic and partial water-soluble components is natural organic matter (NOM). Humic substances, which give natural waters their brownish-yellow hue, are considered the most common route for NOM in soil, sediments, and natural waters. NOM is primarily composed of non-humic fractions, such as carbohydrates, amino acids, and proteins, and humic fractions, such as humic acid (HA) and fulvic acid (FA). A

model structure for aquatic humic acid matter is shown in Figure 1 [1].

Natural organic matter (NOM), a complicated heterogeneous mixture of organic substances that is frequently found in all surface, ground, and soil waters, has had a negative effect on drinking water treatment. The presence of NOM causes numerous issues in the methods used to purify drinking water, and the characteristics and quantity of NOM can have a big impact on how effective these procedures are. NOM, in drinking water treatment, reacts with

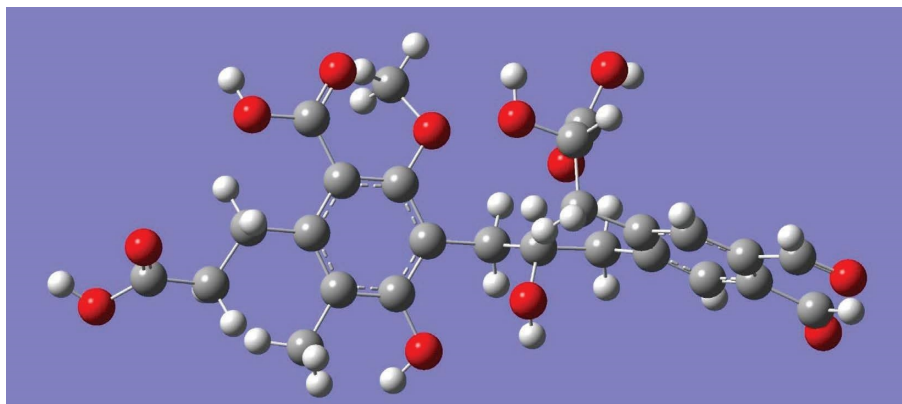


FIGURE 1: Hypothetical model structures of humic matter of aquatic environment.

disinfectants and increases the amount of disinfection by-products, affecting water quality in terms of taste, color, and odor [2].

Due to its distinct physical and chemical characteristics, humic acid (HA), a ubiquitous natural organic matter (NOM) generated from the remains of animals, plants, and microorganisms, has drawn significant attention from academics. The abundance of oxygen-containing functional groups found in HA, such as phenolic OH and COOH, may facilitate the complexation of heavy metals and metal oxides [3, 4].

The NOM is an important precursor for creating disinfection by-products (DBPs) [5]. The concentration of NOM in the surface water is about $2.47 \text{ mg}\cdot\text{L}^{-1}$ [6]. The presence of large amounts of such matter in water leads to the formation of trihalomethanes (THMs) and haloacetic acids (HAAs), which are suspected to be carcinogenic compounds. According to the EPA standards, the maximum concentration levels of THMs and HAAs are 80 and $60 \mu\text{g}\cdot\text{L}^{-1}$, and the goal values have been reduced to 40 and $30 \mu\text{g}\cdot\text{L}^{-1}$, respectively. The amount of NOM in water bodies depends on the climate, soil characteristics, and topography of the region [7]. The effects of NOM on the water include the creation of natural dyes, odor, and taste. In addition, the combination of NOM with inorganic substances can affect corrosion, stability, and alkalinity of water, increasing metal(loid) solubility in water. Moreover, during water treatment stages, NOM reacts with metal coagulants, chemical disinfectants, and oxidants, reducing the UV disinfectant and disturbing the adsorption and filtration processes [8].

The most common processes used to remove organic matter from drinking water are coagulation and flocculation, followed by sedimentation or flotation and finally filtration. Most of the NOM can be removed by coagulation and flocculation. However, low weight hydrophilic molecules can reduce the efficiency of the method compared to high weight hydrophobic molecules [9]. Other methods for removing NOM include ion exchange resins, activated carbon filtration, membrane filtration, and advanced oxidation processes. None of these methods can effectively remove all organic matter in water, except for the ion exchange resin technique, which can remove hydrophilic NOM [10].

NOM can be removed from drinking water using a variety of treatment methods, the most common and cost-effective of which are coagulation and flocculation, followed by sedimentation/flotation and sand filtration. Coagulation can remove the majority of NOM; however, the hydrophobic fraction and high molar mass compounds of NOM are removed more efficiently than the hydrophilic fraction and low molar mass compounds [11].

Coagulation is one of the most widely used water and wastewater treatment processes. The use of coagulation to remove NOM from drinking water supplies has piqued the interest of researchers all over the world because it is efficient and helps to avoid the formation of disinfection by-products (DBPs). Nonetheless, as NOM in water fluctuated more (concentration and composition), the efficiency of conventional coagulation was significantly reduced, necessitating the development of enhanced coagulation processes by optimizing operating conditions (primarily coagulant amount and pH), developing more efficient inorganic or organic coagulants, and coupling coagulation with other water treatment technologies [12, 13].

Carbon nanotubes are considered an alluring class of materials, which exhibit a wide range of unique qualities and have a wide range of uses. Oxidation, grafting with polymers, introducing magnetic particles, and hybridization with other materials can all be used to functionalize carbon nanotubes. Van der Waals forces, π - π stacking, hydrophobic contacts, hydrogen bonds, and electrostatic interactions are all part of the adsorption process. However, expense and hydrophobicity really limit practical usage [14, 15].

Recently, nanoparticles have been widely used in water treatment and purification. Carbon nanotubes (CNTs) are new adsorbents that were accidentally discovered by the Japanese scientist Ijima in 1991, and scientists found that CNTs can effectively remove dioxins, hydrogen, ammonium, ozone, nitrogen, and methane from the air, as well as cadmium, copper, zinc, fluoride, 1,2-dichlorobenzene, and THMs from water [16]. Also, Liu et al. proved that CNTs can also remove NOM from water efficiently [17]. The combination of the CNTs with iron oxide nanoparticles increases their adsorption capacity (more than carbon and activated carbon nanotubes). Separating the sorbent by a simple magnetic process is another advantage of this combination.

TABLE 1: Physical and chemical characteristics of wetland water.

Parameter	Unit of measure	Value (mean \pm SD)
pH	—	8.2 \pm 0.4
Color	TCU	140 \pm 15
Turbidity	NTU	32 \pm 6
Total hardness	mg·L ⁻¹ CaCO ₃	382 \pm 35
Alkalinity	mg·L ⁻¹ CaCO ₃	229 \pm 35
Sulfate	mg·L ⁻¹	27 \pm 9
Manganese	mg·L ⁻¹	0.021 \pm 0.015
Chloride	mg·L ⁻¹	59 \pm 5
Calcium	mg·L ⁻¹	98 \pm 10
Magnesium	mg·L ⁻¹	31 \pm 4
EC	μ S·cm ⁻¹	546 \pm 56
Iron	mg·L ⁻¹	0.51 \pm 0.1

Also, previous studies found that MWCNTs can decrease the pollutants from aqueous solutions and sediments [18–20]. Due to the presence of NOM in drinking water and its related problems, different methods have been used and proposed to remove these substances. As mentioned, the applied methods do not have the ability to remove the NOM effectively, and the implementation and operation of such methods is not economical [17]. However, the use of adsorbents is considered due to the simple operation and low energy consumption [21]. Among the different kinds of adsorbents, magnetic carbon nanotubes (MCNTs) have recently received a lot of attention due to their very high adsorption capacity. Moreover, the uncontrolled release of MWCNTs into the aquatic environment could have negative health effects as well as ecological issues. Consequently, the addition of magnetic nanoparticles to MWCNTs will modify them and create a substance that can be isolated from aqueous solutions using a magnetic field, keeping it out of the environment [18, 22].

Magnetic carbon nanotubes (MCNTs), composed of carbon nanotubes (CNTs) and magnetic nanoparticles (MNPs), have great application exploration potentials due to their superior physical and chemical properties, such as unique magnetism and high enrichment performance [23]. Because the adsorption of HA results in a polyanionic organic coating on Fe₃O₄, changing the surface characteristics, binding HA to Fe₃O₄ affects the sorption. According to reports, complex HA and Fe₃O₄ have a higher capacity for adsorbing metal cations than either HA or Fe₃O₄ alone [3, 24].

In this study, the adsorption rate of HA has been investigated by using multi-walled carbon nanotubes (MWCNTs) coated with iron oxide (Fe₃O₄). Also, influencing factors on the removal rate of HA such as pH, contact time, initial concentration of HA, adsorbent concentration, and mixing rate were studied.

2. Materials and Methods

2.1. Study Area. Choghakhor Wetland which is located in Chaharmahal and Bakhtiari Province was selected as the natural sampling site. The samples were taken by a combination method from different parts of the wetland (north, south, east, and west) with a distance of 10 and 0.5 meters

from the shore and depth, respectively [1]. Physical and chemical parameters include color, turbidity, pH, total hardness, total dissolved solids, total alkalinity, and electrical conductivity, and important ions such as sulfate, iron, manganese, carbonate, bicarbonate, chloride, calcium, magnesium, nitrate, nitrite, and phosphate were measured. In order to know the changes in the amount of natural organic matter (HA), sampling was done in different seasons. Table 1 shows the physical and chemical characteristics.

2.2. Chemicals and Reagents. The chemicals and reagents used for the study were of analytical grade and supplied by Merck and Sigma-Aldrich. The chemicals used in this study were MWCNTs, humic acid, ferrous, ferric chlorides, hydrochloric acid sodium hydroxide, and ethanol. Humic acids (Sigma-Aldrich, Germany) were used to prepare a synthetic solution containing a certain amount of natural organic compounds. Other chemicals such as NaOH, FeCl₃·6H₂O, HNO₃, and HCL were purchased from Merck, Germany. Also, a (0.1 N) sodium hydroxide (0.1 N) were used to adjust the pH. All the required solutions were prepared with deionized water. In order to clean the containers from any pollutants and residues, all the glass containers were washed with nitric acid (10%) overnight. All the synthetic and real sample experiments were done in triplicate. The amount of humic acids was measured using a spectrophotometer (DR5000, HAC, USA) at 254 nm, based on method 5910B of the standard method book.

2.3. Preparation and Oxidation of MWCNTs. The MWCNTs were produced by the chemical vapor deposition method. In order to purify and increase the removal efficiency, the nanotubes were oxidized in two steps. Initially, 5 g of non-oxidized MWCNTs was poured into 100 ml of nitric acid and was stirred for 12 hours at 70°C. After 12 hours, the solution was allowed to cool to the room temperature. Then, the mixture was passed through the fiberglass filter (cellulose nitrate, 0.45 μ), washed with deionized water, and placed in the oven at 63°C for 6 hours. The next step was to oxidize MWCNTs by refluxing 50% nitric acid at 120 C for 12 hours while stirring. Then, the final product was filtered, washed with double distilled water, and dried overnight in the oven [21, 22].

2.3.1. Synthesis of MWCNTs-Fe₃O₄. In order to prepare MWCNTs-Fe₃O₄, 11.92 g of ferric chloride (FeCl₃) and 4.4 g of ferrous chloride (FeCl₂) were dissolved in 600 mL of deionized water, and then 4 g of oxidized MWCNTs was added and shaken for 2 hours, at 70°C. After cooling, the pH was slowly increased using sodium hydroxide (5 M) and the process was continued until deposit was observed at the bottom of the container. The product was separated by magnet and then washed by distilled water and ethanol, respectively. The magnetization of the product can be defined according to the following equation:



It is known that produced iron oxide is in the form of Fe_3O_4 . The achieved mixture was dried in an oven at 100°C for 2 hours [22, 25–27].

2.3.2. Batch Adsorption of NOM by MWCNTs- Fe_3O_4 . Stock solution of natural organic matter (HA) ($5, 10, \text{ and } 20 \text{ mg}\cdot\text{L}^{-1}$) was prepared by mixing a known amount of humic acid (HA). These concentrations were selected due to their proximity to the concentrations of NOM in wetlands and contaminated sources of drinking water. Then, the removal of HA was investigated at pH 3, 5, 7, and 9 and contact times of 20, 40, 60, and 90 minutes with a mixing speed of 60, 80, 100, and 120 rpm. Also, 0.02, 0.05, 0.1, and 0.15 g of MWCNTs- Fe_3O_4 as the adsorbent were added in the bottles, which contained 100 mL NOM solutions. Then, the containers were covered with aluminum foil and placed on a rotating shaker and were shaken to ensure that the adsorption process was balanced. At the desired intervals, solution samples were taken and passed through a $0.45 \mu\text{m}$ filter. The residual HA as a natural organic matter (NOM) in solutions was measured by a TOC analyzer [28].

2.3.3. Design of Experiments. In this study, Taguchi's method was used to design experiments. Taguchi method were used to analyze the data and to determine the optimum conditions of the test. The criterion for selecting the parameter as the optimal signal to noise ratio (S/N) is more in Taguchi analysis. The method of calculating the S/N ratio will be different according to the type of goal optimization.

Considering that in this study, the percentage of humic acid removal is considered as the response, the goal is to maximize the response. The S/N ratio is calculated as equation (2). To investigate the effect of the factors and determine the optimal conditions for the removal of NOM, four factors consisting of time, pH, adsorbent concentration, and mixing speed were considered at four levels. After analyzing the relevant data and determining the optimal condition, real samples were tested three times at optimal conditions without pH manipulation. Data were analyzed using Minitab software and the Taguchi method. The following equations were used to calculate the S/N.

$$\frac{S}{N} \text{ (signal to noise)} = -\log(\text{MSD}), \quad (2)$$

$$\text{MSD} = \frac{1/Y_1^2 + 1/Y_2^2 \dots + 1/Y_n^2}{n}, \quad (3)$$

where MSD is the minimum average square of standard deviations, Y_n represents the percentage of NOM removal, and n represents the number of samples. The experiments designed with 16 modes with different conditions are shown in Table 2.

Considering that the aim of the study was to estimate the optimal values of the factors in three concentrations of 5, 10,

and 20 mg per liter separately, for each of the three mentioned concentrations, the mean graphs and signal-to-noise ratio were presented. Taguchi method experiments are presented in Figure 2. The results of the removal percentage for these three concentrations (5, 10, and 20 mg/liter) are shown in Tables 3–5, respectively.

3. Results and Discussion

3.1. Characteristics of Nanotubes Modified with Iron Oxide. Highscore plus X'Pert software was used to identify the phase. Based on Figure 3, it is clear that in this sample, a weak and relatively wide peak can be seen at an angle about 26° , which is related to the diffraction of plates (002) of carbon nanotubes. Also, by matching the rest of the extreme peaks with the reference codes, it has been determined that these peaks are related to the crystal structure of Fe_3O_4 with reference code JCPDS No. 96-900-2320 has a cubic crystal structure and space group Fd-3m. In this structure, diffraction planes (220), (311), (400), (422), (511), (440), (135), and (301) are at angles $30.1^\circ, 35.7^\circ, 43.2^\circ, 53.9^\circ, 57.1^\circ, 62.9^\circ, 66.4^\circ, \text{ and } 75.3^\circ$ are observed respectively.

These results indicate the complete surface modification of carbon nanotubes by magnetite nanoparticles so that X-rays could not completely pass through the magnetite shell on these nanotubes, and only a very weak peak of these carbon nanotubes was detected. The Rietveld method and MAUD software have been used to examine small quantities related to this sample. This method is a technique proposed by Hugo Rietveld for use in the identification of crystalline materials. In this technique, the height, width, and position of each peak in its X-ray diffraction pattern can be used to determine many structural aspects of the material. The Rietveld technique, in order to fit the theoretical values on the measured values, uses the least squares method [29, 30]. The results of this method are shown in Figure 4.

Based on Figure 4, it is observed that the laboratory analysis results are acceptable, matching with Rietveld analysis result. This confirms the reliability of the results of this analysis. According to this analysis, the crystal size for the magnetite phase is 17.85 nm, the microstrain is 0.005%, and the lattice parameter is 8.348 angstroms.

Based on SEM results of carbon nanotube particles, the diameters of raw CNTs were varying from $0.2 \mu\text{m}$ to $1.97 \mu\text{m}$ with an average diameter of $0.65 \mu\text{m}$; the histogram shows that about 87% of the particles have a diameter of less than 1 micrometer and about 13% of the particles have a diameter between 1 and 2 micrometers. According to the analyzed shape and the resulting histogram with the help of Anix software, it is quite evident that the particles are cylindrical in shape with specific dimensions or multi-faceted in terms of their length (Figures 5 and 6(a)).

Analysis of MWCNTs- Fe_3O_4 by SEM confirmed the presence of iron oxide nanoparticles on the surface of MWCNTs- Fe_3O_4 . Based on the 102 investigated particles, the diameters of MWCNTs- Fe_3O_4 were varying from 48 nm to 143 nm with an average diameter of 77 nm, and the histogram shows that about 79% of the particles have a diameter of less than 88 nm and about 17% of the particles have a size less than

TABLE 2: Experimental variables according to the Taguchi method.

Number of sample	pH	Mixing time (min)	Mixing speed (min)	NT concentration (g·L ⁻¹)
1	3	20	60	0.2
2	3	40	80	0.5
3	3	60	100	1
4	3	90	120	1.5
5	5	20	80	1
6	5	40	60	1.5
7	5	60	120	0.2
8	5	90	100	0.5
9	7	20	100	1.5
10	7	40	120	1
11	7	60	60	0.5
12	7	90	80	0.2
13	9	20	120	0.5
14	9	40	100	0.2
15	9	60	80	1.5
16	9	90	60	1

108 nm. According to the analyzed shape and the resulting histogram with the help of Anix software, it is quite evident that the particles have uniform spherical shapes in terms of morphology (Figures 5 and 6(b)). The comparison of two SEM images shows that adding iron oxide to the sample changes the morphology and average particle size from 650 nm to 77 nm. Therefore, we can claim that the sample has become nanosized after adding iron oxide. Figure 5. shows the SEM images of raw nanotubes and coated with iron particles with low and high magnification in (a, b, c, d), respectively. Also, images (e) and (f) show the particle size of raw and coated nanotubes, respectively.

3.2. Results of Batch Experiments. The results of experiments performed at concentrations of 5, 10, and 20 mg·L⁻¹ of humic acid are shown in Tables 3–5, respectively. According to the obtained results, the highest percentage of HA removal in concentrations of 5, 10, and 20 mg·L⁻¹ was 86.6%, 84.87%, and 95.41%, respectively, at the same conditions (pH = 3, mixing time: 90 minutes, mixing speed: 120 rpm, and absorbent concentration: 1.5 g·L⁻¹). The highest removal percentage was obtained at a concentration of 20 mg·L⁻¹ of HA.

All of the synthetic samples were tested at optimal conditions. The mean removal percentage of HA in synthetic samples at optimal conditions is shown in Table 6. Based on the obtained results, as shown in Table 6, the mean percentage of HA removal at optimal conditions in synthetic and real samples was 83%. Also, all real samples were tested under optimal conditions. The average removal percentage of HA in real samples in optimal conditions was 76.9 ± 5.46%.

Experiments demonstrated that MWCNTs-Fe₃O₄ can adsorb NOM from water to an acceptable level. Consistent with our results, Hyung and Kim revealed that hydrophobic NOM removal by nanocarbon tubes is described as a dominant and effective mechanism [31]. Multi-walled carbon nanotubes are capable of NOM removal at any degree of hydrophobicity and molecular weight [32]. Yang et al. found that oxidized MWCNTs were appropriate adsorbents for solidification and preconcentration of Ni (II) from aqueous solutions [33].

3.3. Effect of pH on the Removal Efficiency. The removal of NOM by MWCNTs-Fe₃O₄ was studied by evaluating it at different pH values of 3, 5, 7, and 9, as shown in Figure 2. Based on our findings, the highest removal efficiency was observed at pH = 3. Hence, with the increase of pH from 3 to 9, the NOM removal rate was decreased. As known, NOM is a non-uniform mixture of organic compounds that enters the water through the decomposition of plants, animal bodies, living and dead microorganisms, and waste products. Generally, NOM molecules are large and have many functional groups that affect their chemical behavior. The electric charge of these functional groups changes with pH variation [1, 22].

On the other hand, oxidized MWCNTs were reported to have a point of zero charge (PZC) of about 4 [34, 35]. It consequently becomes protonated and exhibits a positive net charge on its surface when it is dissolved in aqueous solutions with pH values lower than its PZC = 4, suggesting that it may effectively adsorb NOM. The net surface charge, however, changes negatively when dissolved in solutions above PZC = 4 due to deprotonation, making it incapable of adsorbing negatively charged NOM [3, 21, 24, 34, 35].

Yin et al. stated that acidic pH increases the acidic functional groups on the carbon surface and changes the oxygen species. The acidic functional groups include carboxyl, quinone, and carboxylic form at low pH on the carbon surface [36]. When the pH of the solution is high, the electrostatic forces in the NOM increase and may reduce its density and thereby adsorption capacity [37], and it refers to more repulsion of the charge. In addition, with increasing pH, in weakly acidic NOM with carboxylic and phenolic moieties, the negative charge increases. Therefore, repulsion between NOM and MWCNTs would increase and prevent further NOM adsorption [28]. Previous studies have also stated that at lower pH, the removal efficiency is higher [31, 32].

3.4. Effect of Mixing Rate on the Removal Efficiency. As shown in Figure 2, the effect of agitation speed on the adsorption capacity of NOM was investigated by varying the agitation

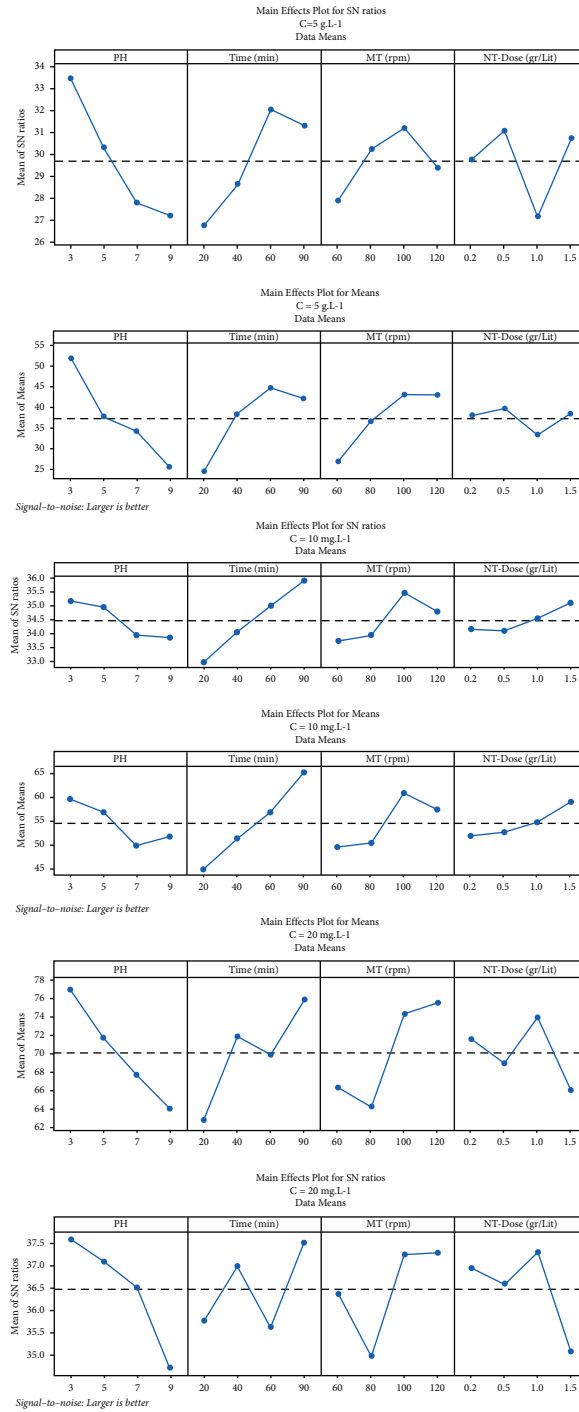


FIGURE 2: Optimal conditions for NOM (HA) removal at different concentrations of HA using the Taguchi method.

speed from 60 to 120 rpm. The percentage of NOM removed has been seen to slightly increase with increased agitation speed. At the concentration of 5 mg.L⁻¹ of NOM, when the mixing rate increases to 100 rpm, at first the NOM removal efficiency increases, and then it decreases. Similar results for concentrations of 10 and 20 mg.L⁻¹ were obtained. Nonetheless, at the concentration of 20 mg.L⁻¹, the removal efficiency slightly increased with the increase of mixing speed. In fact, the speed of 100 rpm at concentrations of 5 and

10 mg.L⁻¹ is optimal while at 20 mg.L⁻¹, 100 and 120 rpm were the best. In a study done by Gupta et al., it was revealed that the adsorption of Cr (III) was decreased at lower mixing speed [21]. It seems that increasing the mixing speed reduces the boundary layer and the strength of the surrounding layer of the adsorbent and makes the mass transfer easier. At low mixing speeds, the mixing operation is not done well. Contact between nanoparticles and contaminants is also reduced, which in turn reduces efficiency. In accordance

TABLE 3: Removal percentage of natural organic matter at a concentration of 5 mg·L⁻¹.

Number of sample	pH	Mixing time (min)	Mixing speed (rpm)	NT concentration (g·L ⁻¹)	Removal efficiency of NOM (%)	
					First repetition	Second repetition
1	3	20	60	0.2	61.11	47.36
2	3	40	80	0.5	73.70	59.48
3	3	60	100	1	84.94	84.78
4	3	90	120	1.5	90.29	95.41
5	5	20	80	1	73.16	62.13
6	5	40	60	1.5	67.27	70.71
7	5	60	120	0.2	79.05	77.55
8	5	90	100	0.5	75.30	63.95
9	7	20	100	1.5	65.93	55.32
10	7	40	120	1	63.26	78.21
11	7	60	60	0.5	75.84	65.21
12	7	90	80	0.2	74.50	65.21
13	9	20	120	0.5	73.70	48.54
14	9	40	100	0.2	66.74	92.21
15	9	60	80	1.5	70.48	21.24
16	9	90	60	1	73.35	66.42

TABLE 4: Removal efficiency of natural organic matter (HA) at a concentration of 10 mg·L⁻¹.

Number of sample	pH	Mixing time (min)	Mixing speed (rpm)	NT concentration (g·L ⁻¹)	Removal efficiency of NOM (%)	
					First repetition	Second repetition
1	3	20	60	0.2	19.4	35.12
2	3	40	80	0.5	62.2	60.25
3	3	60	100	1	57.9	50.78
4	3	90	120	1.5	55.8	86.6
5	5	20	80	1	15.1	45.21
6	5	40	60	1.5	29	20.12
7	5	60	120	0.2	71.8	35.12
8	5	90	100	0.5	52.6	60.21
9	7	20	100	1.5	19.4	41.35
10	7	40	120	1	9.7	60.12
11	7	60	60	0.5	41.9	25.21
12	7	90	80	0.2	48.3	15.31
13	9	20	120	0.5	18.3	10.36
14	9	40	100	0.2	47.2	40.65
15	9	60	80	1.5	33.3	15.65
16	9	90	60	1	16.2	17.21

with our finding, previous studies have proved that as the mixing speed increases, the removal efficiency improved [38, 39].

3.5. Effect of Adsorbent Dose on the Removal Efficiency.

Adsorbent dosage has an important effect on absorption capacity. The removal efficiency of NOM at different concentrations of adsorbent ranging from 0.2 to 1.5 g·L⁻¹ at an optimal condition was examined. The results showed that the effect of adsorbent dose on the removal efficiency at different concentrations of NOM was different. At a concentration of 5 mg·L⁻¹, initially with increasing amount of carbon nanotubes from 0.2 to 0.5 g·L⁻¹, the adsorption capacity increased, and the maximum adsorption occurs at a concentration of 0.5 g·L⁻¹. Also, by increasing the adsorbent dose from 0.5 to 1 g·L⁻¹, the removal efficiency of NOM was increased. Figure 2 shows the effect of adsorbent dose on the removal efficiency of NOM. Although increasing

the adsorbent dose increases the removal efficiency of NOM, due to the desaturation of some active pores on the adsorbent surface and the lack of use of its maximum capacity, the adsorption per unit mass of the adsorbent decreases. Also, increasing the amount of adsorbent can cause turbidity and thus reduce the efficiency of the treatment [40]. It seems that different conditions such as aggregation of nanotubes affect the amount of added nanotubes and the removal efficiency. Hence, it was revealed that when carbon nanotubes accumulate in solution and form bands, the removal efficiency of NOM decreases due to lower level of adsorption capacity. Also, in the presence of glucose, accumulation of these nanomaterials usually occurs [41]. This is as a result of the faster agitation speed improving the diffusion of NOM toward the adsorbents' surface.

3.6. Effect of Contact Time on the Removal Efficiency.

The adsorption behavior of HA by MWCNTs-Fe₃O₄ was

TABLE 5: Removal percentage of natural organic matter at a concentration of 20 mg·L⁻¹.

Number of sample	pH	Mixing time (min)	Mixing speed (rpm)	NT concentration (g·L ⁻¹)	Removal efficiency of NOM (%)	
					First repetition	Second repetition
1	3	20	60	0.2	43.6	45.65
2	3	40	80	0.5	50.6	50.63
3	3	60	100	1	63.9	62.21
4	3	90	120	1.5	86.4	84.87
5	5	20	80	1	46.8	55.17
6	5	40	60	1.5	47.9	48.21
7	5	60	120	0.2	59.1	50.12
8	5	90	100	0.5	75.2	73.31
9	7	20	100	1.5	42.5	49.91
10	7	40	120	1	48.4	55.87
11	7	60	60	0.5	50.6	55.74
12	7	90	80	0.2	49	48.42
13	9	20	120	0.5	40.9	34.93
14	9	40	100	0.2	50.6	69.32
15	9	60	80	1.5	62.9	50.21
16	9	90	60	1	64.5	41.00

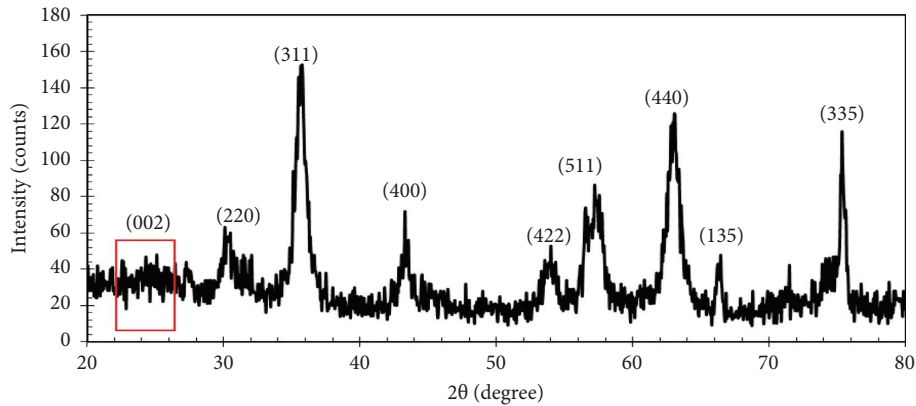


FIGURE 3: X-ray diffraction pattern of surface-modified carbon nanotubes by nanomagnetite.

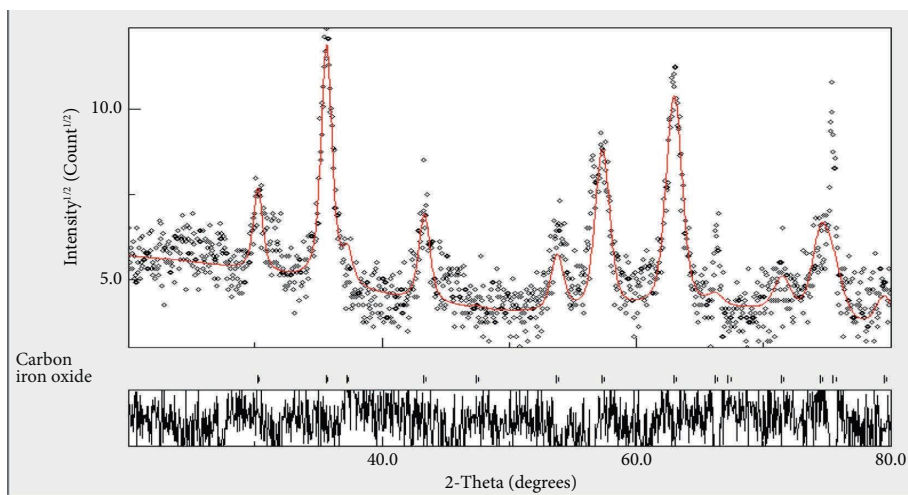


FIGURE 4: Calculation of quantitative values obtained by X-ray test using Rietveld method for carbon nanotube samples modified with nanomagnet surface.

evaluated in relation to the effect of contact time by changing the equilibrium time from 20 minutes to 90 minutes at a concentration of HA of 5, 10, and 20 mg·L⁻¹, adsorbent

dose of 1.5 g·L⁻¹, and pH 3. As shown in Figure 2, with increasing contact time, the amount of adsorbed NOM onto MWCNTs-Fe₃O₄ increased at all concentrations. At the

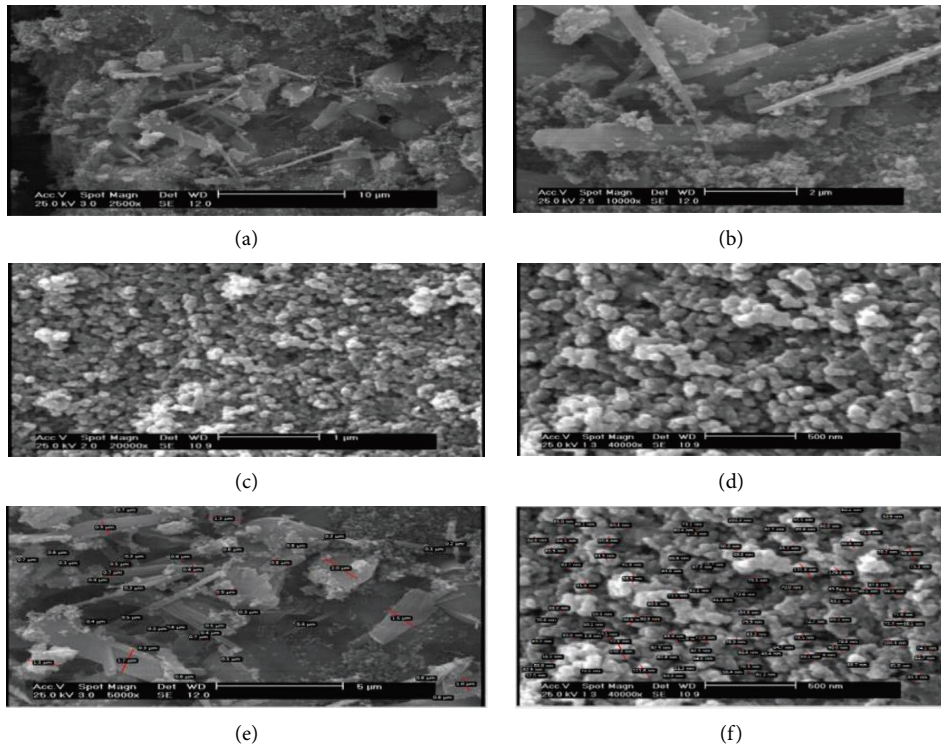


FIGURE 5: SEM images of low magnification MNCNTs (a) and high magnification MNCNTs (b). SEM images of low magnification MNCNTs/Fe₃O₄ (c) and high magnification MNCNTs/Fe₃O₄ (d). SEM images showing the size of the particles of MWCNTs (e) and MWCNTs-Fe₃O₄ (f).

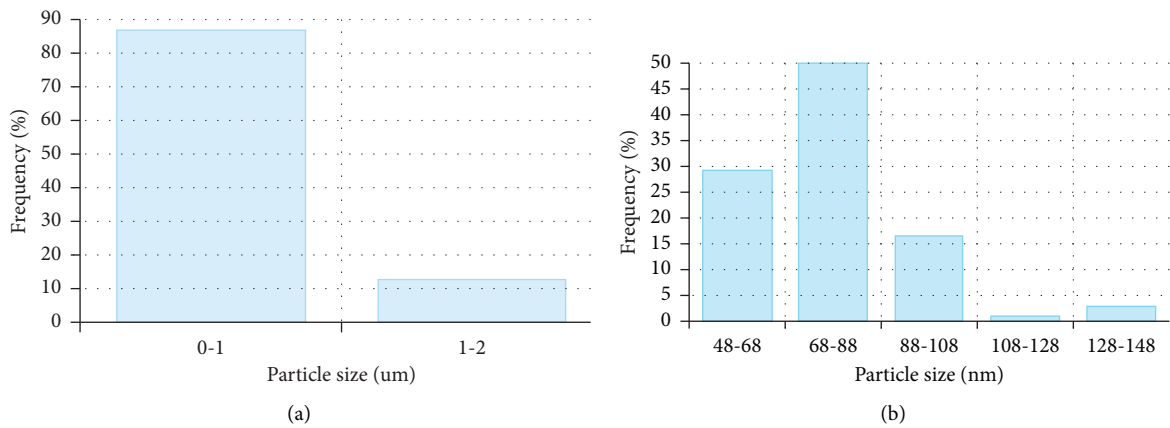


FIGURE 6: Histogram of carbon nanotubes (a) before and (b) after coating with MWCNTs-Fe₃O₄.

TABLE 6: Removal percentage of HA in synthetic samples at optimal conditions.

NOM concentration (HA) (mg·L ⁻¹)	pH	Contact time (min)	Mixing speed (rpm)	NT concentration (g·L ⁻¹)	Mean ± SD* (%)
5	3	60	100	0.5	66.1 ± 8.2
10	3	90	100-120	1.5	82.3 ± 8.66
20	3	90	100	1	64.4 ± 7.3

*Repeated in triplicate.

concentration of 5 mg·L⁻¹ of HA, the efficiency of organic matter removal initially increases and then slightly decreases up to 60 minutes. The percentage removal was enhanced

a little when the contact time was increased from 60 to 90 minutes. At concentrations of 10 and 20 mg·L⁻¹ of HA, with increasing contact time, the removal efficiency also

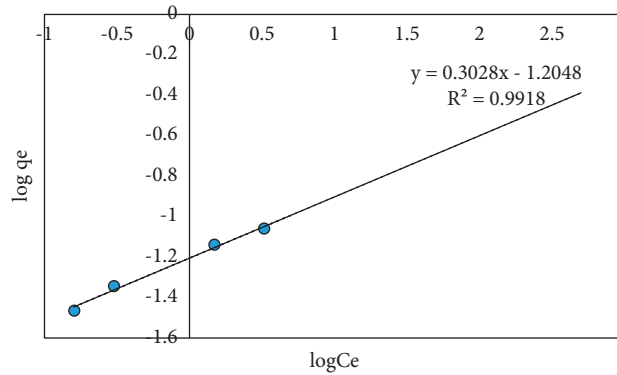


FIGURE 7: Freundlich isotherms for the as-produced MWCNTs-Fe₃O₄.

increased [11, 21]. No further increase in removal efficiency with time was observed for MWCNTs-Fe₃O₄ after 90 min. Naghizadeh et al. have shown that with increasing contact time, adsorption of HA by CNTs increased [28].

3.7. Adsorption Isotherms. Adsorption isotherm is one of the important factors in designing the adsorption systems. This parameter is a key factor in determining the capacity of an adsorbent and optimizing the adsorbent consumption. In this study, Langmuir and Freundlich adsorption isotherms were used to investigate the adsorption mechanism [22, 26, 27, 42]. Linear equation of the Langmuir isotherm is given in the following equation:

$$\frac{C_e}{q_e} + \frac{1}{q_m \times b} + \frac{C_e}{q_m}, \quad (4)$$

where q_e is the amount of adsorbent per unit mass of adsorbent in $\text{mg}\cdot\text{g}^{-1}$, C_e is the equilibrium concentration of the adsorbent in the solution after adsorption in $\text{mg}\cdot\text{L}^{-1}$, and q_m is the Langmuir constant obtained in the curve (C_e/q_e) vs. C_e . The linear equation of the Freundlich isotherm is as follows:

$$\text{Log}q_e - \text{Log}k_f = \frac{1}{n}\text{Log}C_e, \quad (5)$$

where q_e is the adsorption capacity at equilibrium in $\text{mg}\cdot\text{g}^{-1}$, C_e is the equilibrium concentration of the adsorbent in $\text{mg}\cdot\text{L}^{-1}$, and K_f and n are the Freundlich constants obtained in the curve $\text{log}q_e$ vs. $\text{log}C_e$, [26, 27]. By plotting of $\text{log}q_e$ vs. $\text{log}C_e$ (Figure 7) yields very good straight lines (correlation coefficient, $R^2 = 0.991$). Adsorption isotherm models were performed for MWCNTs-Fe₃O₄ at pH = 3, contact time 90 min, adsorbent amounts 0.2–1.5 g per 100 mL, NOM concentration of $5 \text{ mg}\cdot\text{L}^{-1}$, at 25°C. The results showed that Freundlich and Langmuir adsorption models had ($R^2 = 0.989$), and the maximum adsorption of $4.2 \text{ mg}\cdot\text{g}^{-1}$ and ($R^2 = 0.991$) and maximum adsorption of $0.060 \text{ mg}\cdot\text{g}^{-1}$, respectively (Table 7 and Figures 7 and 8).

When the Langmuir and Freundlich isotherms are compared, the Freundlich isotherm has a better fitting model with a higher correlation coefficient ($R^2 = 0.9918$) than the

Langmuir isotherm ($R^2 = 0.9897$). Because MWCNTs-Fe₃O₄ have a larger surface area for metal adsorption, this indicates the applicability of monolayer coverage of NOM on the adsorbent's surface. The high Freundlich isotherm correlation coefficient also indicates that NOM is strongly adsorbed to the surface of MWCNTs-Fe₃O₄. As a result, it has been demonstrated that MWCNTs-Fe₃O₄ have a high potential for use as an adsorbent for the removal of NOM in water.

3.8. Adsorption Process Using Magnetic Composite. Magnetic composites have a redox mechanism and biodegradation to remove organic pollutants. One of the proposed mechanisms for pollutant adsorption by magnetic carbon nanotubes is the π - π interaction between sp^2 hybridized carbon atoms of carbon nanotubes and the aromatic backbone of organic materials. Another is the increased diffusion of organic matter on the surface of CNTs because of their large surface area and pore volume. Anionic matter interacts electrostatically with positively charged functional groups on the CNT surface, and cationic matter interacts electrostatically with negatively charged functional groups on the CNT surface. The elimination of organic contaminants with aromatic skeletons is facilitated by π - π interaction with the π -electron rich CNTs [14, 43] (Figure 9).

Magnetic carbon nanotubes (MCNTs), which are composed of carbon nanotubes (CNT) and magnetic nanoparticles (MNPs), have great exploration and application potential due to their superior physical and chemical properties, such as distinct magnetism and high enrichment performance [23].

Magnetite is an amphoteric solid, which can develop charges in the protonation and deprotonation reaction of Fe-OH sites on surface. This process is controlled by the pH and ion strength in aqueous medium. At pH lower than the PZC (pH < 7.9), the surface charge is positive, and electrostatic interaction between HA and Fe₃O₄ is dominant under acidic conditions [3, 44].

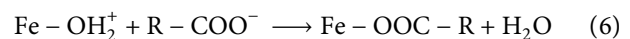
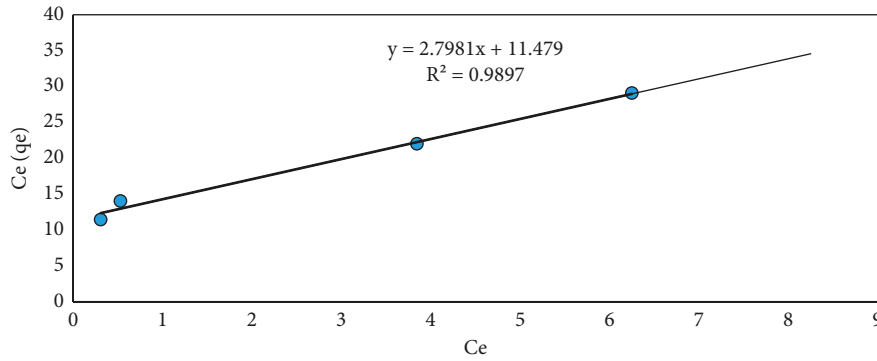
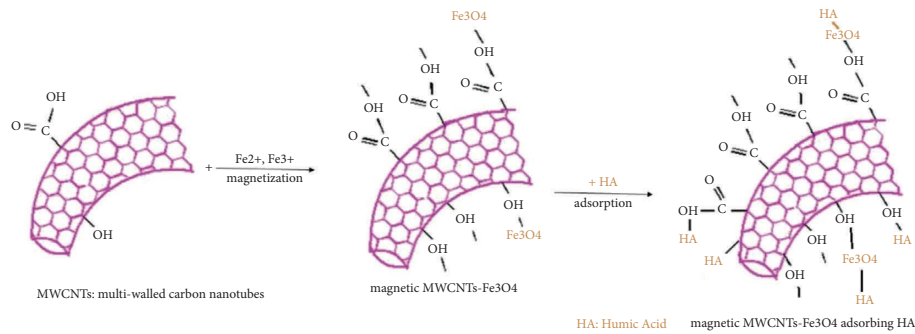


TABLE 7: Fixed and correlation coefficients of Langmuir and Freundlich isotherm models for NOM.

Isotherms	Isotherm equations	Fixed coefficients and correlation coefficients of isotherms		
Langmuir	$1/q_e = 1/q_m k_L C_e + 1/q_m$	q_m (mg·g ⁻¹) 4.2	K_L 0.087	R^2 0.989
Freundlich	$\text{Log } q_m = \text{Log } K_f + 1/n \text{ Log } C_e$	K_f 0.060	n 3.7037	R^2 0.991

FIGURE 8: Langmuir isotherms for the as-produced MWCNTs-Fe₃O₄.FIGURE 9: Illustration of the adsorption mechanism of HA on the composite MWCNTs-Fe₃O₄.

4. Conclusion

MWCNTs were utilized for activated carbon preparation, and then Fe₃O₄ magnetic nanoparticles were embedded on MWCNT adsorbent by the impregnation method for removing HA from aqueous solution. The prepared nanocomposite was characterized by techniques such as SEM and XRD. The results confirmed the correct formation of MWCNTs-Fe₃O₄ nanocomposite. According to this analysis, the crystal size for the magnetite phase is 17.85 nm, the microstrain is 0.005%, and the lattice parameter is 8.348 angstroms.

The Taguchi method was found to be a valuable tool to find optimal conditions for removing HA. The carbon nanotubes' modification with iron oxide (MWCNTs-Fe₃O₄) with a high removal efficiency and perfect magnetic separation performance was examined by considering influencing parameters including the initial concentration, mixing rate, contact time, adsorbent dosage, and pH. The present study demonstrated that HA removal using MWCNTs-Fe₃O₄ increases as both the adsorbent dosage and contact time increase. When the agitation speed was

increased from 60 to 120 rpm, the percentage uptake increased slightly, with 120 rpm producing slightly higher removal for HA. The optimum conditions for the present research were determined, including pH = 3, contact time = 90 min, mixing rate: 120 rpm, and adsorbent dosage = 1.5 g·L⁻¹. The removal efficiencies of synthetic HA at 5, 10, and 20 mg·L⁻¹ concentrations were 86.6%, 84.87%, and 95.41%, respectively. Also, the removal efficiency of actual HA from Choghakhor Wetland was obtained at 77%. The results of this study indicated that MWCNTs-Fe₃O₄ nanocomposite could be satisfactorily used for removing HA from aqueous environments due to high adsorption and easy and quick separation.

Nomenclature

NOM:	Natural organic matter
HA:	Humic acid
EPA:	Environmental Protection Agency
DBPs:	Disinfection by-products
XRD:	X-ray diffraction (XRD)
SEM:	Scanning electron microscopy

FA:	Fulvic acid
THMs:	Trihalomethanes
MNPs:	Magnetic nanoparticles
MWCNTs:	Multi-walled carbon nanotubes
S/N:	Signal to noise
MSD:	Minimum average square of standard deviations
NT:	Nanotube
PZC:	Point of zero charge
HAAs:	Haloacetic acids.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors thank the vice Chancellery for Research of Shahrekord University of Medical Sciences for financially support of the study (Grant No.:1573).

References

- [1] J. Edzwald, *Water Quality & Treatment: A Handbook on Drinking Water*, McGraw-Hill Education, New York, NY, USA, 2011.
- [2] Y. Zhang, X. Zhao, X. Zhang, and S. Peng, "A review of different drinking water treatments for natural organic matter removal," *Water Supply*, vol. 15, no. 3, pp. 442–455, 2015.
- [3] Q. Du, S. Zhang, J. Song, Y. Zhao, and F. Yang, "Activation of porous magnetized biochar by artificial humic acid for effective removal of lead ions," *Journal of Hazardous Materials*, vol. 389, Article ID 122115, 2020.
- [4] M. Liu, W. Chen, M. Ding et al., "Removal of humic acid from aqueous solution by a carbon nanotubes/reduced graphene oxide composite hydrogel," *Desalination and Water Treatment*, vol. 253, pp. 122–137, 2022.
- [5] H.-C. Kim and M.-J. Yu, "Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control," *Water Research*, vol. 39, no. 19, pp. 4779–4789, 2005.
- [6] M. Zazouli, "Determination of hydrophobic and hydrophilic fractions of natural organic matter in raw water of Jalalieh and Tehranspars water treatment plants (Tehran)," *Journal of Applied Sciences*, vol. 7, no. 18, pp. 2651–2655, 2007.
- [7] R. Fabris, C. W. Chow, M. Drikas, and B. Eikebrokk, "Comparison of NOM character in selected Australian and Norwegian drinking waters," *Water Research*, vol. 42, no. 15, pp. 4188–4196, 2008.
- [8] V. Naddeo, V. Belgiorno, and R. M. Napoli, "Behaviour of natural organic matter during ultrasonic irradiation," *Desalination*, vol. 210, no. 1–3, pp. 175–182, 2007.
- [9] J. G. Jacangelo, J. DeMarco, D. M. Owen, and S. J. Randtke, "Selected processes for removing NOM: an overview," *Journal of the American Water Works Association*, vol. 87, no. 1, pp. 64–77, 1995.
- [10] A. Matilainen, E. T. Gjessing, T. Lahtinen, L. Hed, A. Bhatnagar, and M. Sillanpää, "An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment," *Chemosphere*, vol. 83, no. 11, pp. 1431–1442, 2011.
- [11] A. Matilainen, M. Vepsäläinen, and M. Sillanpää, "Natural organic matter removal by coagulation during drinking water treatment: a review," *Advances in Colloid and Interface Science*, vol. 159, no. 2, pp. 189–197, 2010.
- [12] H. Dayarathne, M. J. Angove, R. Aryal, H. Abuel-Naga, and B. Mainali, "Removal of natural organic matter from source water: review on coagulants, dual coagulation, alternative coagulants, and mechanisms," *Journal of Water Process Engineering*, vol. 40, Article ID 101820, 2021.
- [13] D. Ghernaout, N. Elboughdiri, S. Ghareba, and A. Salih, "Coagulation process for removing algae and algal organic matter—an overview," *OALib*, vol. 7, no. 4, pp. 1–21, 2020.
- [14] F. Mashkoo, A. Nasar, and Inamuddin, "Carbon nanotube-based adsorbents for the removal of dyes from waters: a review," *Environmental Chemistry Letters*, vol. 18, no. 3, pp. 605–629, 2020.
- [15] Z. Kang, X. Jia, Y. Zhang et al., "A review on application of biochar in the removal of pharmaceutical pollutants through adsorption and persulfate-based AOPs," *Sustainability*, vol. 14, no. 16, Article ID 10128, 2022.
- [16] M. I. Kandah and J.-L. Meunier, "Removal of nickel ions from water by multi-walled carbon nanotubes," *Journal of Hazardous Materials*, vol. 146, no. 1–2, pp. 283–288, 2007.
- [17] F. F. Liu, J. L. Fan, S. G. Wang, and G. H. Ma, "Adsorption of natural organic matter analogues by multi-walled carbon nanotubes: comparison with powdered activated carbon," *Chemical Engineering Journal*, vol. 219, pp. 450–458, 2013.
- [18] P. Xu, M. Chen, G. Zeng et al., "Effects of multi-walled carbon nanotubes on metal transformation and natural organic matters in riverine sediment," *Journal of Hazardous Materials*, vol. 374, pp. 459–468, 2019.
- [19] H. Sadegh, G. R. Shahryari, A. Masjedi, Z. Mahmoodi, and M. Kazemi, "A review on carbon nanotubes adsorbents for the removal of pollutants from aqueous solutions," *International Journal of Nano Dimension*, vol. 7, 2016.
- [20] A. Khodabakhshi and H. Asgarian, "Removal of mercury (II) from aqueous solutions by multiwalled carbon nanotubes coated with manganese oxide," *Journal of Shahrekord University of Medical Sciences*, vol. 21, no. 6, pp. 258–264, 2019.
- [21] V. Gupta, S. Agarwal, and T. A. Saleh, "Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes," *Water Research*, vol. 45, no. 6, pp. 2207–2212, 2011.
- [22] T. J. Al-Musawi, N. Mengelzadeh, F. Ganji, C. Wang, and D. Balarak, "Preparation of multi-walled carbon nanotubes coated with CoFe₂O₄ nanoparticles and their adsorption performance for Bisphenol A compound," *Advanced Powder Technology*, vol. 33, no. 2, Article ID 103438, 2022.
- [23] J. Guo, H. Jiang, Y. Teng et al., "Recent advances in magnetic carbon nanotubes: synthesis, challenges and highlighted applications," *Journal of Materials Chemistry B*, vol. 9, no. 44, pp. 9076–9099, 2021.
- [24] Y. Ai, C. Zhao, L. Sun, X. Wang, and L. Liang, "Coagulation mechanisms of humic acid in metal ions solution under different pH conditions: a molecular dynamics simulation," *Science of the Total Environment*, vol. 702, Article ID 135072, 2020.
- [25] M. Yegane Badi, A. Azari, H. Pasalari, A. Esrafil, and M. Farzadkia, "Modification of activated carbon with

- magnetic Fe₃O₄ nanoparticle composite for removal of ceftriaxone from aquatic solutions,” *Journal of Molecular Liquids*, vol. 261, pp. 146–154, 2018.
- [26] A. Khodabakhshi, M. Amin, and M. Mozaffari, “Synthesis of magnetite nanoparticles and evaluation of its efficiency for arsenic removal from simulated industrial wastewater,” *Iranian Journal of Environmental Health Science & Engineering*, vol. 8, no. 3, pp. 189–200, 2011.
- [27] A. Khodabakhshi, F. Mohammadi-Moghadam, K. Shakeri, and S. Hemati, “Equilibrium and thermodynamic studies on the biosorption of lead (II) by living and nonliving biomass of *penicillium notatum*,” *Journal of Chemistry*, vol. 2022, Article ID 3109212, 9 pages, 2022.
- [28] A. Naghizadeh, S. Nasser, A. M. Rashidi, R. Rezaei Kalantary, R. Nabizadeh, and A. H. Mahvi, “Adsorption kinetics and thermodynamics of hydrophobic natural organic matter (NOM) removal from aqueous solution by multi-wall carbon nanotubes,” *Water Supply*, vol. 13, no. 2, pp. 273–285, 2013.
- [29] C. Hernandez, F. Ferreira, and D. Rosa, “X-ray powder diffraction and other analyses of cellulose nanocrystals obtained from corn straw by chemical treatments,” *Carbohydrate Polymers*, vol. 193, pp. 39–44, 2018.
- [30] X. Ju, M. Bowden, E. E. Brown, and X. Zhang, “An improved X-ray diffraction method for cellulose crystallinity measurement,” *Carbohydrate Polymers*, vol. 123, pp. 476–481, 2015.
- [31] H. Hyung and J.-H. Kim, “Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters,” *Environmental Science and Technology*, vol. 42, no. 12, pp. 4416–4421, 2008.
- [32] S. G. Wang, X. W. Liu, W. X. Gong, W. Nie, B. Y. Gao, and Q. Y. Yue, “Adsorption of fulvic acids from aqueous solutions by carbon nanotubes,” *Journal of Chemical Technology and Biotechnology*, vol. 82, no. 8, pp. 698–704, 2007.
- [33] S. Yang, J. Li, D. Shao, J. Hu, and X. Wang, “Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: effect of contact time, pH, foreign ions and PAA,” *Journal of Hazardous Materials*, vol. 166, no. 1, pp. 109–116, 2009.
- [34] W. Gao, L. B. Alemany, L. Ci, and P. M. Ajayan, “New insights into the structure and reduction of graphite oxide,” *Nature Chemistry*, vol. 1, no. 5, pp. 403–408, 2009.
- [35] C. Lu and H. Chiu, “Adsorption of zinc (II) from water with purified carbon nanotubes,” *Chemical Engineering Science*, vol. 61, no. 4, pp. 1138–1145, 2006.
- [36] C. Y. Yin, M. K. Aroua, and W. M. A. W. Daud, “Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions,” *Separation and Purification Technology*, vol. 52, no. 3, pp. 403–415, 2007.
- [37] L. Joseph, J. R. Flora, Y.-G. Park, M. Badawy, H. Saleh, and Y. Yoon, “Removal of natural organic matter from potential drinking water sources by combined coagulation and adsorption using carbon nanomaterials,” *Separation and Purification Technology*, vol. 95, pp. 64–72, 2012.
- [38] A. Rahmani, M. Samadi, and R. Noroozi, “Hexavalent chromium removal from aqueous solutions by adsorption onto synthetic nano size ZeroValent iron (nZVI),” *Engineering and Technology*, World Academy of Science, vol. 74, pp. 80–83, 2011.
- [39] B. Tawabini, S. Al-Khaldi, M. Atieh, and M. Khaled, “Removal of Mercury from Water by Multi-Walled Carbon Nanotubes,” *Water Science and Technology*, vol. 61, 2010.
- [40] M. Sulak, E. Demirbas, and M. Kobya, “Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran,” *Bioresource Technology*, vol. 98, no. 13, pp. 2590–2598, 2007.
- [41] Q. Zaib, I. A. Khan, N. B. Saleh, J. R. V. Flora, Y. G. Park, and Y. Yoon, “Removal of bisphenol A and 17 β -estradiol by single-walled carbon nanotubes in aqueous solution: adsorption and molecular modeling,” *Water, Air, and Soil Pollution*, vol. 223, no. 6, pp. 3281–3293, 2012.
- [42] J. Bu, L. Yuan, H. Jiang, and C. Wang, “Study on removal of methylene blue by condensation self-assembled graphene oxide/thiourea composite adsorbent,” *Sustainability*, vol. 14, no. 22, Article ID 15290, 2022.
- [43] N. Agasti, V. Gautam, N. Pandey et al., “Carbon nanotube based magnetic composites for decontamination of organic chemical pollutants in water: a review,” *Applied Surface Science Advances*, vol. 10, Article ID 100270, 2022.
- [44] S. Koesnarpadi, S. J. Santosa, D. Siswanta, and B. Rusdiarso, “Synthesis and characterization of magnetite nanoparticle coated humic acid (Fe₃O₄/HA),” *Procedia Environmental Sciences*, vol. 30, pp. 103–108, 2015.