Adsorption of Humic Acid on Multi-Walled Carbon Nanotubes

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A R T I C L E I N F O

A B S T R A C T

Background: Natural organic matters (NOMs) have the main role in formation of trihalomethanes. These compounds are in natural water sources due to biological activities. In the presented study, adsorption and separation of humic acid as an index of natural organic matters using multi-walled carbon nanotubes is evaluated.
Methods: The experiments were carried out in bath adsorption reactors with different concentrations of humic acid. The effects of pH, adsorbent dose, national concentrations of humic acid and contact time as study variables were tested in separated experiments, as well as, kinetic and isotherm models of the adsorption process were determined.
Results: The results showed that the adsorption follows Freundlich isotherm model and pseudo second-order kinetic equation. The removal percent of humic acid reached to higher than 90% with dosage of 1g/l of nanotube.
Conclusion: Adsorption of humic acid from water by multi-walled carbon nanotubes is an efficient alternative pretreatment method in water treatment plants.

1. Introduction

Organic and natural materials act as a precursor to the development of disinfection by-products (DBPS) [1]. These organic compounds can create in the water resources through natural processes and pollute them [2, 3].

Chlorine gas and hypochlorite are used in drinking water purification processes for disinfection. But these chemicals react with natural organic substances that are present in water and form compounds that are harmful to human health. As an example, the reaction between free chlorine and organic compounds causes the production of disinfection by-products such as Trihalomethanes (THMSs) that are carcinogen [4, 5, 6]. In 1970, the carcinogenicity of chloroform (as a trihalomethane produced by chlorination of drinking water) was confirmed on the mice [7].

Trihalomethanes are also the first type of halogenated disinfectants that are found in treated drinking water [8].

Also, organic matter plays an important role in

the transfer of hydrophobe and metal materials such as lead, aluminum, zinc and radioactive materials during water treatment [9, 10, 11, 12].

In natural waters, organic matter× often has humic nature, causing yellow or brown× in water [9]. Blue humates are usually divided into two groups of humic acid (HA) and fulvic acid (FA), depending on their acidity or alkaline solubility.

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Natural organic matter can be removed from raw water in several ways, which includes conventional coagulation and separation of flocculates by settling or suspension, filtration using various media, membrane filtration, and removal of ion exchange resins, Oxidation, adsorption and biological processes [13, 14, 15, 16].

Most of the water treatment plants have been designed based on the removal of physical and microbial contaminants, and no measures have been taken to remove or reduce chemical contaminants such as organic compounds. On the other hand, the change in the water treatment structure and the use of advanced treatment processes to remove disinfection by-products due to financial constraints or lack of specialized technical personnel and experts who are usually required to use these processes is not easily possible. Therefore, using the available and low cost facilities in order to production of drinking water should be provided to consumers.

The adsorption process is one of the methods used to remove the organic matter. The adsorption on the various materials such as granular and powdered activated carbon, ash, bentonite, cellulose phosphate, biomass, coke, and Chinese soil are used [17]. Carbon nanoparticle and carbon nanotubes are other adsorbents which have been considered in recent years.

The comparison between carbon nanotubes and other adsorbents, such as activated carbon, by researchers suggests that carbon nanotubes are better adsorbents for organic compounds in water

works. The high adsorption capacity of organic pollutants by carbon nanotubes is mainly due to their porous structure and the existence of surface functional groups at the surface of these adsorbents [7].

Carbon nanotubes have unique chemical and physical properties that increase the use of these nanotubes in piezoelectric sensors, voltammetry electrodes, and electrochemical biological sensors.

Also, the behavior of carbon nanotube adsorption is another factor in their application in environmental activities. Carbon nanotubes have more addsorption capacity than other carbon compounds, such as porous graphitic carbon (PGC). Because carbon nanotubes are arranged in the form of large graphite lamellas alongside each other and produce weak inter-molecular Van der waals forces, the compounds effectively are adsorbed by the nanotubes. Flat shapes with polar characteristics and surface electric charges with π bands and free electron pairings can absorb more on the surface of carbon nanotubes. One of the other characteristics of carbon nanotubes is the high surface-to-volume ratio of these adsorbents, which has greatly influenced their use as absorbent [18]. Researchers have used many carbon nanotubes to remove organic compounds, which can be referred to Ehrampoush et al. In their study, the maximum adsorption capacity of humic acid on adsorbent in acidic conditions was 37.31 mg [17].

In 2011, Fernando et al. In order to remove red-colored M-2BE used aqueous solutions of multi-wall carbon nanotubes and activated carbon, which carbon nanotubes showed a higher adsorption than activated carbon [19].

In the present study a kind of Multi-Walled Carbon Nanotube (MWCNTs) was used in order to removal of humic acid (HA) as a natural organic matter from aqueous solution in a batch adsorption experiments.

2. Materials and Methods

The purchased nanotubes were the product of the pioneering Iranian Nanotechnology Company.

The outer diameter of the MWCNTs was 20-30 nm and its inner diameter was 10-5 nm. Its length was 10-30 micrometers and its specific surface area was 110 m^2/g and the purity of carbon nanotubes was> 95%. These nanotubes have been produced by chemical vapor deposition (CVD).

In this study humic acid, product of Sigma Aldrich was used. In this study, the effects of initial humic acid concentration, pH, and contact time and adsorption dose as research variables on the adsorption capacity and efficiency were investigated. Samples of water were synthesized synthetically and using humic acid in the laboratory. To prepare the samples, a stock solution of humic acid of 1000 mg / l was prepared first, and solutions of 20, 40, 60, 80, 100, 150, 200 and 250 milligrams per liter were made for calibration. The samples were also prepared with Stock solution with the required concentrations for batch experiments.

2.1. Batch Adsorption Experiments

The batch adsorption experiments were performed in 250 ml erlenmeyer flasks. After adding 100 ml of a solution with a specific concentration of humic acid, the required amount of nanotube was added to the erlenmeyer flask.

After adjusting other conditions the erlenmeyer flasks were placed in the shaker incubator, the rate of shaking and the temperature were set, and after the required time for the adsorption, were removed from the shaker incubator. Samples were centrifuged at 4000 rpm for half an hour to separate the nanoparticles from the sample solution. All experiments were repeated three times with blanks and control samples for considering non-adsorption removal processes.

The amount of humic acid absorbed by carbon nanotubes was calculated as follows:

$q = (C_0-C) v/m$

q The amount of humic acid adsorbed on the MWCNTs or adsorption capacity (mg/g). C_0 and C are initial concentration and final concentration of humic acid after adsorption operation (mg/l). V

is the volume of sample solution (1) and m is adsorbent dose (g).

Measurements of the unknown and standardized humic acid were performed with the UV / VISILE spectrometer (DR 5000).

3. Results and Discussion

Effect of contact time on adsorption: In order to investigate the effect of contact time on humic acid adsorption, batch adsorption experiments were conducted with a sample of 50 mg/l humic acid and adsorbent dose of 1 g/ l at 15 to 280 minutes.

Results are shown in Fig. 1. The amount of humic acid removal initially has a steep slope, which after 1.5 hour the slope of the graph is reduced and fixed.
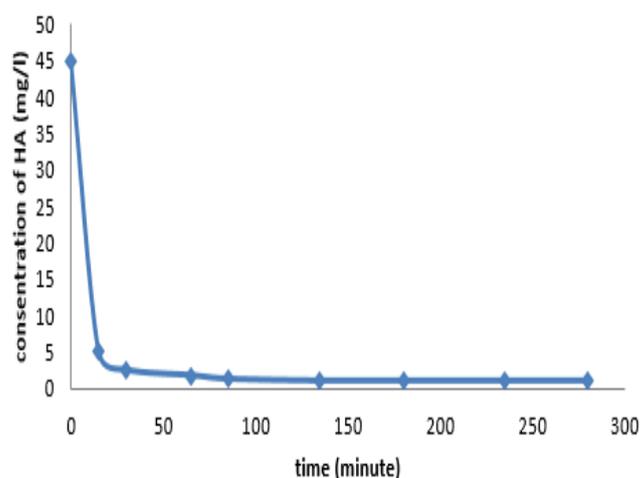

Fig. 1: Effect of Time on Humic Acid Concentration.

Effect of adsorbent doses: The role of different adsorbent doses on the humic acid removal was examined in the batch experiments were conducted with initial concentration of 20 mg/ l of humic acid and 1.5 hours mixing time. The results of this study which are presented in Fig. 2. Showed that increasing the adsorbent dose increased the humic acid removal efficiency. However, the amounts of adsorption capacity decreased and were 42.6, 40.5, 26.75, 21.78, 18, 15.83 mg/g, respectively.of study (p <0.05). The most and least significant relationships were in the fields of environmental health and occupational therapy respectively.
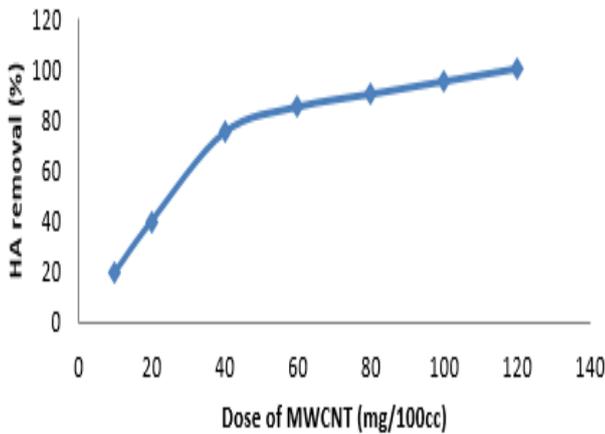
Fig. 2: Effect of adsorbent dose on the humic acid removal percentage.
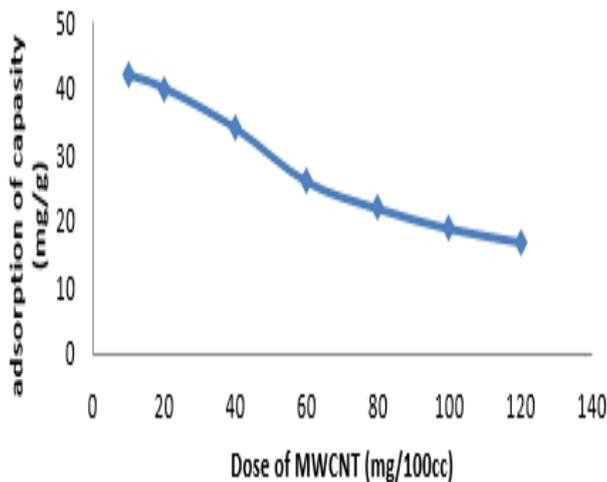

Fig. 3: Effect of adsorbent dose on absorbance capacity.

Determination of pH Effect: To determine the effect of PH, an humic acid solution was prepared at a concentration of 20 mg / l, pH of 4, 7, 10 and a carbon nanotube 40 mg / 100 cc. At pH 4,7,10, the obtained adsorption capacity were 31.42, 30.05, and 20.82, respectively. The results of this experiment are shown in Fig. 3.

Adsorption isotherm models: Langmuir and Freundlich adsorption isotherm models were used to express the association between adsorbed humic acid and its equilibrium concentration. Concentrations of 300, 200, 100, 50, 10 mg / l were prepared with pH 7 and the absorbent dose of 100 mg per 100 cc of solution was used. After the equilibrium time, it was centrifuged and filtered for 1.5 hours at 170 rpm at 25 °C, and the residual
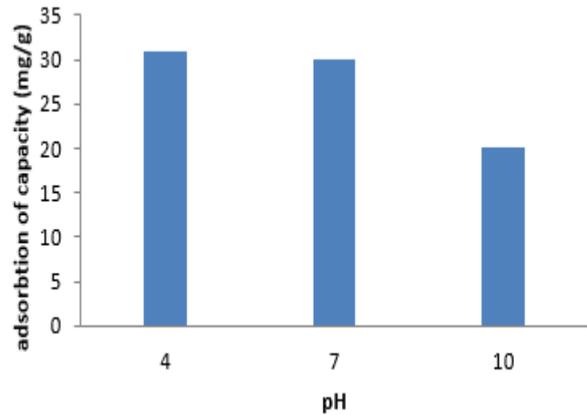

Fig. 4: Effect of PH on the adsorption capacity of MWCNT.

Acid concentration were measured. The linear equations of these models were used to study the matching of the data with isotherm models. The linear equations of these models are as follows: Langmuir linear equation

$$Ce/q_e = Ce/q_{max} + (1/KLq_{max})$$

Freundlich linear equation

$$Log\ q_e = log\ K + 1/n\ logC_e$$

In the above equations, qe is adsorption capacity or the amount of adsorbate material per adsorbent mass at time of equilibrium (mg /g), Ce is concentration of soluble matter in the solution after adsorption (mg /l), q_{max} maximum adsorption capacity (mg/g), K_L is the Langmuir constant (l/mg), K_f is Freundlich constant [20].

Table 1: Parameters adsorption isotherms models.

Adsorption Isotherm	Description of isotherm models		
	Isotherm Constants	Isotherm constant values	R^2
Ce/q_e=Ce/q_max + (1/K_Lq_max)	K_L q_{max}	0.3985 7.56	0.782
Log q_e = log K_f + l/n log c_e	K_f l/n	1.66 5.2575	0.9753

The result show that humic acid adsorption on multi-walled carbon nanotubes follows the Freundlich model.
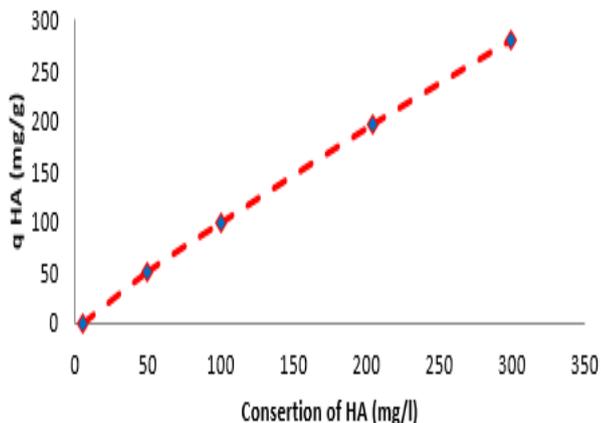
Fig. 5: Effect of initial concentration of humic acid on adsorption capacity (mg/g).
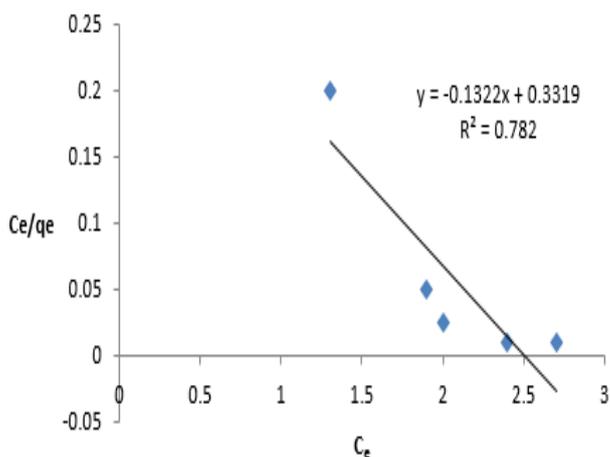

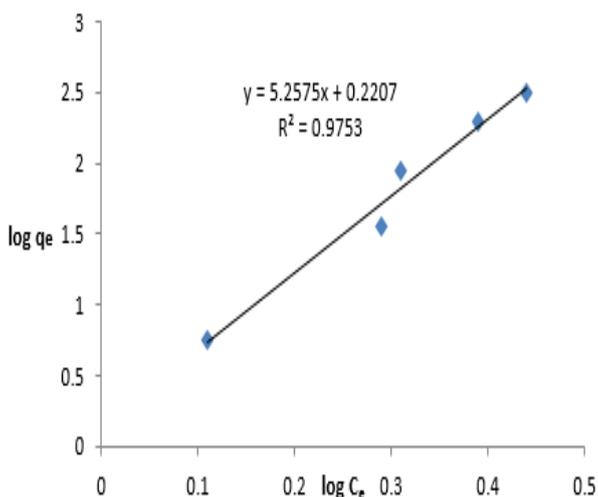**Fig. 6:** Langmuir adsorption isotherm of humic acid on MWCNTs.

Fig. 7: Freundlich adsorption isotherm of humic acid on MWCNTs.

3.1. Determination of adsorption kinetics

Second-order kinetic equations were used to analyze the experiment's data. The following equations are as follows [20]:

Linear equation of pseudo first-order model

$$Ln\ (C) = In\ (C_0) - K_1\,t$$

Linear equation of pseudo first-order model

$$1/C = 1/C_0 - K_2\,t$$

In these equations, K^{-1} is the pseudo-first-order reaction rate constant (min^{-1}), C and C_0 are initial and final concentrations respectively, K_2 is pseudo second order velocity constant (min^{-1}). The results show that humic acid adsorption on MWCNTs is following Pseudo first order.

This study showed that by increasing the contact time, the amount of adsorption capacity increases and after 1.5 hours the system reaches to equilibrium. This is due to the fact that, at the early time of process, vacant sites are highly available for adsorption and, with increasing time and adsorption of more humic acid, a repulsive force forms between adbsorbed and the remaining acid in the solution, and the available sites decline.

Thus, the adsorption rate is gradually reduced.

These results are consistent with the findings of Chungsying Lu et al., Who worked on NOM adsorption on carbon nanotubes, and a 4-hour equilibrium time was reported [21].

With increasing amount of adsorbent dose, the adsorption rate is also higher, which is due to the increase in active adsorbent sites, but the amount of adsorption of humic acid on the mass unit of adsorbent decreases which is due to lack of full usage of adsorbent capacity [22].

The results of this study indicate that adsorption under acidic conditions is better. And under alkaline conditions, the amount of adsorption decreases, which is due to the fact that, under alkaline conditions, the density and torsion of the NOM are reduced and, therefore, adsorption does not perform well [23].

Table 1: Parameters adsorption kinetic models.

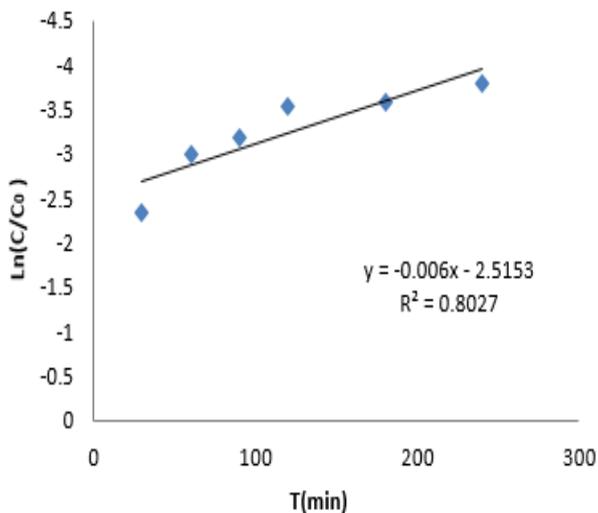| Pseudo second order kinetic			Pseudo first order kinetic			Initial concentration of HA (mg/l)
Model	R^2	K_2 (min^{-1})	Model	R^2	K_1 (min^{-1})	
Y=0.0025x+0.3809	0.89	0.0025	Y=-0.006x-2.5153	0.80	- 0.006	50

Fig. 8: Pseudo-first order kinetic adsorption in adsorption of humic acid by MWCNTs.
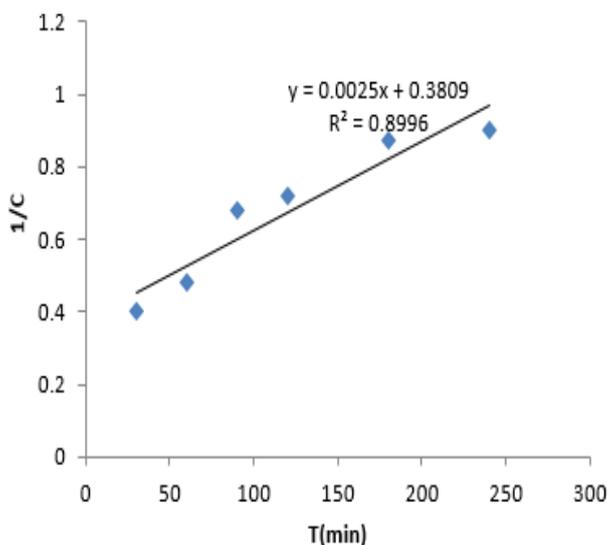

Fig. 9: Pseudo-second order kinetic adsorption in adsorption of humic acid by MWCNTs.

The results show that by increasing the initial concentration of humic acid, the adsorption of humic acid by adsorbent also increases, which is consistent with the findings of other researches about adsorption of similar adsorbates on the carbon nanotubes such as work of Gholami et al., and, this is due to the fact that when the adsorbate concentration gradient increases, the driving force for the motion of humic acid from the solution to the absorbent surface and overcomes the resistance of the mass transfer between the solution and the adsorbent surface [24]. As a result, the rate of transfer of humic acid from the solution to the interface of the liquid and absorbent increases [20].

The results of the calculations show that the adsorption of humic acid by multi-walled carbon nanotubes follows the Freundlich isotherm with the R^2=0.9753. Freundlich isotherm model represents a multiple adsorption. Kinetic studies show the adsorption rate at different times. The study of kinetics of adsorption showed that in this study, the adsorption of humic acid by carbon nanotubes follows a pseudo-second-order kinetic model with R^2=0.8996. Nasseri et al., Who worked on absorbance of natural organic matter on formed carbon nanotubes, reported that the adsorption process follows the Freundlich isotherm with R^2=0.99 [23]. In an investigation carried out by Asgari for the adsorption of humic acid by zeolite, the adsorption process followed the first-order kinetics [25].

4. Conclusion

The results of this study showed that MWCWT is a good alternative in order to removal of humic acid from aqueous solutions. MWCWT can also adsorb other organic compounds, therefor using of this adsorbent in the water treatment plants is recommended. In many countries, dam or natural

lakes are the main secures of water supply, and these lakes are suitable environment for growth of plants which are the secures of natural organic compounds such as humic acid.

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