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Using Modified Multi-Walled Carbon Nanotubes with Ultrasonic Homogenizer for BTEX Removal from Aqueous Solutions

Hamidreza Pourzamani[1], Iman Parseh[2], Mostafa Hadei[3], Fatemeh Rashidashmagh[4], Mohammad Darvish[1], Saed Fadaei[1*]

[1] Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran.
[2] Department of Environmental Health Engineering, School of Health, Yasuj University of Medical Sciences, Yasuj, Iran.
[3] Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran.
[4] Section of sanitary engineering, Department of water Management, School of Civil Engineering and Geosciences, Delft University of Technology, Delft, Netherlands.

Abstract

Background: BTEX refers to a volatile compound with single aromatic ring in petroleum including benzene, toluene, ethyl benzene, and xylenes. Due to its flammability, toxicity and carcinogenicity properties, BTEX has many adverse effects on human health. This study aimed to evaluate the efficiency of multi-walled carbon nanotube (MWCNT) modified with an ultrasonic homogenizer (UH) to remove BTEX from aqueous solutions.
Methods: MWCNT was modified in different concentrations, times and intensities. Then, the best condition was selected. After modification based on the design of experiments (DOE), 16 experiments were arranged at 4 levels with 4 factors. Samples required for simulation were built according to the standard methods and then analyzed by gas chromatography mass.
Results: The results revealed that the optimum conditions for modified carbon nanotubes were obtained at concentration of 30% sodium hypochlorite, time of 5 seconds, and intensity of 50 dB. The optimum conditions for initial BTEX concentration, MWCNT dose, contact time, and pH were 100 mg/L, 2000 mg/L, 20 min and 7 respectively.
Conclusions: The results indicated that carbon nanotubes modified with homogenizer are a simple and effective technique to remove BTEX from the environment.

Keywords: Nanotubes, Carbon, Water quality, Chromatography, Gas.
*Corresponding to: Fadaei S, Email: saed_fadaei@hlth.mui.ac.ir
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Introduction

Benzene, Toluene, Ethylbenzene and Xylene (BTEX) are volatile and monoaromatic compounds that are common constituents in petroleum products.[1] Aromatic compounds have a high tendency to accumulate in groundwater but they can also contaminate the soil and air.[2] This compound has harmful effects on human health including skin and sensory irritation, central nervous system depression, respiratory problems, leukemia as well as disturbance of the kidney, liver and blood systems.[3] In the United States, the permitted levels of benzene, toluene, Ethylbenzene, and mixed xylenes in drinking water are 0.005, 1, 0.7 and 10 parts per million (ppm) respectively.[4] Since the BTEX has flammability, toxicity and carcinogenicity properties, the presence of small amounts of these compounds in the water can result in detrimental effects on water quality. It can also be a threat to the health and life of humans.[5] There are various conventional methods to treat and remove these chemicals from different polluted environments.[6] Commonly used methods for this purpose usually include biological

treatment,[7] membrane filters and adsorption with activated carbon or artificial zeolite.[5,8] The adsorption is a widely utilized method due to the simplicity, effectiveness and ease of use.[6,9] The use of nanomaterials for removal of contaminants from the environment is a new process and has found great popularity in recent years due to special properties of these compounds.[10] Carbon nanotubes (CNTs) are unique, one-dimensional macromolecules with great thermal and chemical stability. Most of the atoms lying on the surface of nanoparticles are not saturated and thus they can easily link with other atoms.[11] Also, these nanomaterials have an outstanding adsorption capacity. These two important properties can contribute to more convenient operation and can accelerate the adsorption as well as removal rate of the pollutant.[9,10] Bina et al. (2014) evaluated the efficiency of BTEX removal by MWCNTs from water and wastewater and found that the benzene, toluene, ethylbenzene and xylene, were removed by 97.7%, 98.5%, 99%, and 99.6% respectively.[7] Ehrampoush et al. (2012) applied carbon nanotubes modified with calcium hypochlorite to remove benzene from aqueous solutions with 4.46% increase in benzene removal rate observed after modification during 1 hour.[12] Khani and Moradi (2013) studied the influence of surface oxidation on the surface and crystalline structure of carbon nanotubes with different oxidants. It was found that the oxidation with acid can create a noticeable change in the diameter and surface of nanotubes.[13] In the present study, a novel method was used to improve the performance of carbon nanotubes for BTEX adsorption which was compared with other common for modification of carbon nanotubes.

Materials and Methods

The materials used in this study included MWCNTs (The BET surface area, pore volume, and pore size distribution were 132.42 (m2/g), 0.58(cm3/g) and 13.21 (nm) respectably) purchased from the Iranian Research Institute of the Petroleum Industry, NaOCl (Merck, Germany, 6-14% active chlorine, analytical grade), NaOH (Merck, Germany) and H2O2 (Merck, Germany, 30% purity). The chemicals used in the study included benzene (Merck, purity: 99.7%), toluene (Merck, purity: 99.7%), ethylbenzene (Merck, purity: 99%) and xylene (Merck, purity: 99%). A stock solution of approximately 100 mg/L of BTEX was prepared by dissolving enough amounts of each component of BTEX. Standard solution contained 100 mg/L of each component of BTEX in deionized H2O (7). The mixture was thoroughly dissolved using an ultrasonic bath (Bandline Sonorex Digitex DT156, Germany) for 60 min and then stirred continuously for 24 h at 25°C. Next, it was placed in the ultrasonic bath again for 30 min[14] and was used to prepare an initial solution of BTEX with 10-100 mg/L concentrations. Finally, standard series and samples were

prepared using deionized H2O to achieve the desired concentrations.

In this study, the experimental design was used to determine the best type of solution, the optimal time and intensity of ultrasonic homogenizer (Bandline, GM3200 and Germany) for modification of multiwalled carbon nanotubes. After modification, MWCNTs were repeatedly washed by distilled water until reaching neutral pH and placed in an oven (Memmert D-91126, Schwabach FRG Company, Germany) at 75°C for 24 h to dry. They were then kept in a desiccator for later use. After modification, carbon nanotubes were used at the time of 8 min, pH=5, BTEX concentration of 10 mg/L and carbon nanotubes dosage of 1000 mg/L l to find the best condition of modification.

All experiments were carried out in 250 ml glass jars. In each experiment, various adsorbent doses (50 to 200 mg) were added to 100 ml of BTEX solution. The initial concentrations (C0) were 10-100 mg/L. Also, the experiments were carried out at different pHs (2 to 11) and retention times (2 to 20 min) (table 1).

Table1. Controlling factors and their levels

Factors	Level 1	Level 2	Level 3	Level 4
BTEX concentration (mg/L)	10	30	70	100
MWCNTs dose (mg/L)	500	1000	1500	2000
Contact time (min)	2	8	14	20
pH	2	5	7	11

The Taguchi orthogonal plan was applied for modification (table 2) and best condition for BTEX removal (Ttable 3). The corresponding factor values were in compliance with the literature.[15,16] The glass flasks were sealed with 20 mm stopper. Headspace within each flask was minimized to exclude any contaminant volatilization phenomena. After preparing all batch setups, the flasks were placed on a shaker (Orbital Shaker Model KS260B, IKA Company, Germany) and stirred at 240 rpm at room temperature for 2-20 min. Before and after each experiment, BTEXs were determined using a gas chromatograph coupled to a flame ionization detector (GC-MS) (Agilent technology 7890A). All experiments were repeated three times and their mean and standard deviation were considered. The control samples (Blank experiments) were considered for measuring the BTEX concentration diminishing due to the evaporation and absorption on the bottle. The solution pH was measured at the start and end of each experiment. The initial pH was corrected using 0.05 M HCl (Merck, Germany, %30 pure) and 0.05 M NaOH (Merck, Germany, %99 pure). The amounts of adsorbed BTEX on the adsorbent (qe, mg/g), distribution ratio (KD, l/g) and removal percentage (%R) were calculated according to Equations 1-3.[17,18]

Table 1. Controlling factors and their levels

(1) $q_e = (C_0 - C_t) \times \dfrac{V}{m}$

(2) $K_D = \dfrac{C_0 - C_t}{C_t} \times \dfrac{V}{m}$

(3) $\%R = \dfrac{C_0 - C_t}{C_0} \times 100$

Where, C0 and Ct (mg/L) are the BTEX concentrations at the start and end of each experiment, V represents the initial solution volume (l) and m is the adsorbent weight (g).

Samples were measured using GC-MSin splitless mode (injection line temperature was 210°C and detector temperature was 250°C). Then, the following temperature program was used for column oven: 36°C for 1 min and with 10°C/min to 90°C, directed to 150°C with 25°C/min rate and held at 150°C for 6 min. Hydrogen gas at a flow rate of 30 ml/min was applied as the fuel. Also, the flow of air and nitrogen gases were 300 and 30 30 ml/min, respectively. The column was CP-sil 5 Cb 25 m with helium (purity 99.995%) as carrier gas at the flow rate of 1.11 ml/min. Static headspace analysis was performed using a CTC PAL-Combi PAL headspace sampler. Optimal experimental values were based on Amin et al. (2013).[17] The headspace gas was injected into GC-MS injector from an automatic headspace sampler after 25 min shaking at 70°C. The injector port was maintained at 250°C and 1 ml volume of headspace was injected in splitless mode.

The design of experiments (DOE) software (Design Expert 6 Stat-Ease, Inc., USA) was applied to determine the effects of pH, adsorbent dose and initial concentrations of BTEX and contact time on removal of BTEX.

The crystal phases of adsorbents were characterized by a powder X-ray diffractometer (XRD, Philips, Co. Nederland). The morphology of the adsorbents was studied via scanning electron microscopy (SEM) (Philips XI30, Philips and Nederland).

Results

The results of X-ray diffraction (XRD)

Figure 1 displays the XRD results of modified carbon nanotubes and unmodified carbon nanotubes with homogenizer used in the removal of BTEX compounds.

Figure 1. XRD results of MWCNT-HM and MWCNT in the removal of BTEX compounds

The results of scanning electron microscopy (SEM)

Figure 2 reveals the SEM image of MWCNT (a) and MWCNT-HM (b) in BTEX removal.

Figure 2: SEM image of MWCNT (a) and MWCNT-HM (b)

The SEM was used to evaluate the surface of carbon nanotubes before and after the modification. The as-prepared CNTs are usually entangled with one another and have closed caps, so their specific surface area is absolutely low (~ 100 m2/g).

Table 2 reports the result of optimal conditions for modification of MWCNTs.

Table 2. The optimal conditions of MWCNT modification
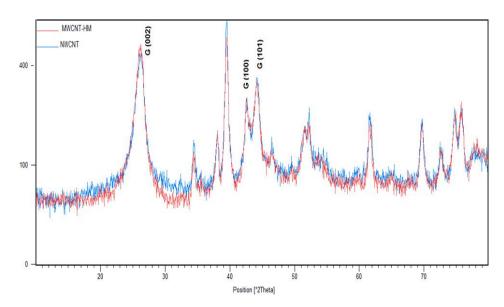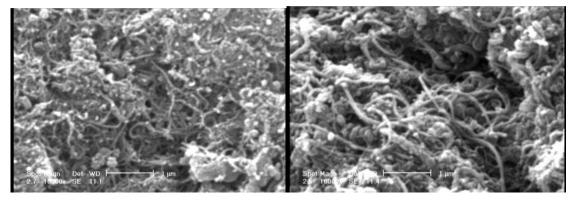
Optimum condition for BTEX removal

Figure 1. XRD results of MWCNT-HM and MWCNT in the removal of BTEX compounds

(a)   (b)

Figure 2. SEM image of MWCNT (a) and MWCNT-HM (b)

Table 2. The optimal conditions of MWCNT modification

Run	Error! No text of specified style in document.solution	Time (s)	Solution concentration (%)	Intensity (dB)	Removal (%)
1	Sodium hydroxide	15	60	30	20.1
2	Sodium hydroxide	5	30	40	21
3	Hydrogen Peroxide	15	30	50	20
4	Hydrogen Peroxide	10	60	40	22.2
5	Distilled water	10	-	40	21.6
6	Distilled water	5	-	50	20.5
7	Sodium hypochlorite	5	30	50	45
8	Sodium hypochlorite	15	60	30	40.8

The optimal conditions of BTEX removal by MWCNTs and modified MWCNTs by homogenizer (MWCNT-HD) were determined using experimental design (table 3).

According to Table 3, in the batch experiments, the MWCNT-HM adsorbed 64.1% BTEX in run 10. Also, in this run, the maximum BTEX uptake occurred for MWCNT by 17.6% removal. As can be seen, the ultrasonic homogenizer is effective in BTEX removal and could increase BTEX removal

by 46.5%.

Table 3. The optimal conditions of BTEX removal by MWCNT-HD and MWCNT

Table 4 reports BTEX removal by MWCNT-HM under optimum conditions.

Table 5 summarizes the effects of the factors and interactions obtained by fractional factorial design.

Table 3.The optimal conditions of BTEX removal by MWCNT-HD and MWCNT

Run	Factors				Secondary BTEX Concentration (Mg/L)		Removal efficiency (%)		qe (mg/g)⁻¹	
	Initial BTEX concentration (mg/L)	Adsorbent Dose (mg/L)	Time (s)	pH	MWCNT	MWCNT-HM	MWCNT	MWCNT-HM	MWCNT	MWCNT-HM
1	120±2.1	500	8	7	102.7±0.3	61.2±0.2	14.4	49	34.5	117.6
2	120±4.3	2000	14	5	100.5±0.1	50.4±0.1	16.2	58	9.7	34.8
3	40±0.8	1500	14	7	33.5±.2	16.5±0.2	16.1	58.7	4.3	15.6
4	280±2.1	500	14	11	240.5±0.2	138.3±0.1	14.1	50.6	79	283.3
5	40±1.2	1000	8	5	35±0.1	22±0.2	12.5	45	5	18
6	120±1.6	1000	2	11	104.1±0.2	67±0.1	13.2	44.2	15.8	53
7	400±3.1	1000	14	2	337.6±0.6	174.8±0.2	15.6	56.3	62.4	225.2
8	40±1.7	2000	20	11	33.6±0.3	17±0.2	15.9	57.5	3.1	11.5
9	120±3.3	1500	2	2	105.8±0.1	69.8±0.1	11.8	41.8	9.4	33.4
10	400±5	2000	20	7	329.6±0.2	143.6±0.7	17.6	64.1	35.2	128.2
11	400±4.6	500	20	5	336.4±0.2	159.2±0.6	15.9	60.2	127.2	481.6
12	400±4.8	1500	8	11	339.2±0.8	174.4±1.1	15.2	56.4	40.5	150.4
13	280±2.3	2000	8	2	237.1±0.1	118.1±0.1	15.3	57.8	21.4	80.9
14	280±2.7	1500	2	5	239.6±0.3	139.4±0.7	14.4	50.2	26.9	93.7
15	40±1.2	500	2	2	35.7±0.1	27.3±0.6	10.6	31.6	8.5	25.3
16	280±4.6	1000	20	7	234.9±0.1	123.2±0.7	16.1	56	45	156.8

Table 4. BTEX removal by MWCNT-HM in optimum condition

Pollutants	Factors				Secondary Concentration (mg/L)	Removal efficiency (%)	(qe) mg/g
	pH	Contact time (Min)	MWCNT-HM Dose (Mg/L)	Initial concentration (mg/L)			
Benzene	7	20	2000	100±1	46.5±0.3	53.5 ۵۳/۵	26.7
Toluene	7	20	2000	100±0.7	39.2±0.1	60.8 ۶۰/۸	30.4
Ethylbenzen	7	20	2000	100±0.7	30.2±0.1	69.8 ۶۹/۸	34.9
Xylene	7	20	2000	100±0.7	27±0.8	73	36.5
BTEX	7	20	2000	400±5	143.6±0.7	64.1 ۶۴/۱	128.2

Table 5. Effects of the factors and interactions obtained by fractional factorial design

Factor/interaction	Degree of freedom	Sum of squares	Mean squares	F value	Probability> F	Contribution (%)
A: BTEX concentration/(mg/L)	3	665.9	222	187.9	<0.0001	31
B: MWCNT-HM dose/(mg/L)	3	587.9	196	165.8	<0.0001	27.4
C: Contact time/min	3	683.2	227.7	192.7	<0.0001	31.8
D: pH	3	38.8	17.3	10	0/0005	1.8
AB interaction	3	131.5	13	37.1	<0.0001	6.1
Lack of fit	15	17.7	1.2	-	-	0.83
Pure error	0	-	-	-	-	0
Residuals	15	17.7	1.2	-	-	0.83

Table 5: Effects of the factors and interactions obtained by fractional factorial design

Figure 3 demonstrates the effect of parameters on BTEX removal. Figure 3(a) indicates that the BTEX adsorption increased from 33.5% to 42.1 % with elevation of the initial BTEX concentration from 10 to 100 mg/L.
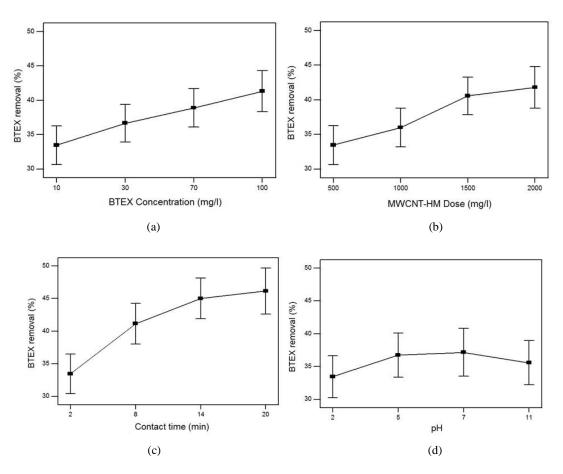
Figure 3. Design expert plot of effect of factors on BTEX removal by MWCNT-HM in: (a) BTEX concentration, (b) MWCNT-HM dose, (c) contact time and (d) pH

Discussion

XRD tests were performed to check the quality of the crystal structure of modified and unmodified MWCNTs. According to studies, graphic carbon G (002), G (100) and G (101) are located at 2θ angles of 25.97, 43.33 and 44.61.[19] However, in this study, it was located at 26.1, 42.6 and 44.2 with minor changes in 2θ angles. The rest of the peaks were related to the non-graphitic carbon and other impurities nanotubes. The peak intensity of G (002) for carbon nanotubes was equal to IMWCNT=433 and IMWCNT-HM=461. Ahmed et al. used the nitric acid to functionalize the carbon nanotubes and could increase the peak intensity to 80 a.u,[20] which can confirm the results of this study. The area under the peak indicates a more regular crystal structure. The increase is more tangible in the case of graphitic carbon G (002) revealing that the crystal structure of graphite and nanotubes improved after modification which it is consistent with the results of Ahmed et al.[20]

Some attempts, such as cutting, cap-opening, or using chemical treatments to create micropores on the walls of the multi-walled carbon nanotubes (MWNTs) have been made to enhance the specific surface area of CNTs.[21] The SEM images (figure 2a) of carbon nanotubes before modification indicate that the distribution of the nanotubes is irregular. In addition,

(a)

(b)

(c)

(d)

the surface of nanotubes is smooth and they are not porous due to adhesion and aggregation at their surface, causing diminished adsorption rate of the nanotubes. Khani et al. studied the effects of surface modification using various oxidants on external and crystal structure of carbon nanotubes and noticed a noticeable change in the diameter and surface of the carbon nanotubes.[13] As can be seen in figure 2b, the modification reduces the aggregation of nanotubes and creates a uniform distribution among them. Ling et al. expressed that it can be due to the addition of the carboxyl functional groups after modification.[13] The results of the present study also revealed that the removal efficiency grows by increasing the pollutant concentration, adsorbent dosage, and contact time.

Table 2 indicates that the modification of MWCNT has been better in sodium hypochlorite 30% solution within 5 min and ultrasonic intensity of 50 dB. It was also found that the MWCNT has had weaker adsorption during the longer time and high ultrasonic intensity. Zhang et al. investigated the modification of the carbon nanotubes by 20% NHO3 during 2 h under ultrasonic radiation. They found that the specific surface area of the carbon nanotubes increased from 49.9 to 55.5 m2/g after modification. They also found that the catalyst particles in the tubes were removed and the length of nanotubes became shorter; finally the internal surface was effectively used causing enhanced specific surface area of the nanotubes.[22] Since the high ultrasonic power is likely to cause damage to the structure and reduce electrical conductivity of MWCNTs, Omastova et

al. used the ultrasonic bath with a power of 64 W and homogenizer ultrasonic with a power of 360 W for modification of MWCNTs to determine the suitable power of modification. They found that modification reduces the electrical conductivity at high power and selected 64 as the optimum power.[23] According to table 2, concerning the BTEX percentage removal, the MWCNT modified by sodium hypochlorite 30 % (Run 7) was selected as the best MWCNT-HM.

As shown in table 4, the maximum and minimum uptakes of pollutants were related to xylene (73%) and benzene (53.5%) respectively. Favorable adsorption with the order of X>E>T>B may be due to the increase in molecular weight (B, 78g<T, 92g<E, X, 106g), solubility (B, 790 mg/L>T, 530 mg/L>E, 152 mg/L>X, 150.5 mg/L), boiling point (B, 80.1∘C<T, 110.7∘C<E, 136.2∘C<X, 138∘C).[6]

The F value test (in table 5) showed that the contact time (31.8%) acted significantly in affecting the adsorption performance. It revealed that the contact time is a significant parameter in determining the adsorption capacity in liquid phase. Pourzamani and et al. research also confirmed this result.[5] Further, the pH influences and the interaction between BTEX concentrations and MWCNT-HM doses seemed less significant according to the F values of 10 and 37.1, for pH and interaction, respectively. The effective parameters in benzene removal had the following order: contact time>BTEX concentration>MWCNT-HM dose>AB interaction>pH.

Amin et al. obtained the same results and observed that the amount of benzene adsorbed increased from 60.5% to 98.6% rising the initial BTEX concentration.[17] Figure 3(b) indicates that the maximum BTEX removal occurs at 2000 mg/L of MWCNT-HM dose. An increase in MWCNT-HM dose directly affects the removal of BTEX, and reseanably with increase in absorption sites, the amount of sorbent increases. Amin et al. surveyed the efficiency of nanomagnetic particles in toluene removal from water and wastewater and found that with the rise of nanomagnetic particles, toluene removal increased. As presented in figure 3(c), expectedly in BTEX removal by MWCNT-HM, the amount of adsorbed BTEX increased from 2 to 20 min. A study conducted by Kennedy et al. in 2007 suggested that by elevating the concentration of pollutants (phenol), activated carbon removal efficiency increased and absorption rate was very high within the first 15 minutes and then decreased; finally at 75 minutes, it reached equilibrium.[24] Figure 3(d) displays that lowest BTEX removal percentage occurred at pH 2 as it increased by raising the pH up to 7 and then diminished. It is likely that the adsorption of BTEX on MWCNT-HM sorbent was because of opposite charges between the sorbent and the BTEX. Su et al. compared the adsorption ability of unmodified carbon nanotube and the carbon nanotube modified with sodium hypochlorite. They observed that the modified carbon nanotubes exhibited better performance within acidic to neutral pHs.[25]

The results indicated that MWCNT-HM had a higher efficiency (about 46 %) for BTEX removal from aqueous solutions in comparison to MWCNT. The MWCNT-HM eliminated benzene and toluene better than ethyl benzene and xylene. Also, the results revealed that the physicochemical properties of MWCNT including crystallization and pores were remarkably improved after the oxidation, and MWCNT adsorbed more BTEX. Therefore, it can be suggested that carbon nanotubes modified with homogenizer constitute a simple and efficient method for removal of BTEX from aqueous solutions.

Acknowledgement

Conflict of Interest

The authors declare that they have no conflict of interest.

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