

WATER QUALITY AND PROTECTION:  
ENVIRONMENTAL ASPECTS

Water and Wastewater Treatment from BTEX  
by Carbon Nanotubes and Nano-Fe<sup>1</sup>

Bijan Bina<sup>a</sup>, Mohammad Mehdi Amin<sup>a</sup>, Alimorad Rashidi<sup>b</sup>, and Hamidreza Pourzamani<sup>a</sup>

<sup>a</sup>Environment Research Center, Isfahan University of Medical Sciences, Isfahan, Iran

<sup>b</sup>Gas Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

E-mail: pourzamani@hlth.mui.ac.ir

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**Abstract**—The removal of benzene, toluene, ethylbenzene, and xylene (BTEX) from aqueous solution by multi- and single-walled carbon nanotubes (MWCNTs and SWCNTs), hybrid carbon nanotubes (HCNTs) and nano-Fe was evaluated for a nanomaterials dose of 1 g/L and a BTEX concentration of 10 mg/L and pH 7. The equilibrium amount ( $q_e$ ) (mg/g) removed by SWCNTs (B: 9.98, T: 9.96, E: 9.97, and X: 9.97 mg/g) was higher than for MWCNTs, HCNTs and nano-Fe in a  $c_0$  of 10 mg/L and for a contact time of 10 min. The  $q_e$  of total BTEX removed via SWCNTs was 39.89 mg/g. The order of uptake for SWCNTs is  $X > T = E > B$ , which is related to the increasing water solubility and the decreasing molecular weight of the compounds. The SWCNTs performed better for BTEX sorption than the MWCNTs, HCNTs and nano-Fe. The results of desorption study show that BTEX adsorbed on SWCNTs can easily be desorbed at  $105 \pm 2^\circ\text{C}$ . It was concluded that recycling CNTs using heat improved the performance of the CNTs. For the first time, better adsorption performance was observed for recycled CNTs than for raw CNTs. SWCNTs are efficient BTEX adsorbents that could be used for cleaning up environmental pollution.

**Keywords:** BTEX, carbon nanotube, nano-Fe, water pollution

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INTRODUCTION

Benzene, toluene, ethylbenzene, and xylene are common water contaminants. BTEX are volatile, monoaromatic compounds that are common constituents in petroleum products [2]. Figure 1 shows the structure of BTEX.

The BTEX compounds are frequently found in groundwater because of leaks in underground storage tanks and pipelines, improper waste disposal practices, inadvertent spills and leaching from landfills [12]. These pollutants have been found to cause many serious health side effects to humans (e.g., skin and sensory irritation, central nervous system depression, respiratory problems, leukemia, cancer, and disturbance of the kidney, liver and blood systems) [1]. The compounds are classified as priority pollutants regulated by the US Environmental Protection Agency (EPA) and were among the target compounds in the EPA's 33–50 programs. Benzene is teratogenic and may be associated with the development of leukemia, and toluene is a suspected depressant of the central nervous system. Because of these health concerns, a maximum contaminant level of 5  $\mu\text{g}/\text{L}$  for benzene is set as the standard for drinking water by the US EPA. The US Public Health Service (1989) has also recom-

mended that drinking water contains no more than 2 mg/L of toluene for lifetime exposure [10, 12]. These compounds have a high polluting potential because of their neurotoxic, carcinogenic and teratogenic properties, and they represent a high risk to the environment and human health [11]. Therefore, BTEX removal from groundwater and surface waters is essential.

BTEX removal from groundwater has been widely studied, and several processes have been successfully applied, including bioremediation, volatilization, oxidation, and adsorption. BTEX removal from water by adsorption on resins [7], raw and thermally modified diatomite [1] and organ clays [3] has already proved to be an interesting application.

Carbon nanotubes (CNTs) are unique, one-dimensional macromolecules that have outstanding thermal and chemical stability. These nanomaterials have been employed for removing many kinds of organic pollutants, such as dioxin and volatile organic compounds from gas phases or 1,2-dichlorobenzene, trihalomethanes, reactive dyes, xylenes, fulvic acids and natural organic matters from aqueous solutions [9]. Zytner et al. investigated the sorption and desorption of BTEX in five media: sandy loam soil, organic top soil, clay soil, peat moss and granular activated carbon (GAC) [16]. The comparisons of CNTs with

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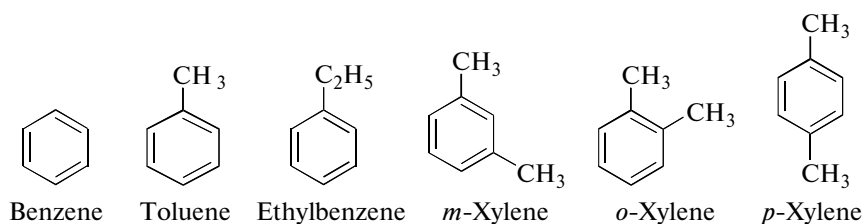


Fig. 1. The structure of BTEX.

other adsorbents such as activated carbon suggest that CNTs are promising organic adsorbents for environmental protection applications. As a result, it is expected that CNTs will also have good adsorption characteristics for BTEX in water and wastewater [4]. The large adsorption capacity of CNTs for organic pollutant is primarily due to their pore structure and the existence of a wide spectrum of surface functional groups. The adsorption mechanism of BTEX on CNTs is mainly attributed to the  $\pi$ - $\pi$  electron donor-acceptor interaction between the aromatic ring of BTEX and the surface carboxylic groups of CNTs [9]. Lu et al. used surface modification of carbon nanotubes to enhance BTEX adsorption from aqueous solutions. The NaOCl-oxidized CNTs have superior adsorption performance toward BTEX compared with many types of carbon and silica adsorbents reported in the literature [9]. Su et al. employed multi-walled carbon nanotubes that were oxidized by sodium hypochlorite (NaOCl) solution to enhance the adsorption of benzene, toluene, ethylbenzene and *p*-xylene in an aqueous solution. Aivalioti et al. studied the removal of BTEX and MTBE (methyl tertiary butyl ether) from aqueous solutions by raw and thermally modified diatomite [1].

These studies have all shown the potential for developing carbon nanotube technologies for treating BTEX in water, which is commonly discharged from many kinds of industrial activities and frequently encountered in the groundwater of gasoline-contaminated sites. However, such studies are still very limited in the literature. There are many types of CNTs that can be used for contaminant removal, but we do not yet know which of them is better for removing specific contaminants. Therefore, a test of the BTEX removal efficiency of different types of CNTs is needed to employ the most efficient CNTs in water and wastewater treatment.

The present study aimed to determine the removal efficiency for benzene, toluene, ethylbenzene, and xylene separately and for total BTEX using single-walled and multi-walled carbon nanotubes, hybrid carbon nanotubes, and nano-Fe and to rank their BTEX removal abilities.

The contribution of this study is the process of regenerating CNTs and nano-Fe as adsorbents of BTEX with temperature instead of with the chemical regener-

ants used in other studies. Furthermore, an evaluation of hybrid CNTs was not found in the literature.

## MATERIALS AND METHODS

### Materials

A mixed suite of 4 organic compounds was employed to evaluate the different nanomaterials. These compounds were chosen to represent a range of solubilities, chemical structures, chemical configurations and relative importance as an environmental pollutant. The chemicals tested in this study were 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 appropriate amounts of each substance in a standard solution that contained 100 mg/L of benzene + 100 mg/L of toluene + 100 mg/L of ethylbenzene + 100 mg/L of xylene in deionized H<sub>2</sub>O. The mixture was mixed thoroughly by using an ultrasonic bath (BANDELIN Sonorex Digtec) for 60 min. Then, it was stirred continuously for 24 h at 25°C. After shaking, the solution was put in an ultrasonic bath again for 30 min and was used to prepare the initial BTEX solution with a 10 mg/L concentration. Finally, standard series and samples were prepared using deionized H<sub>2</sub>O to achieve the desired concentrations.

### Experimental Conditions

Batch adsorption experiments were conducted using 110 mL glass bottles with the addition of 100 mg of adsorbents and 100 mL of BTEX solution at an initial concentration ( $c_0$ ) of 10 mg/L, which was chosen to be representative of low BTEX levels in water polluted with gasoline. The glass bottles were sealed with 20 mm stoppers. The headspace within each beaker was minimized to exclude any contaminant volatilization phenomena. The glass bottles from the batch experiments were placed on a shaker (Orbital Shaker Model OS625) and were stirred at 240 rpm at room temperature for 10 min. The solution samples were then allowed to settle for 2 min. The supernatant was filtered through 0.45  $\mu$ m filters to remove suspended CNTs. A magnetic field column was used to separate suspended nano-Fe. Finally, the BTEX concentration

**Table 1.** BTEX removal by MWCNT, SWCNT, HCNT and nano-Fe at  $C_0 = 10$  mg/L and contact time of 10 min

Adsorbent	Benzene		Toluene		Ethylbenzene		Xylene	
	$c_t$ , mg/L	removal percent, %	$c_t$ , mg/L	removal percent, %	$c_t$ , mg/L	removal percent, %	$c_t$ , mg/L	removal percent, %
MWCNT	0.23	97.70	0.15	98.5	0.10	99.0	0.04	99.6
SWCNT	0.03	99.74	0.02	99.8	0.02	99.7	0.01	99.9
HCNT	0.04	99.58	0.05	99.5	0.04	99.6	0.03	99.7
Nano-Fe	0.32	96.80	0.23	97.7	0.16	98.4	0.09	99.2

in the liquid phase was determined using GC/MS chromatography. All of the experiments were repeated three times, and only the mean values were reported. Blank experiments, without the addition of adsorbents, were also conducted to ensure that the decrease in BTEX concentration was not due to adsorption on the wall of the glass bottle or volatilization. The solution pH was measured at the beginning ( $pH_{in}$ ) and at the end ( $pH_{fin}$ ) of each experiment. The  $pH_{in}$  was adjusted to neutral using 0.05 M HCl or 0.05 M NaOH. The amount of adsorbed BTEX on the adsorbents ( $q_e$ , mg/g) was measured, and the percent removal (%R) was calculated as follows:

$$q_e = (c_0 - c_t) \frac{V}{m}, \quad (1)$$

$$\%R = \frac{c_0 - c_t}{c_0} \times 100, \quad (2)$$

where  $c_0$  and  $c_t$  (mg/L) are the BTEX concentrations at the beginning and after a certain period of time,  $V$  is the initial solution volume (L), and  $m$  is the adsorbent weight (g).

#### Chemical Analysis

An Agilent Technologies system consisting of a 5975C Inert MSD with a Triple Axis Detector equipped with a 7890A gas chromatograph with a split/splitless injector was used for the quantification and confirmation of the polycyclic aromatic hydrocarbons. A fused silica column, HP-5 ms (5% phenyl–95% dimethylpolysiloxane; 30 m  $\times$  0.25 mm I.D., 0.25  $\mu$ m), was employed with helium (purity: 99.995%) as the carrier gas at a flow rate of 1 mL/min. The column temperature was programmed as follows: 40°C for 10 min, increasing to 120°C at 10°C/min and holding for 2 min. The injector port was maintained at 250°C, and a 1 mL volume of headspace was injected in splitless mode (2.0 min). The effluent from the GC column was transferred via a transfer line held at 280°C and fed into a 70 eV electron impact ionization source held at 280°C. The analysis was performed in the selected ion monitoring (SIM) mode. The data were acquired and processed by the data analysis software.

Static headspace analysis was performed using a CTC PAL-Combi PAL headspace sampler. The

experimental parameters of the headspace sampler were as follows: incubation time, 25 min; incubation temperature, 70°C; sample loop volume, 1 mL; syringe/transfer line temperature, 110°C; flash time, 2 min with  $N_2$ ; loop fill time, 0.03 min; injection time, 1 min; and sample volume, 10 mL in 20 mL vials. No NaCl was added to the samples.

The pH measurements were made with a pH-meter (EUTECH, 1500).

#### Adsorbents

During the experimental procedure, four different nanomaterials were tested: (1) single-walled carbon nanotubes, (2) multi-wall carbon nanotubes, (3) hybrid carbon nanotubes, and (4) nano-Fe. TEM images of SWCNTs (1–2 nm), MWCNTs (10 nm), HCNTs (a hybrid of MWCNTs and Silica), and nano-Fe (20–40 nm) shown in Figs. 2a–2d, respectively. These nanomaterials were purchased from the Iranian Research Institute of the Petroleum Industry. HCNTs were a hybrid of MWCNTs and Silica so that open the tubes of MWCNT as a sheet instead of tube.

#### Recycling Method

The reversibility of the sorbents that were used for BTEX removal from aqueous solution was evaluated via 2 successive adsorption cycles followed by 2 successive desorption cycles. Recycling was also conducted at  $105 \pm 2^\circ\text{C}$  and 24 h in an oven (Memmert D-91126, Schwabach FRG). All samples were replicated at least in triplicate.

#### Analysis of Data

For the data analysis, design of experiments (DOE) software (Design Expert 6) was used. In this software, the analysis was done with a general factorial plan.

## RESULTS AND DISCUSSION

#### Adsorption Performance

Table 1 shows the BTEX removal percent for MWCNTs, SWCNTs, HCNTs and nano-Fe under an initial BTEX concentration of 10 mg/L, an adsorbent

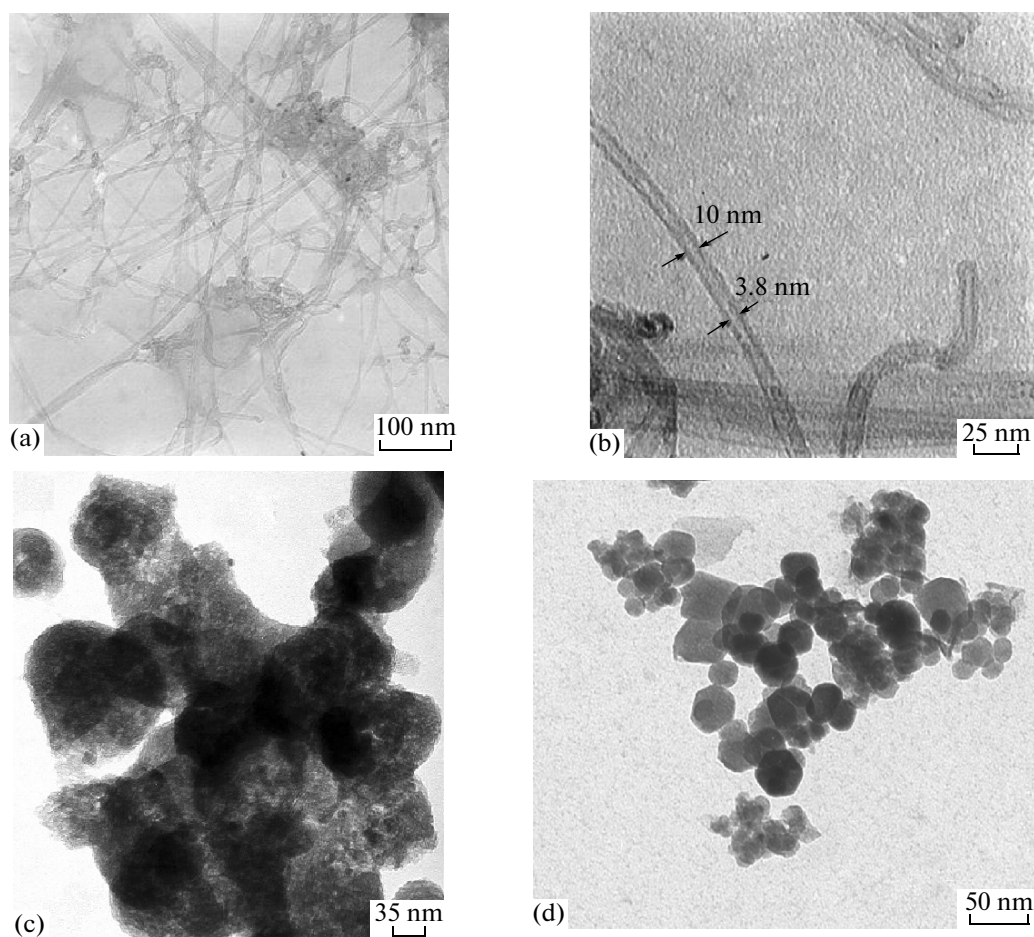


Fig. 2. TEM image of: (a) SWCNT, (b) MWCNT, (c) HCNT, and (d) nano-Fe.

concentration of nanomaterial of 1000 mg/L, a contact time of 10 min and shaking at 240 rpm.

Based on the DOE analysis, there was no difference between HCNTs and SWCNTs in terms of benzene removal (values of “Prob >  $|t|$ ” greater than 0.1). However, there were difference between MWCNTs, SWCNTs and nano-Fe for benzene removal (values of “Prob >  $|t|$ ” less than 0.05). A comparison of toluene removal in carbon nanotubes and nano-Fe indicated that, there was a difference between MWCNTs, HCNTs, nano-Fe and SWCNTs for toluene removal (values of “Prob >  $|t|$ ” less than 0.05). A comparison of carbon nanotubes and nano-Fe for ethylbenzene removal showed that MWCNTs, SWCNTs, HCNTs and nano-Fe had significantly different removal rates for ethylbenzene (values of “Prob >  $|t|$ ” less than 0.05). Also, there were significant differences between the carbon nanotubes and nano-Fe for xylene removal. SWCNTs had better benzene, toluene, ethylbenzene, and xylene removal than the other investigated nanoparticles in this study.

Figure 3 shows the BTEX removal by MWCNTs, SWCNTs, HCNTs, and nano-Fe and a comparison

between them. SWCNTs were better than HCNTs, MWCNTs, and nano-Fe at removing BTEX.

Figure 4 indicates the equilibrium amounts of benzene, toluene, ethylbenzene and xylene and BTEX adsorbed on MWCNTs, SWCNTs, HCNTs, and nano-Fe ( $q_e$ ) with a  $c_0$  of 10 mg/L and a contact time of 10 min.

Based on Fig. 4, it is evident that the  $q_e$  for MWCNTs and SWCNTs follow the following order:  $X > E > T > B$ ; for HCNT, the order is  $E > X > T > B$  and for nano-Fe, the order is  $X > T > E > B$  for a  $c_0$  of 10 mg BTEX/L. This order of adsorption may be attributed to the decreasing solubility (B, 1790 mg/L > T, 530 mg/L > E, 152 mg/L > X, insoluble), the increasing molecular weight (B, 78 g < T, 92 g < E, X, 106 g) [1] and the increasing boiling point (B, 80.1°C < T, 110.7°C < E, 136.2°C < X, 144°C) of the different compounds [5].

Lu et al. also showed evidence that the  $q_e$  increased with  $c_0$  and roughly follows the order  $E > X > T > B$  for a  $c_0$  of 60 mg/L and  $X > E > T > B$  for a  $c_0$  of 200 mg/L [9]. Also Aivalioti et al. indicated that adsorbent preference for BTEX in the diatomite adsorbents decreases in the following order:  $p$ -xylene > ethylbenzene >

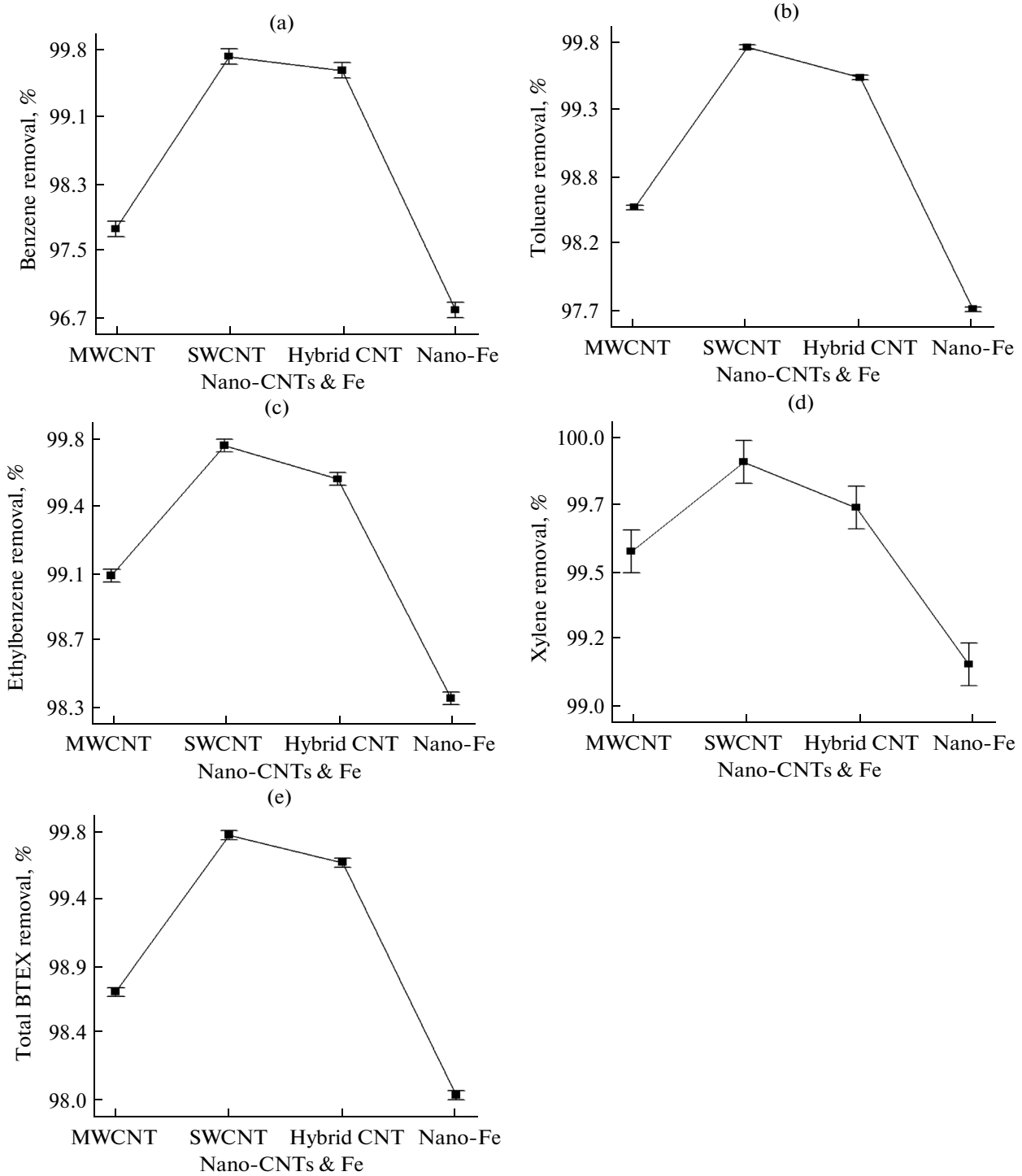
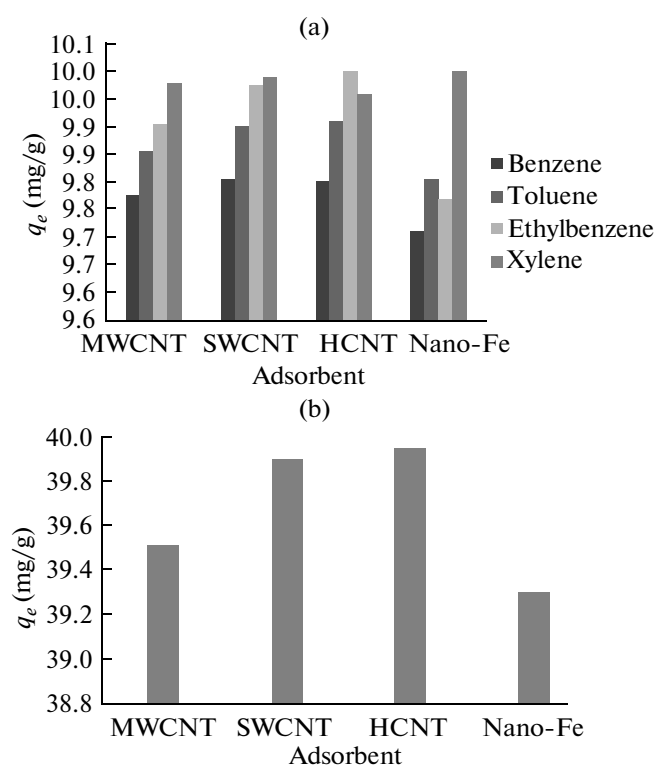


Fig. 3. Design expert plot for MWCNT, SWCNT, HCNT and nano-Fe in: (a) benzene, (b) toluene, (c) ethylbenzene, (d) xylene, and (e) total BTEX removal with a  $c_0$  of 10 mg/L.

*o*-xylene > toluene > benzene [1]. Daifullah and Girgis indicated that the adsorption of BTEX proceeds in the following order: xylene > ethylbenzene > toluene > benzene [4]. Su et al. found that the  $q_e$  of BTEX adsorption (at a  $c_0$  of 200 mg/L, contact time of 240 min and 600 mg/L of adsorbent concentration) by

CNT (NaOCl) were 212, 225, 255 and 274 mg/g for B, T, E and X, respectively, and that favorable adsorption occurred in the following order: X > E > T > B [13].

It was also found that the  $q_e$  for SWCNTs was higher than for HCNTs, MWCNTs, and nano-Fe.



**Fig. 4.** Equilibrium amount of (a): benzene, toluene, ethylbenzene, and xylene and (b): total BTEX adsorbed on CNTs and nano-Fe with a  $c_0$  of 10 mg/L.

With a  $c_0$  of 10 mg/L, the SWCNTs showed the greatest  $q_e$  (B: 9.98, T: 9.96, E: 9.97, X: 9.97 mg/g). The  $q_e$  of total BTEX for SWCNTs was 39.89 mg/g.

The equilibrium amount ( $q_e$ ) sequence is SWCNTs > HCNTs > MWCNTs > nano-Fe. This result implies the presence of chemically inherited groups that lead to direction of the affinity for BTEX removal, irrespective of the texture characteristics. This indicates that the adsorption of BTEX on CNTs is dependent on the surface chemical nature and the porosity characteristics. Similar findings have been reported in the literature for

the adsorption of BTEX on activated carbon [4]. Used of silica with MWCNT as HCNT, silica cause opens the tubes of MWCNT and produce sheet that have more area than MWCNT for BTEX adsorption. It is response for more removal of BTEX by HCNT than MWCNT.

It is important to identify the adsorption mechanism of BTEX on CNTs. Because no significant pH variation during adsorption was observed, it is suggested that the  $\pi$ - $\pi$  electron donor-acceptor mechanism involving the carboxylic oxygen atom on the CNT surface as the electron donor and the aromatic ring of BTEX as the electron acceptor is responsible for the uptake of BTEX by CNTs [9]. Similar conclusions have been drawn in the literature for the adsorption of BTEX on multi-walled carbon nanotubes [13].

Furthermore, the electrostatic interaction between the BTEX molecules and the SWCNT surface may also explain the observation of high BTEX adsorption via the single-wall CNTs. Because the BTEX molecules are positively charged [9], the adsorption of BTEX is thus favored for adsorbents with a negative surface charge. This results in more electrostatic attraction and thus leads to a higher BTEX adsorption.

Comparisons for  $q_e$  from this study with various adsorbents, such as SWCNTs, MWCNTs, powdered activated carbon (PAC) and granular activated carbon reported in the literature are given in Table 2. Under analogous conditions, the present SWCNTs show better performance for BTEX adsorption than do other adsorbents. This suggests that the SWCNTs are efficient BTEX adsorbents. Because the costs of commercially available CNTs are continuously decreasing, it may be possible to utilize these novel nanomaterials for BTEX removal in water and wastewater treatment in the near future.

#### CNT and Nano-Fe Recycling

Repeated availability is an important factor for an advanced adsorbent. Such an adsorbent not only pos-

**Table 2.** Comparisons of  $q_e$  via various adsorbents (T—temperature, °C; S/L—solid/liquid, g/mL;  $c_0$ —initial concentration, mg/L)

Adsorbents	$q_e$ (mg/L)				Condition	Reference
	Benzene	Toluene	Ethylbenzene	Xylene		
MWCNT	9.8	9.8	9.9	9.9	T = 10, S/L = 0.1/100, $c_0$ = 10	This study
SWCNT	9.98	9.98	9.98	9.98	T = 10, S/L = 0.1/100, $c_0$ = 10	This study
Hybrid CNT	9.97	9.95	9.96	9.96	T = 10, S/L = 0.1/100, $c_0$ = 10	This study
Nano-Fe	9.7	9.8	9.8	9.8	T = 10, S/L = 0.1/100, $c_0$ = 10	This study
CNT	18.1	80.1	81.1	147.8	T = 25, S/L = 0.06/100, $c_0$ = 200	[9]
GAC	183.3	194.1	—	—	T = 30, S/L = 0.15/100, $c_0$ = 35–442	[14]
PAC	40	40	—	—	S/L = 0.1/40, $c_0$ = 100	[6]
Activated carbons	4.76	5.5	6.75	7.33	T = 25, S/L = 0.1/100, $c_0$ = 10	[4]

**Table 3.** BTEX removal by raw and recycled MWCNT, SWCNT, HCNT and nano-Fe at  $c_0 = 10$  mg/L and contact time of 10 min

Adsorbent	Benzene		Toluene		Ethylbenzene		Xylene	
	$c_t$ , mg/L	removal percent, %	$c_t$ , mg/L	removal percent, %	$c_t$ , mg/L	removal percent, %	$c_t$ , mg/L	removal percent, %
MWCNTrec1	0.013	99.9	0.039	99.6	0.03	99.7	0.12	99.8
SWCNTrec1	0.013	99.9	0.033	99.7	0.02	99.7	0.02	99.8
HCNTrec1	0.015	99.8	0.05	99.5	0.04	99.5	0.08	99.2
Nano-Fe rec1	0.014	99.9	0.03	99.7	0.03	99.7	0.06	99.4
MWCNTrec2	0.015	99.8	0.02	99.7	0.015	99.8	0.06	99.4
SWCNTrec2	0.014	99.9	0.02	99.8	0.012	99.9	0.03	99.6
HCNTrec2	0.015	99.8	0.02	99.8	0.02	99.8	0.15	99.4
Nano-Fe rec2	0.02	99.8	0.04	99.5	0.02	99.8	0.16	99.4

sesses higher adsorption capability but also should show better desorption properties, which will significantly reduce the overall cost for the adsorbent.

Although nanoparticles and CNTs show more BTEX sorption capacities in aqueous solution, their very high unit cost currently restricts their potential use in water treatment. Thus, testing the reversibility of sorbents that could be used for BTEX removal is required to reduce their replacement cost. For this purpose, as a part of the study, the probability of used SWCNT, MWCNT, HCNT and nano-Fe recycling was investigated. Table 3 shows the BTEX removal percent by MWCNTs, SWCNTs, HCNTs and nano-Fe that was recycled in the first cycle (MWCNTrec1, SWCNTrec1, HCNTrec1 and nano-Fe rec1) and the second cycle (MWCNTrec2, SWCNTrec2, HCNTrec2 and nano-Fe rec2) under an initial BTEX concentration of 10 mg/L, a nanomaterial concentration of 1000 mg/L, a contact time of 10 min and shaking at 240 rpm. Figure 5 compares raw SWCNTs, MWCNTs, HCNTs and nano-Fe with their recycling performance in cycles 1 and 2.

It is apparent that CNTs can be reused for the removal of BTEX through a large number of water and wastewater treatment and regeneration cycles. The presence of metal catalysts in raw CNTs that may remain through the chemical process used to functionalize CNTs may be removed by heating, causing better adsorption performance for recycled CNTs than for raw CNTs. In addition, the structure and nature of the carbon surface were changed after thermal treatment, including the increase in graphitized structure and the decrease in surface functional groups and negative charges [8]. These could also be reasons why CNTs were able to adsorb more BTEX after recycling.

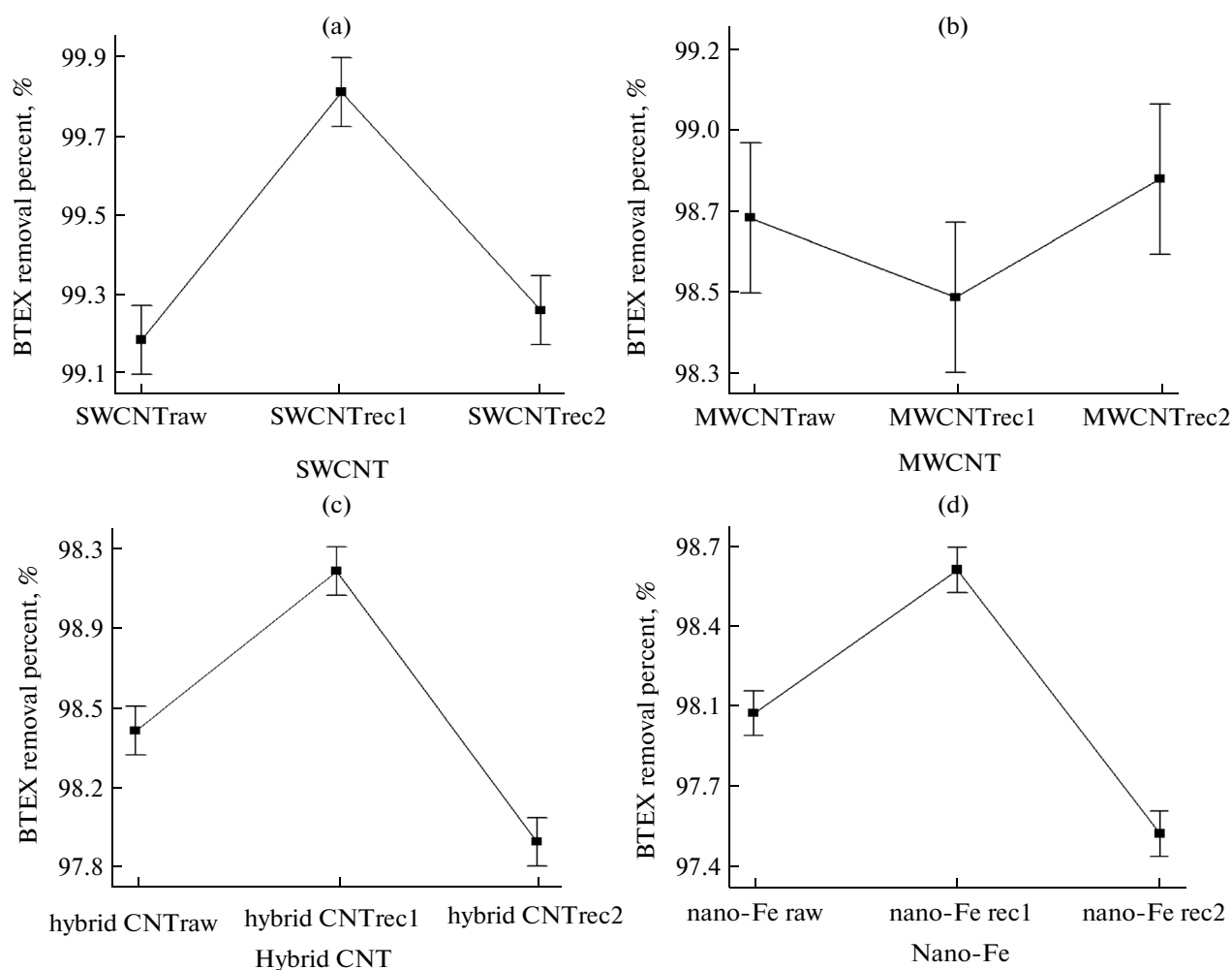
The results show that the BTEX adsorbed by the SWCNTs could be easily desorbed by temperature; therefore, SWCNTs can be employed repeatedly in water and wastewater management.

This is the key factor determining whether a novel but expensive sorbent can be accepted by the field or

not. It is expected that the unit cost of CNTs will be further reduced in the future by recycling heat processes. SWCNTs and MWCNTs appear to be potentially cost effective BTEX sorbents for water and wastewater treatment. The desorption differences between CNTs and carbonaceous materials such as black carbon, coal, and kerogen in soils/sediments that are composed of almost the same element may be due to their distinct geometric structures. The carbonaceous materials exhibit a high degree of porosity and extended interparticulate surface area, whereas CNTs are one-dimensional hollow nanosized tubes as well as aggregates. CNTs easily adhere to each other and form bundles due to strong van der Waals interactions. The adsorption sites are therefore defined for the entire bundle instead of individual nanotubes. There are four possible groups of adsorption sites on bundles: the interior of individual tubes, the interstitial channels between nanotubes, the external groove sites, and the outer surface sites of individual tubes on the peripheral surface of the bundles. The interior of individual tubes is only available in open-ended tubes; the interstitial channels are applied for large tube diameters, while grooves and the external surface are the most important for adsorption [15]. Therefore, it is inferred that most of the BTEX molecules are located on the external adsorption sites. Moreover, CNTs cannot form closed interstitial spaces in their aggregates. Hence, all of the adsorbed BTEX is released by the temperature. The sorbent weight loss was neglected in the recycling processes. The weight loss can be attributed to the evaporation of adsorbed water and the elimination of carboxylic groups and hydroxyl groups on the CNT wall [9].

## CONCLUSIONS

We concluded that SWCNTs showed a higher adsorption capacity for BTEX removal than HCNTs, MWCNTs, and nano-Fe. The  $q_e$  for MWCNTs and SWCNTs follow the following order: X > E > T > B; for HCNT, the order is E > X > T > B and for nano-Fe, the



**Fig. 5.** Design expert plot for raw and recycled: (a) SWCNT, (b) MWCNT, (c) HCNT, and (d) nano-Fe in BTEX removal with a  $c_0$  of 10 mg/L.

order is  $X > T > E > B$  for a  $c_0$  of 10 mg BTEX/L. It appears that xylene isomers are the components with the highest adsorption tendency on CNTs and benzene is the component with the lowest adsorption tendency. The equilibrium amount ( $q_e$ ) sequence is SWCNTs > HCNTs > MWCNTs > nano-Fe. HCNT had a higher adsorption capacity than MWCNT because silica cause opens the tubes of MWCNT and produce sheeted carbons that have more area than MWCNT for BTEX adsorption.

After recycling nanomaterials over 2 cycles, SWCNTs and MWCNTs were shown to be efficient BTEX sorbents that can be regenerated and reused in water and wastewater treatment applications. Furthermore, heating could be upgraded produced improved adsorption on recycled CNTs and nano-Fe compared with raw CNTs.

The metal catalysts in raw CNTs may be removed during heating, causing better adsorption performance for recycled CNTs than for raw CNTs.

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