



**BTEX Removal from Aqueous Solution by
Modified Multi-Walled Carbon Nanotubes With Ozone**
Remoção de BTEX de Solução Aquosa por
Nanotubos de Carbono de Paredes Múltiplas com Ozônio

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Abstract

Modification of multi-walled carbon nanotube (MWCNT) via ozone was carried out to enhance removal of BTEX from aqueous solution. MWCNT was oxidized by ozone (MWCNT-O₃) generator at %80 intensity for 5 min and in 30% NaOCl solution. The images of scanning electron microscopy (SEM) results indicated that the MWCNT-O₃ have a lower degree of entanglement with increased porosity compared to the non-modified MWCNT. X-ray diffraction (XRD) test showed that structural crystallization was increased following the modification. After change, the Fourier transform infrared (FTIR) analysis showed that the peaks corresponded to the hydroxyl and carboxylic acid groups in MMWCNT-O₃ were more intense than those in non-MMWCNT. The optimum condition for initial BTEX concentration, MWCNT-O₃ dose, contact time, and pH was 100 mg/L, 2000 mg/L, 20 min, and 5 respectively. In this optimum condition the efficiency of MWCNT-O₃ were increased by %43.5. This study concludes that this method is easy to use and also that ozone is an effective modifier for MWCNT in removal of BTEX compounds from the environment.

Keywords: BTEX; Ozone; Nanotubes; Aqueous Solution

Resumo

Modificações de nanotubos de carbono de paredes múltiplas (MWCNT) por ozônio foi realizada, melhorando a remoção de compostos BTEX de solução aquosa. MWCNT foi oxidado por gerador de ozônio (MWCNT-O₃) em intensidade de 80% por 5 minutos em solução de 30% de NaOCl. A análise das imagens de microscopia eletrônica de varredura (SEM) indicou um baixo grau de emaranhamento com porosidade aumentada quando comparada ao MWCNT não modificado. Os testes de difração de raios-X (DRX) mostraram que a cristalização estrutural foi aumentada, seguindo a alteração dos nanotubos. Após as alterações, a análise de infravermelho de Fourier (FTIR) mostrou que os picos correspondentes aos grupos de hidroxila e ácido carboxílico em MMWCNT-O₃ foram mais intensos que aqueles dos MWCNT não modificados. A condição ótima para concentração inicial de BTEX, dose de MWCNT-O₃, tempo de contato e pH foi de 100 mg/L, 2000 mg/L, 20 min, e 5, respectivamente. Nessa condição ótima, a eficiência do MWCNT-O₃ foi aumentada em 43,5%. Este estudo conclui que este método é simples de ser utilizado e que o ozônio é um modificador efetivo para MWCNT na remoção de compostos BTEX do meio ambiente.

Palavras-chave: BTEX; Ozônio; Nanotubos; Solução aquosa

1 Introduction

Nowadays, excessive use of energy resources and raw materials in industries, oil and its products, are considered as the source of a large number of environmental pollutants (de Oliveira & de Oliveira Loureiro, 1998). Benzene, toluene, ethylbenzene, and xylene collectively known as BTEX, are widely used as industrial solvents in fine chemical and petrochemical industries. The Environmental Protection Agency (EPA) classified BTEX as priority pollutants that tend to pose significant threat to human health and environment due to their toxic and carcinogenic properties (Van Agteren *et al.*, 1998, Murata *et al.*, 1999, Pourzamani *et al.*, 2014a). BTEX petroleum products are in the form of volatile organic compounds, single ring, nonionic, and nonpolar (Su *et al.*, 2010, Bielefeldt & Stensel, 1999, Pourzamani *et al.*, 2014b). The EPA standard for BTEX in drinking water are 0.005 mg/L for benzene, 1 mg/L for toluene, 0.7 mg/L for ethylbenzene, and 10 mg/L for xylene isomers (Reusser & Field, 2002). BTEX contribute to major environmental problems such as global warming, stratospheric ozone depletion, photochemical ozone formation, and odor nuisance (Sarafray-Yazdi *et al.*, 2008). These organic compounds are flammable, toxic, carcinogenic, and mutagenic. The presence of these compounds in water, even at low concentrations, is of the most concern. The removal of these compounds from the water resource is essential to ensure safe water (Li *et al.*, 2010; Pourzamani *et al.*, 2015b). Conventional methods for treating are complex and dependent to areas that have been contaminated with BTEX. The methods used for removing BTEX from water and wastewater commonly include biological treatment, membrane filters, adsorption by activated carbon, and zeolite adsorption (Fakhru'l-Razi *et al.*, 2009; Moura *et al.*, 2011; Sanjay *et al.*, 2013). The comparisons of CNTs with other adsorbents, such as activated carbon made by the fore going researchers, suggest that the CNTs are promising adsorbents for environmental protection applications (Lu & Su, 2007). Ozonation can modify the surface property of an activated carbon such as specific surface area, pore volume, and functional group. Su *et al.* (2010) oxidized carbon nanotube (CNT) by NaOCl to enhance its benzene, toluene, ethylbenzene, and p-xylene (BTEX) adsorption capacity. The study indicated that the CNTs (NaOCl) are efficient in adsorbing of BTEX from water and wastewater. Chiang *et al.* (2002) studied the effect of ozone

treatment on the adsorption of volatile organic carbon (VOC) exemplified by methyl ethyl ketone (MEK) and benzene. Results indicated that ozonation can increase the specific surface area of activated carbon from 783 ± 51 to 851 ± 25 m²/g, partially due to increasing microspores. Manchester *et al.* (2008) reported that modified activated carbon by ozone increased the efficiency of mercury absorption. Hemraj-Benny *et al.* (2008) survived the effect of ozonolysis on the pore structure, surface chemistry, and bundling of single-walled carbon nanotubes and found that ozonolysis likely opens end caps and introduces holes into the sidewalls of tubes, which may occur through an oxidation of carbon atoms located on the nanotube surface, resulting in the formation of oxygen-containing functional groups. This study aimed to improve the adsorption capacity of (MWCNT) modified by ozone for removal of BTEX from aqueous solution and to determine the significance and optimum conditions for BTEX removing.

2 Materials and Methods

The materials used in this study include MWCNT, purchased from the Iranian Research Institute of the Petroleum Industry, NaOCl (Merck, Germany, 6-14% active chlorine, analytical grade). The chemicals tested in this study were benzene (Merck, purity: 99.7%), toluene (Merck, purity: 99.7%), ethylbenzene (Merck, purity: 99.7%), and Xylene (Merck, purity: 99.7%). A BTEX stock solution, approximately 100 mg/L, 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 H₂O. The mixture was thoroughly solved using an ultrasonic bath (Bandline Sonorex Digitex DT156, Germany) for 60 min, and then stirred continuously for 24 h at 25°C. After shaking, the solution was again put in an ultrasonic bath for 30 min (Bina *et al.*, 2012) and then used to prepare the initial solution of BTEX with 10-100 mg/l concentrations. Standard series and samples containing desired concentrations of BTEX were made using deionized water.

2.1 Adsorbent

The MWCNTs was oxidized by ozone generator (OWA-1000, Taiwan) for 5 min and %80 intensity in 30% NaOCl solution (140 mL H₂O +

60 mL NaOCl from Merck, Germany, %70 pure). The MWCNT was repeatedly washed with distilled water until reaching neutral pH. Then, it was put in an oven (Memmert D-91126, Schwabach FRG Company, Germany) at 75°C for 24 h to dry. The dried MWCNT was kept in a desiccator for later use.

2.2 Experimental Conditions

All of the batch experiments were conducted in 250 mL glass flasks. In each experiment, different amounts of the adsorbents, from 50 to 200 mg, were added to 100 mL of BTEX solution, with initial concentrations (C_0) of 10-100 mg/L. In addition, these variables were examined at different pH varying from 2 to 11 and retention time from 2 to 20 min (Table 1). These concentrations were chosen as representatives of the low BTEX level in gasoline polluted water. 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 in room temperature for 2-20 min. Before and after each experiment, BTEX was determined using a gas chromatograph coupled to a flame ionization detector (GC-FID) (Agilent technology 7890A). All of the experiments were repeated 3 times, and only the mean and standard deviation values were reported. Blank experiments, without any addition of adsorbents, were also conducted to ensure the decrease in the BTEX concentration that actually has been adsorbed on glass bottle wall or via volatilization. The pH was measured at the beginning (pH_{in}) and at the end (pH_{fin}) of each experiment. The initial pH was adjusted using 0.05 M HCl (Merck, Germany, %30 pure) and 0.05 M NaOH (Merck, Germany, %99 pure). The amount of adsorbed BTEX on adsorbent (q_e , mg/g), distribution ratio (K_D , L/g) and removal percentage (%R) were calculated according to Equations 1-3.

| 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 |

Table 1 Controlling factors and their levels.

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

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

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

where C_0 and C_t (mg/L) are the BTEX concentrations at the beginning and at the end of each run, V is the initial solution volume (L), and m is the adsorbent weight (g).

2.3 Chemical Analysis

Initial samples were quantified via GC-FID at injection line temperature of 210°C with split less mode and detector temperature of 250°C. The following temperature program was used for column oven: 36°C for 1 min, 10°C/min to 90°C, direct to 150°C with 25°C/min rate and hold at 150°C for 6 min. The hydrogen gas was used as the fuel (flow 30 mL/min), air flow was 300 mL/min, and nitrogen was used as a makeup gas at a flow rate of 30 mL/min. 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. Experimental optimum parameters of the headspace sampler were based on Amin et al. article (Amin *et al.*, 2014). The headspace gas was injected into GC-FID injector from an automatic headspace sampler after 25 min shaking at 70°C. No NaCl was added to the samples, and the pH was determined using a pH meter (Cyberscan pH1500, Thermo Fisher Scientific Inc., Netherland). The injector port was maintained at 250°C, and 1 mL volume of headspace was injected in split less mode.

2.4 Data Analysis

Design of experiments (DOE) software (Design Expert 6 Stat-Ease, Inc., USA) was used to ascertain the individual effects of pH, adsorbent dose, initial concentrations of BTEX, contact time on removal of BTEX data analysis, and also experiments number reduction.

2.5 Characterizations of Adsorbents

The crystal phase of adsorbents was characterized by a powder X-ray diffractometer (XRD, Philips, Co. Nederland). The morphology of the adsorbents was studied by a scanning electron microscopy (SEM) (Philips XI30, Philips, Nederland). The surface functional groups of the adsorbents were detected by a Fourier Transform Infrared Ray (FTIR) Spectrometer (JASCO, FT/IR-6300, Japan) in the range of 400-4000 cm^{-1} .

3 Results

3.1 Modification of Carbon Nanotubes With Ozone

Table 2 shows the percent removal of BTEX in different conditions by MWCNT modified with ozone.

| Solution | Concentration of Substrate (%) | Time (min) | Ozone Dose (%) | Removal (%) |
|---------------------|--------------------------------|------------|----------------|-------------|
| Sodium hypochlorite | 30 | 5 | 80 | 49.5 |
| Sodium hypochlorite | 60 | 15 | 20 | 43 |

Table 2 Different conditions for modification of MWCNT with ozone.

3.2 Scanning Electron Microscopy Study (SEM)

The morphology of adsorbents were observed by using SEM. Figure 1A shows the SEM images of carbon nanotubes treated with ozone and Figure 1B shows the unmodified carbon nanotube.

3.3 X-Ray Diffraction (XRD)

Crystallographic structure of functionalized MWCNT was confirmed by X-ray diffraction (XRD) measurements. Figure 2 gives a XRD pattern of MWCNT and MWCNT- O_3 .

3.4 Analysis of Infrared Spectroscopy (FTIR)

FTIR testing for chemical bonds and functional groups attached to the carbon nanotubes were used. Figure 3 shows the results of FTIR for MWCNT and MWCNT- O_3 .

3.5 BTEX Removal by MWCNT- O_3 at Different Conditions

The percent removal of MWCNT- O_3 was evaluated by using different conditions. Table 3

and Figure 4 show the benzene removal in the MWCNT- O_3 . The estimated effects of the factors and their interactions can be seen in Table 4.

| Run | Factors | | | | Response1: BTEX | | |
|-----|---------------------------|---------------------------------|--------------------|----|-----------------|-------|----------------|
| | BTEX Concentration (mg/L) | MWCNT- O_3 dose (mg/L) | Contact Time (min) | pH | c_t (mg/L) | R (%) | q_t / (mg/g) |
| 1 | 120±1.4 | 500 | 8 | 7 | 64.9±0.2 | 45.9 | 110.1 |
| 2 | 120±3.2 | 2000 | 14 | 5 | 50.1±0.1 | 58.2 | 34.9 |
| 3 | 40±1.2 | 1500 | 14 | 7 | 18.4±0.2 | 54 | 14.4 |
| 4 | 280±1.6 | 500 | 14 | 11 | 134.1±0.1 | 52.1 | 29.17 |
| 5 | 40±1.2 | 1000 | 8 | 5 | 20±0.2 | 49.4 | 19.7 |
| 6 | 120±2.9 | 1000 | 2 | 11 | 59.9±0.1 | 50.1 | 60.1 |
| 7 | 400±3.9 | 1000 | 14 | 2 | 176.4±0.2 | 55.9 | 223.6 |
| 8 | 40±3.9 | 2000 | 20 | 11 | 16.6±0.2 | 58.4 | 11.7 |
| 9 | 120±3.3 | 1500 | 2 | 2 | 63.1±0.1 | 47.4 | 37.9 |
| 10 | 400±6 | 2000 | 20 | 7 | 155.2±0.7 | 61.2 | 122.4 |
| 11 | 400±5 | 500 | 20 | 5 | 158.8±0.6 | 60.3 | 48.2 |
| 12 | 400±5 | 1500 | 8 | 11 | 174±1.1 | 56.4 | 150.4 |
| 13 | 280±3.2 | 2000 | 8 | 2 | 116.2±0.1 | 58.5 | 8.1.9 |
| 14 | 280±2.7 | 1500 | 2 | 5 | 131.3±0.7 | 53.1 | 99.1 |
| 15 | 40±1.3 | 500 | 2 | 2 | 24.6±0.6 | 38.5 | 30.8 |
| 16 | 280±5.1 | 1000 | 20 | 7 | 128.2±0.7 | 54.2 | 157.7 |

Table 3 Removal of BTEX by MWCNT- O_3 in different conditions.

Table 4 shows the effect of the interaction between these factors and the removal of BTEX by MWCNT- O_3 .

| Factor-Interaction | DF | Sum of Squares | Mean Squares | F Value | Prob > F | Contribution (%) |
|------------------------------|----|----------------|--------------|---------|----------|------------------|
| A: BTEX concentration (mg/L) | 3 | 374.6 | 124.9 | 922.8 | < 0.0001 | 34.4 |
| B: MWCNT- O_3 Dose | 3 | 408.7 | 136.2 | 1006.5 | < 0.0001 | 37.5 |
| C: Contact time (min) | 3 | 163.6 | 54.5 | 403 | < 0.0001 | 15 |
| D: pH | 3 | 68.1 | 22.7 | 167.9 | < 0.0001 | 6.2 |
| AB Interaction | 3 | 69.8 | 23.3 | 172 | < 0.0001 | 6.4 |
| Lack of Fit | 15 | 2 | 0.14 | | | 0.2 |
| Pure Error | 0 | | | | | 0 |
| Residuals | 15 | 2 | 0.14 | | | 0.2 |

Table 4 the effect of the factors on removal of BTEX by MWCNT- O_3

4 Discussion

Modification of carbon nanotubes with ozone gas is a relatively new technique that features high-performance, low price, and easy in operation (Li

et al., 2008). Ozone improves surface properties of carbon nanotubes such as specific surface area, pore volume, and surface functional groups (Pourzamani *et al.*, 2015a). According to Table 2, the best modification of carbon nanotubes occurred in 30% solution of sodium hypochlorite for 5 minutes by 80% of the production of ozone. Chiang *et al.* results indicated that ozonation increase the specific surface area of activated carbon from 783 ± 51 to 851 ± 25 m^2/g (Chiang *et al.*, 2002). Increased in surface area, micro pore volume, and mesopore volume of CNTs depend on several, intertwined factors, including the degree of purity, surface functionality, density of surface groups, as well as the state of aggregation of the carbon tubes (Hemraj-Benny *et al.*, 2008).

Figure 1 shows the SEM images of MWCNT- O_3 (Figure 1A) and MWCNT (Figure 1B). It is clear from Figure 1A that the surface of the MWCNT- O_3 is porous and its structure is homogenous. Figure 1B shows that the untreated MWCNT surface structure is smooth and agglomerated. Ozonation can modify the surface property of an activated carbon such as surface area and pore volume. Ozone reacts with the physical structure of the activated carbon enlarging the pore size and creates new pores. Increase in pore structure is seen at the micro pore (Chiang *et al.*, 2002). Benny *et al.* studied the influence of O_3 and $\text{O}_3/\text{H}_2\text{O}_2$ in purification of MWCNT and found that a large amount of contaminant material, such as amorphous carbon is substantially removed after ozonolysis (Hemraj-Benny *et al.*, 2008). How does this purification process occur? Upon ozonolysis, amorphous carbon detritus, onions, and nanoparticles become heavily functionalized with oxygenated groups (Mawhinney *et al.*, 2000), and thereby have increased solubility in polar solvents, which are used to wash these samples (Banerjee & Wong, 2002). In addition, ozone is expected to etch away at oxidize the graphitic shells, coating the iron metal particles, exposing these metal impurities to removal by further chemical treatment (Hemraj-Benny *et al.*, 2008).

Figure 2 gives a XRD pattern of MWCNTs and MWCNT- O_3 . The sharp peak at 517° comes from G (002) substrate and the other peaks lying at 280 and 356 attribute to G (100), G (101) which are located at 43.33 and 44.61, respectively. Ahmed *et al.* (2013) investigated the compression of functionalization of multi walled carbon nanotubes treated by olive oil

and nitric acid. The results showed that the nitric acid could increase the peak intensity in the 80 au. As shown in Figure 4, the peaks at G (002), G (100), G (101) for MWCNT were increased, the sharpness of the peak indicates that the graphite structure of the MWCNT was oxidized without significant damage (Chiang *et al.*, 2011; Woointranont *et al.*, 2011).

As shown in Figure 4, modified with different antioxidants creates different functional groups on the surface of carbon nanotubes, including alcoholics, carboxylic acids, aldehydes, ketones, and esters (Gupta & Saleh, 2011b). The hydroxyl group peak in the spectra of the modified MWCNT is more intense than that in the non-modified MWCNT spectra. In addition, other bands at $1400\text{--}1730$ cm^{-1} corresponding to $-\text{C}=\text{O}$, $-\text{COO}-$, and $-\text{COOH}$ groups were all reinforced after treatment, especially a new peak at 1718 cm^{-1} can be assigned to $\text{C}=\text{O}$ stretching of the carboxylic acid group (Shojaosadati *et al.*, 2010). Since no significant pH variation during adsorption as well as direct relationship between BTEX adsorption and surface carboxylic groups of the MWCNT were observed, it was suggested that the π - π electron-donor-acceptor mechanism involving the carboxylic oxygen atom of the MWCNT surface as electron donor and the aromatic ring of BTEX as electron acceptor is responsible for the uptake of BTEX by MWCNT (Ren *et al.*, 2011). Table 3 shows the best condition and maximum BTEX removal for MWCNT- O_3 . Table 3 indicates that the maximum removal of BTEX was happen in run 10, that is 61.2% of the total BTEX was removed. The comparison of BTEX removal in same condition (run 10) with MWCNT and MWCNT- O_3 illustrated that MWCNT- O_3 (61.2%) has better performance than MWCNT (17.7%). Figure 4 shows the removal of BTEX at different concentrations, MWCNT- O_3 doses, contact time, and pH for determining the optimum conditions of BTEX removal by MWCNT- O_3 . Figure 4A shows that the BTEX adsorption increased from 40% to 46.5% with raising the initial BTEX concentration from 10 to 100 mg/L . (Qadri *et al.*, 2009) obtained similar results and showed that the amount of dye adsorbed increased from 3.6 mg/g^{-1} to 35 mg/g^{-1} as the dye concentration increased from 3.69 to 184 mg/L . Figure 4B indicates that, according to our expectation, an increase in MWCNT dose directly affects the removal of BTEX, while the optimum condition of MWCNT dose was selected to be 2

g/L. Figure 4C shows that the highest rate of BTEX adsorption occurs for 20 min. In BTEX removal by MWCNT-O₃, the amount of adsorbed BTEX increased from 2 to 20 min. Figure 4D shows that the removal efficiency was in minimum level, at pH = 7, and maximum level at pH = 5. According to the Figure 4, optimum conditions to removal of BTEX are 100 mg/L BTEX concentration, adsorbent dose 2000 mg/L, contact time 20 min, and pH 5. As shown in Table 4, the statistical significance between parameters was tested by comparing the mean square against the experimental error. In this case, five effects have prob> F less than 0.05 and indicated that they are significantly different from zero at the 95%

confidence level (Amin *et al.*, 2013). Interaction between BTEX concentration with MWCNT-O₃ dose and pH seemed to be less significant because of the F-values, 172 and 167.9, respectively. Also, the contact time contributed to the major part in affecting the adsorption capability, i.e. 37.5%. The results showed that the higher initial concentration of adsorbent enhanced the sorption process and it's reasonable. The effective parameters in BTEX removal were following the order of:

MWCNT-O₃ dose > BTEX concentration > Contact time > AB Interaction > pH.

Figure 1 SEM images of carbon nanotubes treated with ozone (a) and unmodified carbon nanotubes (b)

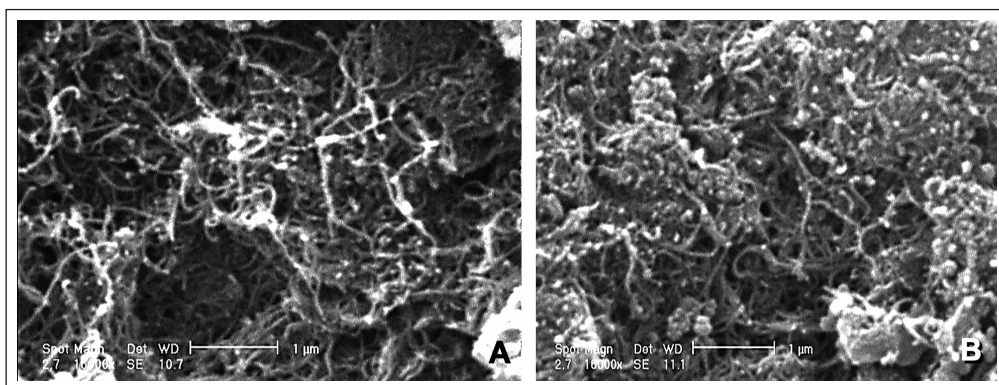


Figure 2 XRD compare images of MWCNT with modified carbon nanotubes with ozone.

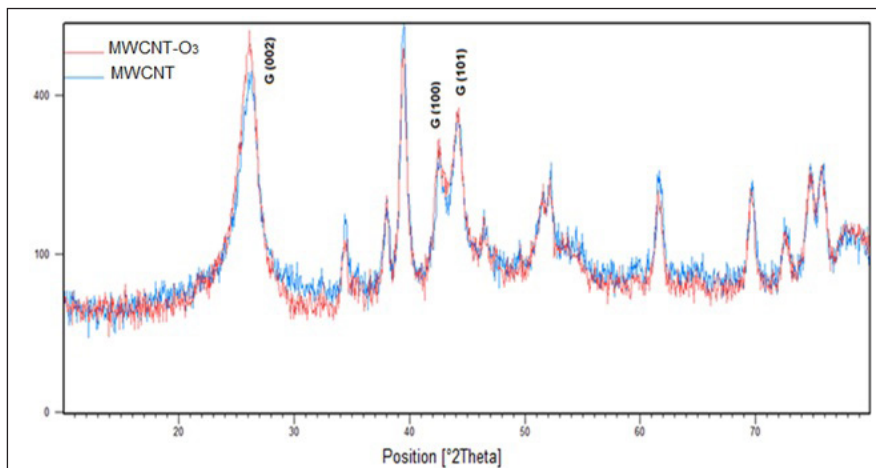
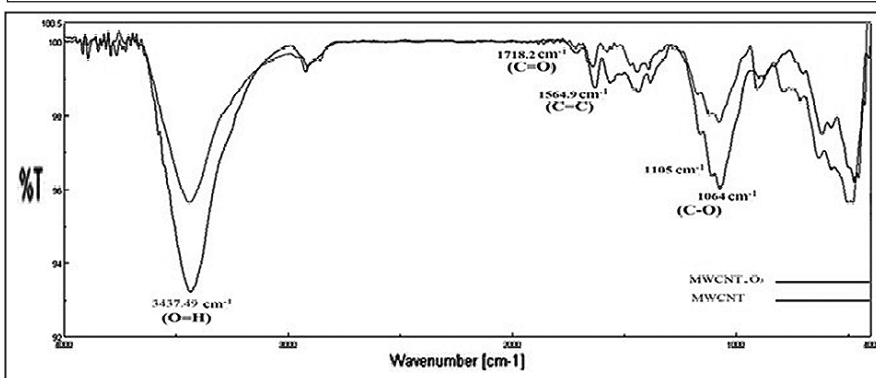


Figure 3 FTIR of MWCNT and MWCNT-O₃.



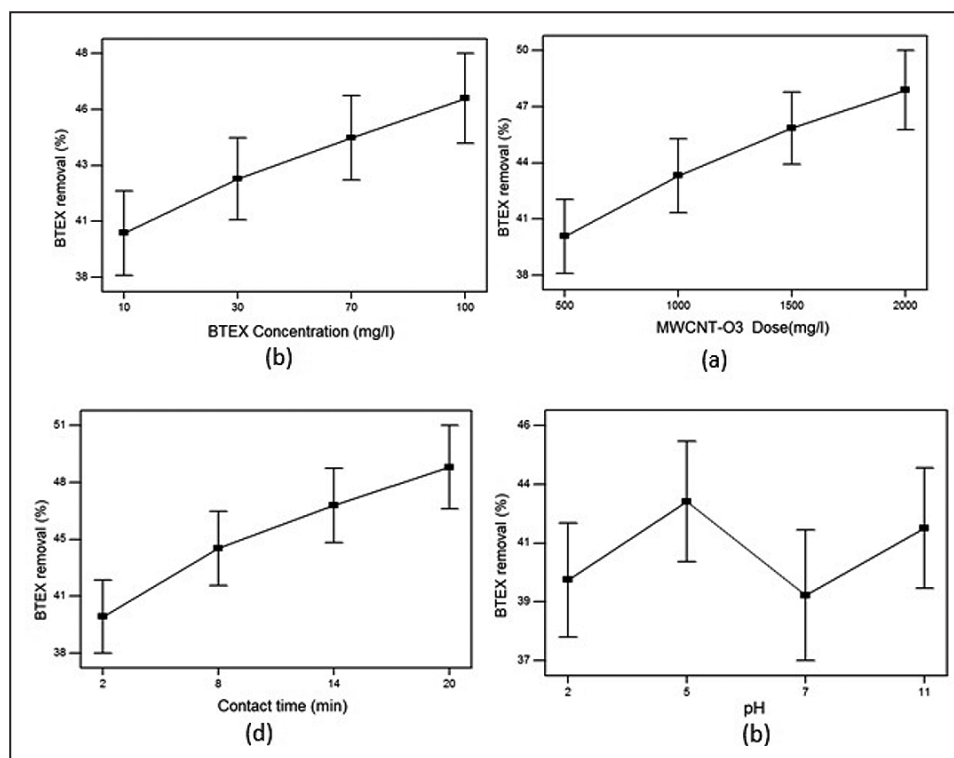


Figure 4 The impact of various factors on the removal of BTEX by MWCNT-O₃: (a) initial concentration of BTEX (b) adsorbent dose (c) contact time (d) pH

5 Conclusion

In this study, MWCNT were oxidized by NaOCl solution in different intensities ozone and time. MWCNT was employed as adsorbents to study their characterizations and adsorption performance of BTEX in an aqueous solution. XRD, FTIR, and SEM test show that the physicochemical properties of MWCNT were greatly improved after the oxidation, including the increase of crystallization, surface carboxylic groups, and pores, which made MWCNT a better adsorbent for BTEX. The optimum condition for initial BTEX concentration, MWCNT-O₃ dose, contact time, and pH was 100 mg/L, 2000 mg/L, 20 min, and 5 respectively. This suggests that the ozone modification is simple and an efficient method for removal of BTEX from aqueous solution.

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