Original Article

Efficiency enhancement of multi-walled carbon nanotubes by ozone for benzene removal from aqueous solution

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ABSTRACT

Aims: Modification of multi-walled carbon nanotubes (MWCNTs) via ozone was carried out to enhance removal benzene from aqueous solutions.

Materials and Methods: Multi-walled carbon nanotubes purchased from the Iranian Research Institute of the Petroleum Industry was oxidized by ozone generator at %80 intensity for 5 min and in 30% NaOCl.

Results: The Fourier transform infrared analysis showed that the peaks corresponded to the hydroxyl and carboxylic acid groups in modified MWCNTs (MMWCNTs) are more intense than that in non-MMWCNTs. The images of scanning electron microscopy indicated that the MMWCNTs have a lower degree of entanglement with increased porosity compared to the nonmodified one. X-ray diffraction test showed that structural crystallization was increased following the modification. After modification, the efficiency of MWCNTs was increased by 20%. The optimum condition for initial benzene concentration, MWCNT dose, contact time, and pH was: 100 mg/L, 2000 mg/L, 20 min, and 5 respectively.

Conclusion: Our research suggested that ozone modification can be a simple method in improvement of the MWCNTs efficiency for removal of benzene from aqueous solution.

Key words: Aqueous solution, benzene, efficiency enhancement, multi-walled carbon nanotube, ozone modification

INTRODUCTION

Benzene is one of the contaminators of air, surface water, and groundwater.[1] Benzene volatile and flammable aromatic hydrocarbon have been used in solvent and exist in many fuels such as petroleum and gasoline.[2] Benzene pollutes groundwater through the leakage from underground storage, pipelines, improper waste disposal, in advertent spills and landfills.[3] Its present concentration limit for drinking water established by the United States Environmental Protection Agency and the German guideline is 1 mg/L.[2] There are concerns about adverse health effects of benzene including cancer, irritation of mucosal membranes, hematological changes, impairment of the central nervous system, respiratory problems and disruption of liver and kidney[4] Benzene can be detected by odor at levels of 2.5 ppm or greater in air, and in water it is detected by taste/odor at levels of 0.5-2.0 ppm.[5] Therefore, removal of benzene from water and wastewater

is essential. Some treatment methods such as chemical oxidation, biological treatment, air stripping and adsorption have been successfully used for the removal of benzene from water and wastewater.[6] The nanometer material is a new functional material, which has attracted much attention due to its special properties. Most of the atoms on the surface of the nanoparticles are unsaturated and can easily bind with other atoms. Nanoparticles have high adsorption capacity. Besides, the operation is simple, and the adsorption process is rapid. So there is a growing interest in the application of nanoparticles as adsorbents.[7] Xu *et al*.[8] used O_2 plasma for surface modification of multi-walled carbon nanotubes (MWCNTs) and found that plasma treatment shows high efficiency for purification of MWCNTs. Su *et al*.[9] oxidized carbon nanotubes (CNTs) by NaOCl to enhance its benzene, toluene, ethylbenzene and p-xylene (BTEX) adsorption capacity, and indicated that the CNTs (NaOCl) are efficient in adsorbing BTEX from water and wastewater. Lu *et al*.[10] fabricated CNTs by the catalytic chemical vapor deposition method and oxidized by HCl, H_2SO_4, HNO_3 and NaOCl solutions for enhancing benzene, toluene, BTEX adsorption in an aqueous solution. Advantage of using ozone in modified of MWCNT (MMWCNT) include high performance, short time to modification, and free of environmental pollution. Disadvantages include causing the salty water and the ozone generator desirable. This study aimed to evaluate the ability of ozone treatment in surface modification and improvement of the adsorption capacity of (MWCNTs) as a new method and to examine its potential application for removal of volatile organic compounds (VOCs) such as benzene from aqueous solution and determine the significance and optimum condition (pH, nano materials dose, initial toluene concentrations and contact time) for removing benzene.

MATERIALS AND METHODS

Materials
The materials used in this study include MWCNTs that purchased from the Iranian Research Institute of the Petroleum Industry, NaOCl (Merck, Germany, %70 pure, analytical grade). A solution of 100 mg/L of benzene was prepared by dissolving appropriate amounts of benzene (Merck, purity: 99.7%, analytical grade) in deionized water. 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 put in ultrasonic bath again for 30 min[11] and was used to prepare initial solution of benzene with 10-100 mg/L concentrations. Standard series and samples containing desired concentrations of benzene were made using deionized water.

Adsorbent
The MWCNTs was oxidized by ozone generator (OWA-1000, Taiwan) for 5 min and %80 intensity in 30% NaOCl solution (140 mL H_2O + 60 mL NaOCl) (Merck, Germany, %70 pure).

The MWCNTs was repeatedly washed with distilled water until reaching neutral pH and put in an oven (Memmert D-91126, Schwabach FRG Company, Germany) at 75°C for 24 h to dry. The dried MWCNTs were then kept in a desiccator for later use.

Experimental conditions
All of the batch experiments were conducted in 250 ml glass flasks. In each experiment, various amounts of the adsorbents, from 50 to 200 mg, were added to 100 ml of benzene 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 benzene 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 set-ups, 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, benzene 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 values were reported. Blank experiments, without the addition of adsorbents, were also conducted to ensure the decrease in the benzene concentration that actually has been adsorbed on glass bottle wall or via volatilization. The solution 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 benzene on adsorbent (qe, mg/g), distribution ratio (K_D, L/g) and removal percentage (%R) were calculated according to Equations 1-3.

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

$$K_D = \frac{C_0 - C_t}{C_t} \times \frac{V}{m} \tag{2}$$

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \tag{3}$$

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

Table 1: Controlling factors and their levels				
Factors	**Level 1**	**Level 2**	**Level 3**	**Level 4**
Benzene 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

MWCNTs: Multi-walled carbon nanotubes

Chemical analysis

Initial samples were quantified via GC-FID at injection line temperature of 210°C, split less mode of 80 ml/min in 2 min and detector temperature of 250°C. The following temperature program was used for column oven: 36°C for 1 min and 10°C/min to 90°C, direct to 150°C with 25°C/min rate and hold in 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 a CP-sil 5 Cb 25 m × 320 μm × 1.2 μm with helium (purity 99.995%) as carrier gas at the flow rate of 1.11 ml/min. The gas chromatography mass spectrometry (GC-MS) was used for determining the benzene in low concentrations after treatment by MWCNTs. The Agilent technologies system consists of 5975°C inert MSD with triple axis detector that is, equipped with a 7890A gas chromatography with a split/splitless injector. A fused silica column, HP-5 ms (5%phenyl-95% dimethylpolysiloxane; 30 m, 0.25 mm I.D., 0.25 μm), was employed with helium (purity 99.995%) as carrier gas at a flow rate of 1 ml/min. The column oven temperature was programmed as follows: 40°C for 10 min, increasing to 150°C at 10°C/min and holding for 2 min. The injector port was maintained at 250°C, and 1 mL volume of headspace was injected in splitless mode (2 min). The effluent from the 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 scan mode. The data were acquired and processed using the data analysis software. 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.[3] The headspace gas was injected into GC-FID or GC-MS injector from an automatic headspace sampler after 25 min shaking in 70°C. No NaCl was added to the samples, and the pH measurements were made with a pH meter (Cyberscan pH1500, Thermo Fisher Scientific Inc., Netherland).

Experimental plan and data analysis

Design of Experiments (Design Expert 6 Stat-Ease, Inc., USA) was used to ascertain the individual effects of pH, doses of MMWCNTs, initial concentrations of benzene, and contact time on the benzene removal. This method was also used for data analysis and to decrease the number of the experiments. The Taguchi orthogonal array plan was applied by four factors at four levels [Table 1]. The matrix involved 16 runs, and each run was triplicated. The corresponding factor values in Table 1 were in compliance with the brain storming and literature.[10,12,13]

Isotherm study was evaluated for benzene adsorption by MWCNTs in optimum condition. MWCNTs dose 2 g/L, contact time 14 min, and pH 8. Water solubility of benzene was estimated to be 1790 mg/L at pH 7. Isotherm fitting tool (ISOFIT) software(Version 2 , Inc., USA) was used to fit isotherm parameters to experimental data. ISOFIT is a software that fits isotherm parameters to experimental data

via the minimization of a weighted sum of squared error (WSSE) objective function.[14] The ISOFIT supports a number of isotherms, including: (1) Brunauer-Emmett-Teller, (2) Freundlich, and (3) Langmuir.

Characterizations of the 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}.

RESULTS AND DISCUSSION

Adsorbent characteristics

Scanning electron microscopy study

The Digimizer software (Digimizer v4.1.1.0, Inc., USA) was applied to detect the diameter of the MWCNTs. It was found that the average diameter of the MWCNTs after treatment was 60 nm. As shown in Figure 1a, in addition to irregular distribution and some agglomerated parts, the surface structure is smooth for untreated MWCNTs. SEM image of the MMWCNTs showed a lower degree of entanglement [Figure 1b]. When MWCNTs aggregate together, they can form bundles or pores that create lots of adsorption sites, such as the interstitial channel, the external groove, and partial coating of the external surface nanometer thick layered carbon.[15] The lower degree of aggregation in the MMWCNTs was attributed to carboxyl groups.[16] It is clear that the surface of the MMWCNTs is porous, and its structure is homogenous. Khani and Moradi[17] studied the influence of surface oxidation on the morphological and crystallographic structure of MWCNTs via different oxidants and found that after treatment with acids, a clear change in diameter and surface roughness
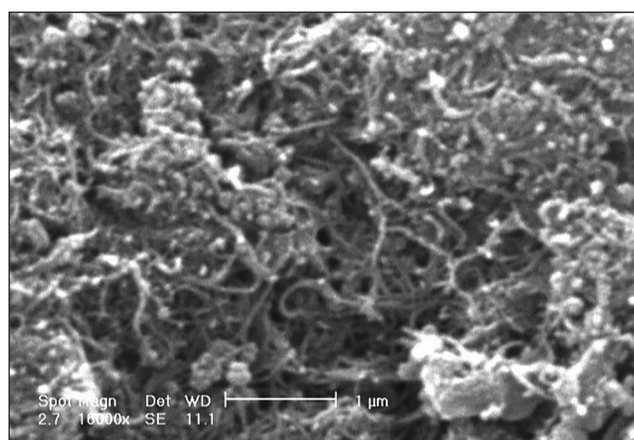

Figure 1a: Scanning electron microscopy images of nonmodified multi-walled carbon nanotubes

was occurred along the tube walls. Through the oxidation process, the diameters of the MWCNTs were narrowed down gradually.

Fourier transform infrared spectra

Fourier transform infrared is mainly used as qualitative technique for evaluation of functional group. Figure 2 shows the FTIR spectra of non-MMWCNT (a) and MMWCNT (b) from 370 to 4000 cm^{-1}. It shows that the bands at 3437, 1629, and 1034 in MMWCNTs is more intense than that in the non-MMWCNTs spectra and a new peak at 1718 cm^{-1} in MMWCNTs can occur. The hydroxyl group peak in the spectra of the MMWCNTs is more intense than that in the non-MMWCNTs spectra. The bands at 3440 and 2915 cm^{-1}are assigned to -OH stretch from carboxylic groups (-COOH and -COH).[18] In addition, other bands at 1400-1730 cm^{-1} corresponding to -C=O, -COO-, and -COOH groups were all reinforced after treatment, especially a new peak at 1718 cm^{-1} can be assigned to C=O stretching of the carboxylic acid group.[19] Peaks around 1034 cm^{-1} can be assigned to C-O stretching vibrations of the carboxylic acid group that increased after modification.[20] Since no significant pH variation during adsorption as well as direct relationship between benzene adsorption and surface carboxylic groups of the MWCNTs were observed, it was suggested that the π - π electron-donor-acceptor

mechanism involving the carboxylic oxygen-atom of the MWCNTs surface as electron-donor and the aromatic ring of benzene as electron-acceptor is responsible for the uptake of benzene by MWCNTs. A diagram of the mechanism for adsorption of benzene on the MWCNTs is shown in Figure 3.[21] These formed functional groups are abundant on the external and internal surface of oxidized MWCNTs, which increase the surface polarity and further alter the surface charges.[10]

X-ray diffraction patterns

X-ray diffraction is used in order to ascertain the quality and crystalline nature of nanotubes as opposed to amorphous carbon materials. Figure 4 shows a XRD pattern of the MWCNTs. The sharp peaks at 25.97 1, 43.33 1, and 44.61 attribute to G (002), G (100), G (101), which are located at 26.1, 42.6, and 44.2, respectively.[22] In the present study, the effects of different NaOCl concentration were evaluated on structural integrity, surface area and pore distribution of the MWCNTs. As shown in Figure 4, the peaks at G (002), G (100), G (101) for MMWCNT was increased which is a sign of its higher crystallization. Woointranont *et al*.[23] investigated the effect of surface modification of CNTs on the formation of nickel oxide/CNT Nano composites, and in the XRD analysis the peak at (002) was decreased. They found that acid-treated method may cause the structural destruction of CNT. It is known that oxidants can alter structural and physical properties of MWCNTs.[24,25]
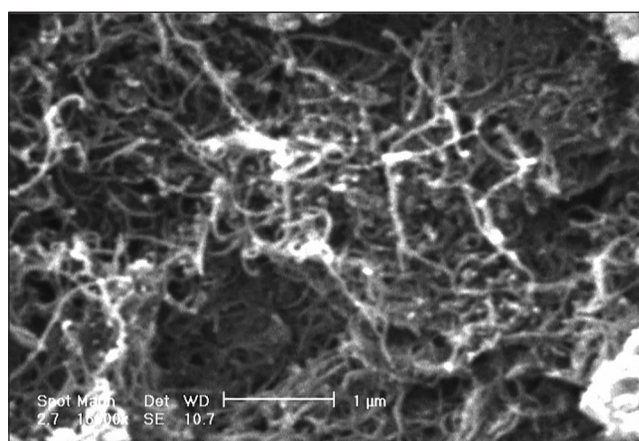

Figure 1b: Scanning electron microscopy images of modified multi-walled carbon nanotubes
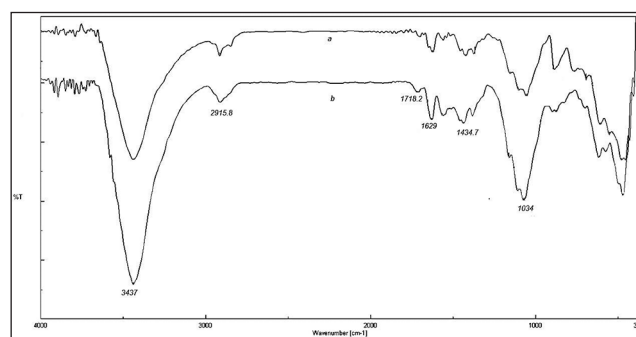

Figure 2: The Fourier transform infrared spectra of (a), nonmodified multi-walled carbon nanotubes (MWCNT) and (b) modified MWCNTs
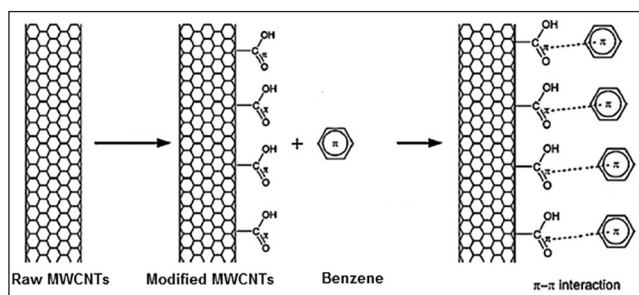

Figure 3: A diagram of the mechanism involved in adsorption of benzene on the modified multi-walled carbon nanotubes
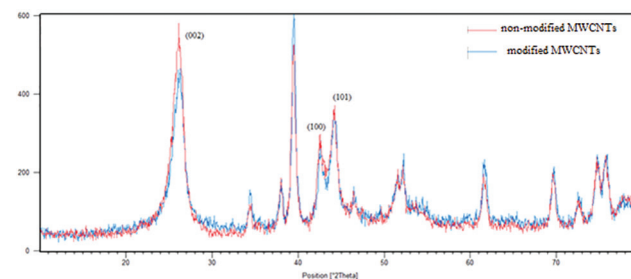

Figure 4: X-ray diffraction patterns of nonmodified multi-walled carbon nanotubes (MWCNTs) and modified MWCNTs composites

Optimum condition for benzene removal

According to Table 2 obtained from DOE software, in the batch experiments, the MMWCNTs adsorbed benzene >33%in run 10. Also for MWCNT the maximum benzene uptake occurs in run 10 and it was only 13% (the table for MWCNT don't added), which is consistent with previous studies.[3]

Run	Factors				Responsel: Benzene			
	Benzene concentration/ (mg/L)	Modified MWCNTs dose/(mg/L)	Time/min	pH	C_t/(mg/L)	R/%	Qe/(mg/g)	K_D (L/g)
1	30 ± 0.2	500	8	7	24.2 ± 0.2	19.2	11.52	36
2	30 ± 0.5	2000	14	5	20.5 ± 1.2	31.5	4.73	11.7
3	10 ± 0.4	1500	14	7	7.4 ± 0.8	26	1.73	5
4	70 ± 0.4	500	14	11	53 ± 0.3	24.3	34.02	96.9
5	10 ± 0.5	1000	8	5	7.5 ± 0.4	25.2	2.52	6.7
6	30 ± 1.2	1000	2	11	23.5 ± 0.4	21.6	6.48	21.9
7	100 ± 1.9	1000	14	2	72.2 ± 0.7	27.8	27.8	76.8
8	10 ± 0.5	2000	20	11	6.7 ± 0.1	33.1	1.66	4
9	30 ± 1.8	1500	2	2	24.3 ± 0.2	18.9	3.78	12.9
10	100 ± 1.2	2000	20	7	66.8 ± 0.5	33.2	16.6	40.7
11	100 ± 2.4	500	20	5	67.1 ±.1.2	32.9	65.8	161.4
12	100 ± 2	1500	8	11	71.1 ± 0.9	28.9	19.27	51.4
13	70 ± 0.9	2000	8	2	48.1 ± 0.5	31.2	10.92	27.9
14	70 ± 1.7	1500	2	5	50.6 ± 0.1	27.7	12.93	34
15	10 ± 0.2	500	2	2	9 ± 0.6	9.6	1.92	10.9
16	70 ± 1.6	1000	20	7	52.2 ± 0.3	25.4	17.78	51.3

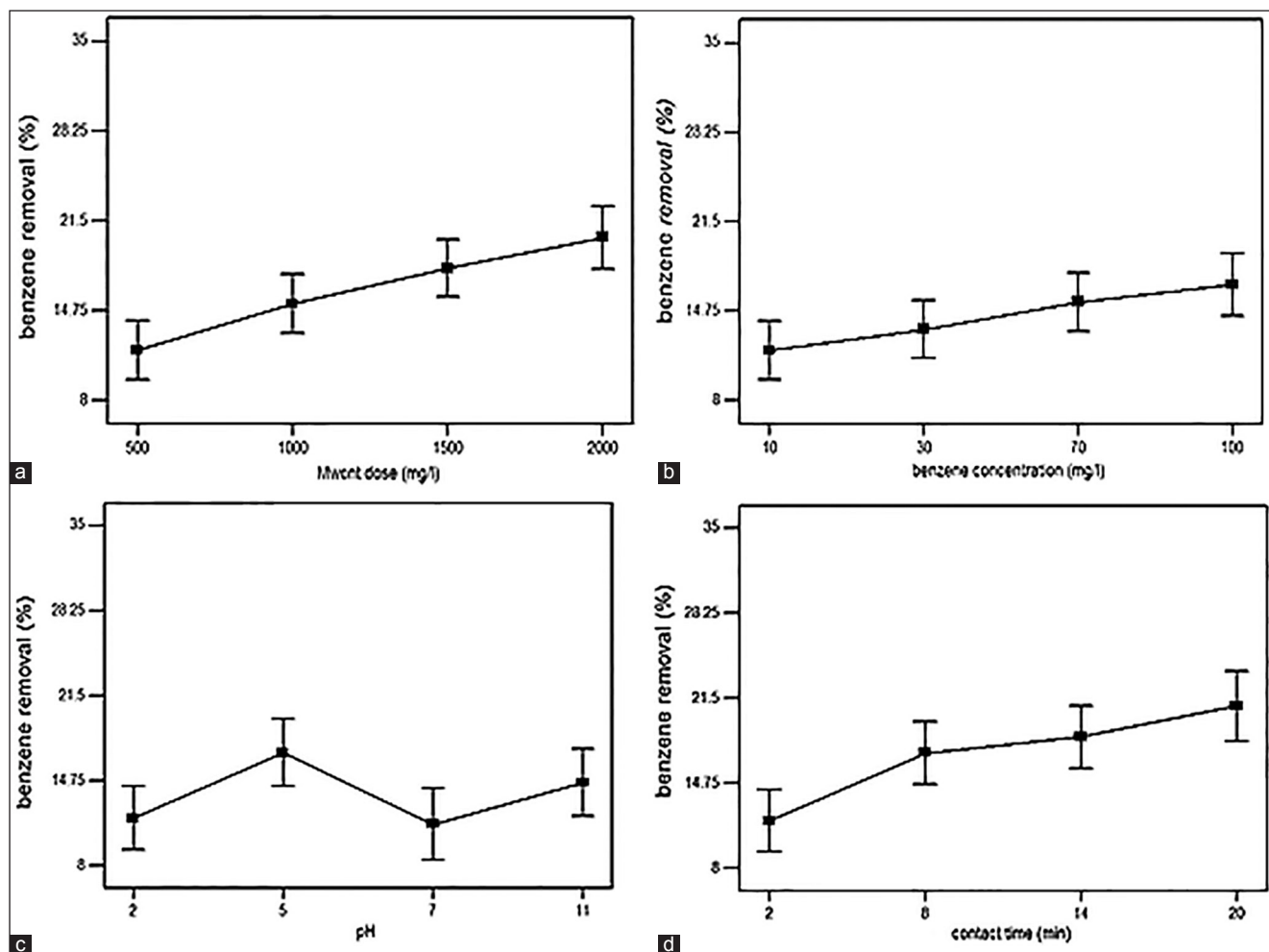MMWCNT: Modified multi-walled carbon nanotube, MWCNTs: Multi-walled carbon nanotubes

Figure 5: Design expert plot of the factors effects on benzene removal by modified multi-walled carbon nanotubes (MMWCNTs): (a) MMWCNTs dose, (b) benzene concentration, (c) pH and (d) contact time

Table 3: The best condition and benzene removal for adsorbents

Adsorbent	Factors				Responsel: benzene		
	Benzene concentration (mg/L)	MWCNTs dose (mg/L)	Time (min)	pH	C_t (mg/L)	R (%)	Qe (mg/g)
Raw MWCNTs	100 ± 0.5	2000	20	7	86.1	13.9	6.95
Modified MWCNTs	100 ± 0.3	2000	20	5	66.8 ± 0.5	33.3	16.6

MWCNTs: Multi-walled carbon nanotubes

Table 4: Effects of the factors and interactions obtained by fractional factorial design

Factor/interaction	Degree of freedom	Sum of squares	Mean squares	F	Probability > F	Percentage of contribution
A: Benzene concentration/(mg/L)	3	320.1	106.7	90.13	<0.0001	26.1
B: MMWCNT dose/(mg/L)	3	485.6	161.8	136.7	<0.0001	39.5
C: Contact time/min	3	172.4	57.4	48.5	<0.0001	14
D: pH	3	166.1	55.4	46.7	<0.0001	13.5
AB interaction	3	76.7	25.5	21.6	<0.0001	6.2
Lack of fit	14	17.76	1.18		—	0.3
Pure error	0				—	0
Residuals	14	17.76	1.18	90.13	—	0.3

MMWCNT: Modified multi-walled carbon nanotube

Figure 5 shows the effect of parameters on benzene removal. Figure 5a shows that in the maximum dose of MWCNTs, most benzene removal happened so that 2 g/L of MWCNTs was selected as an optimum dose of the adsorbent. As shown in Figure 5b, with raising the initial benzene concentration from 10 to 100 mg/L, the benzene adsorption increased from 11.7% to 16.8%. Su *et al.*[9] used NaOCl-oxidized CNTs to removal BTEX and obtained similar results. Figure 5c indicates that by increasing the pH values from 2 to 5 the benzene removal percentage was increased. Then, in pH 7 the lowest benzene adsorption occurred, and by raising the pH to 11, benzene removal was increased again. Figure 5d shows that the removal of benzene was increased rapidly with time, and the highest amount of benzene adsorption was occurred in 20 min.

Table 3 shows the best condition and maximum benzene removal for raw MWCNTs and MMWCNTs.

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 probability > F < 0.05 which indicate that they are significantly different from 0 at the 95% confidence level.[3] The F value test showed that the MMWCNT dose acted significantly in affecting the adsorption performance. Besides, the pH influences and the interaction between benzene concentrations and MMWCNT doses seemed less significant because of the F values of 46.7 and 21.6, for pH and interaction, respectively. Also Su *et al.*[9] observed that the change in pH_{in} has insignificant effects on BTEX adsorption, reflecting high stability of MWCNT (NaOCl) as BTEX adsorbents in a wide range of solution pH. Effective factors on the benzene removal followed this order: MWCNTs dose > benzene concentration > contact time > pH > adsorbate concentration and adsorbent dose interaction.

Table 5: Summary of selected diagnostics for benzene adsorption by modified MWCNTs

Isotherms	AICc	R^2y	R^2N	M^2	Linearity assessment
BET	29.19	0.977	0.836	9.5×10^{-2}	Nonlinear
Langmuir	18.4	0.969	0.811	1.1×10^{-10}	Linear
Freundlich	30.4	0.969	0.811	1.37×10^{-1}	Nonlinear

AICc: Multi model ranking, R^2y: Correlation between measured and simulated observation, R^2N: Correlation between residual and normality, M^2: Linssen measure of nonlinearity, MWCNTs: Multi-walled carbon nanotubes, AICc: Corrected akaike information criterion, BET: Brunauer-Emmett-Teller

Isotherm study

Isotherm fitting tool is a software program that fits isotherm parameters to experimental data via the minimization of a WSSE objective.[14] As shown in Table 5, with ISOFIT reported in the output file, the corrected akaike information criterion values indicate that the Langmuir isotherms expression provides the best fit of benzene adsorption by MMWCNTs. The results of earlier studies[26] on adsorption of benzene from aqueous solutions onto activated carbon showed that the Langmuir equation could describe the experimental data fairly better than Freundlich equation.[2]

CONCLUSIONS

In this study, ozone was used to modify the surface characteristics of MWCNTs and enhance its adsorption property. The FTIR, XRD, and SEM analyses show that physicochemical properties of the MWCNTs such as structure and surface nature were greatly improved after oxidation, which resulted in its benzene adsorption capacity to be increased up to 20%. The optimum condition for initial benzene concentration, MWCNT dose, contact time, and pH was: 100 mg/L, 2000 mg/L, 20 min, and 5 respectively. It is concluded that modification of the MWCNTs by ozone

is new method for removal of VOCs such as benzene from water and wastewater.

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