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# Adsorption of toluene, ethylbenzene and xylene isomers on multi-walled carbon nanotubes oxidized by different concentration of NaOCl

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**Abstract** Multi-walled carbon nanotubes (MWCNTs) were fabricated and oxidized by different concentrations of sodium hypochlorite (NaOCl) solutions. The untreated MWCNTs and modified MWCNTs were employed as adsorbents to study their characterizations and adsorption performance of toluene, ethylbenzene and xylene isomers (TEX) in an aqueous solution. The physicochemical properties of MWCNTs were greatly affected after oxidation, which influences TEX adsorption capacity. The 3% NaOCl-oxidized MWCNTs shows the greatest enhancement in TEX adsorption, followed by the 30% NaOCl. More interestingly, the 15% NaOCl-oxidized MWCNTs has lower adsorption capacities than untreated MWCNTs. The adsorption mechanism of TEX on treated MWCNTs is attributed to the combined action of hydrophobic interaction,  $\pi$ - $\pi$  bonding interaction between the aromatic ring of TEX and the oxygen-containing functional groups of MWCNTs and electrostatic interaction. 3% NaOCl solution could not only introduce much oxygen-containing functional groups on MWCNTs, but also lead to less damage for the pore structure. This suggests that the CNTs-3% NaOCl is efficient adsorbent for TEX and that they may possess good potential for TEX removal in wastewater treatment.

**Keywords** adsorption, toluene, ethylbenzene and xylene isomers (TEX), multi-walled carbon nanotube, surface oxidation

## 1 Introduction

It's a global concern that soil and water were contaminated with organic substances such as BTEX (benzene (B), toluene (T), ethylbenzene (E), and xylene isomers (X)) from leaking storage tanks of service stations or the petroleum industry and improper disposal of hazardous wastes. Since BTEX are flammable, toxic and carcinogenic substances, the presence of excessive amounts of BTEX in aqueous surroundings may have a greatly adverse impact on water quality and thus endanger public health and welfare. Consequently, sustainable, efficient wastewater and cost effective treatment for BTEX is significantly needed.

Carbon nanotubes (CNTs) have aroused widespread attention as a new type of adsorbents due to their outstanding ability for the removal of various inorganic and organic pollutants from large volumes of wastewater. CNTs, a new member of the carbon family, were first discovered by Iijima in 1991 [1]. Since then, CNTs have been the focus of considerable research because of their unique physicochemical properties such as functional mechanical, thermal, the diameter and length of the tubes, and the morphology, or nanostructure, and have been termed 'materials of the 21st century' [2]. Because of their highly porous and hollow structure, large specific surface areas, surface functional groups and hydrophobic surfaces, CNTs show strong interactions with organic compounds. For the removal of various organic pollutants in the environment, adsorption of aromatic compounds, such as BTEX [3–9], polyaromatics [10–13], chlorophenols [14,15], 1,2-dichlorobenzene [16,17], nitrobenzenes [18], phenolic compounds [19], amino acid [20], herbicide [21], natural organic matters [22–24], and dyes [25,26] on CNTs has been investigated experimentally or numerically.

The adsorption capacity of organic pollutant via CNTs is mainly attributed to the pore structure and the existence of surface functional groups. Chemical oxidation modification of CNTs plays an important role in changing the surface area and pore size distribution [27], and thus, the adsorption capacity. Although relationships between adsorption and surface area as well as pore volume of CNTs can be constructed, changes in pore sizes and structures may lead to condensation of adsorbents to different degrees. Chemical oxidation of CNTs also affects the maximum adsorption capacity because of the modification in the surface morphology and surface functional groups. Activation of CNTs under various conditions with chemicals such as  $\text{HNO}_3$ ,  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NaOCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{KOH}$ , and  $\text{NaOH}$  has been widely reported [28,29]. The metallic impurities, amorphous carbon, and catalyst support materials are removed after oxidation process and the surface characteristics are altered due to the introduction of new surface functional groups [30]. A modification of CNTs with specific physicochemical properties can be easily achieved by chemical modification [28] or thermal treatment [31] to make them that have the best performance for particular purposes. Although chemical oxidants could remove impurities most effectively, damage the pore structure and introduce oxygen-containing surface groups on CNTs to some extent, the degree of pore structure damage and the amount of oxygen-containing groups are greatly influenced by the concentration of oxidant and experimental condition. However, such studies are still very limited in the literature about adsorption performance on CNTs oxidized by different concentration oxidants.

In this paper, MWCNTs were synthesized by the floating alcohol catalytic chemical vapor deposition (ACCV) methods [32], and a highly efficient and nondestructive purified approach has been studied detailed in our previous work [33]. Based on our previous research results, the small-diameter multi-walled carbon nanotubes have been oxidized by NaOCl solutions with different concentration, and then employed as adsorbents to study their physicochemical properties and adsorption characteristics of TEX in aqueous solutions. Adsorption mechanisms will be better understood by investigating the adsorption properties affected by different concentration NaOCl solutions between MWCNTs and TEX organic chemicals along with groundwater environmental conditions.

## 2 Materials and methods

### 2.1 Chemicals and reagents

All chemicals, such as sodium hypochlorite, toluene, ethylbenzene, xylene, were purchased from Sinopharm Group Co. (Shanghai, China). They were of analytical grade or better and used directly without further purification.

### 2.2 MWCNTs preparation and purification

The present MWCNTs were prepared by the ACCVD method. Alcohol was used as carbon feedstock, ferrocene as catalyst, and thiophene as growth promoter. Ferrocene and thiophene were dissolved in alcohol to prepare solutions with different concentrations of ferrocene and thiophene. A quartz tube (self-made device) of 3 cm in diameter and 1 m in length was heated up to temperatures between  $1000^\circ\text{C}$  and  $1150^\circ\text{C}$  using a tubular furnace (ECFK-8-13, Shanghai Grand Yield High-temp. Tech. Ind. Co., Ltd, China) with a heating length of 70 cm. In the process of raising the temperature, Ar flow was initiated in the quartz tube in order to eliminate oxygen from the reaction chamber. The alcohol solution dissolved with ferrocene and thiophene was supplied by an electronic squirmer pump (BT100-1L, Baoding Longer Precision Pump Co., Ltd, China) and sprayed through a nozzle with an Ar flow. After several hours of pyrolysis, the supply of alcohol was terminated, and the sample was collected from a glass bottle connected to the quartz tube.

The pristine sample in a quartz boat (self-made device) was put in a quartz tube and heated in air at  $400^\circ\text{C}$  for 45 min to oxidize Fe nanoparticles. Air was introduced into the quartz tube at a slow rate to provide oxygen continuously. After air oxidation, the oxidized sample was further heat-treated at  $800^\circ\text{C}$  or  $900^\circ\text{C}$  for 60 min under the protection of Ar gas, and then refluxed in  $3\text{ mol}\cdot\text{L}^{-1}$   $\text{HNO}_3$  for 3 h. The samples after acid treatment were filtered on a  $0.22\text{ }\mu\text{m}$  millipore polycarbonate membrane and rinsed with distilled water until the pH value of the filtrate became neutral. The purified MWCNTs will be referred as as-grown CNTs in the following text.

### 2.3 Surface modification and characterization of MWCNTs

After the purification treatment, the purified MWCNTs samples were oxidized by different concentration of NaOCl (70% purity). The different concentrations were 30% NaOCl (70 mL  $\text{H}_2\text{O}$  + 30 mL NaOCl) solution, 15% NaOCl (85 mL  $\text{H}_2\text{O}$  + 15 mL NaOCl) solution and 3% NaOCl (97 mL  $\text{H}_2\text{O}$  + 3 mL NaOCl) with magnetic stirring at ambient temperature for 12 h, which will be referred as CNTs-30% NaOCl, CNTs-15% NaOCl, and CNTs-3% NaOCl in the following text. After oxidation, the mixture was filtered through a  $0.22\text{ }\mu\text{m}$  millipore polycarbonate membrane and the filtered solid was washed using deionized water repeatedly, until the solution pH became neutral. The filtered solid was dehydrated subsequently using vacuum drying oven at  $120^\circ\text{C}$  for 8 h. The microstructure and morphology of initial and NaOCl modification samples were analyzed by Scanning Electron Microscope (SEM, JSM-6400F, JEOL, Ltd. Japan).  $\text{N}_2$  adsorption experiments using a automatic specific surface area/pore size distribution measurement (BELSORP-miniII, BEL Japan, Inc., Japan) were conducted to investigate the

porosity of MWCNTs. All samples were outgased at 200°C in a nitrogen flow for 4 h prior to the measurement. Nitrogen adsorption data were recorded at the liquid nitrogen temperature (77 K). The specific surface area of MWCNTs was calculated according to the BET equation from the adsorption data in the relative pressure from 0.04 to 0.2. The pore volumes were estimated to be the liquid volume of adsorption ( $N_2$ ) at a relative pressure of 0.99. The micropore size distribution ( $< 2$  nm) was determined by micropore analysis method (MP method) derived from the curvature of the t-plot, which was calculated from  $N_2$  adsorption isotherm. And the mesopore size distribution (2–50 nm) was determined by the Barrett–Joyner–Halenda method (BJH method). Details about these analytical methods can be found in previous publications [34,35]. X-ray diffraction (XRD, Bruker D8 Advance, Bruker AXS, Germany) experiments were performed to study the crystallization of MWCNTs before and after NaOCl modification. XRD was operated at 40 kV and 40 mA. Nickel-filtered Cu K $\alpha$  radiation was used in the incident beam. Micro-Raman spectrometer (LabRam-1B, Dilor, France) was used to further characterize the structural integrity of the as-grown CNTs and oxidized CNTs, with a spectral resolution of 1.2  $cm^{-1}$  per pixel, using a He-Ne laser at an excitation wavelength of 632.8 nm. The surface functional groups of adsorbents were detected by a Fourier transform infrared ray (FTIR) spectrometer (NICOLET 5700, America Spectrum One, Perkin Elmer, MA, USA) from 4000 to 400  $cm^{-1}$ . Zeta potentials of adsorbents were measured at pH 7. Samples were prepared identically to those of the batch experiments. Thirty measurements were made for each sample on a zeta potential analyzer (Zetasizer Nano-Zs, Malvern Instrument Co., UK) and the average was taken as the zeta potential of MWCNTs.

#### 2.4 Batch adsorption experiments

To avoid volatilization loss of TEX from the solid/solution system, batch adsorption experiments were conducted in 50 mL crimp neck headspace vial equipped with pre-assembled cap and teflon septa, with 20 mg MWCNTs and 50 mL TEX solution of different initial concentrations ranging from 10 to 110  $mg \cdot L^{-1}$ , which resulted in almost no headspace. The TEX solubility is not high (T, 515  $mg \cdot L^{-1}$  > p-X, 198  $mg \cdot L^{-1}$  > m-X, 175  $mg \cdot L^{-1}$  > E, 152  $mg \cdot L^{-1}$  > o-X, 130  $mg \cdot L^{-1}$ ). The employed T, E, p-X, m-X, and o-X were diluted using deionized  $H_2O$  to the desired concentrations with ultrasonic cleaner for mixing uniformity. Timing of the sorption period started as soon as the solution was poured into the bottle and sealed. Sample bottles were shaken on a shaker (TS-2102C, Shanghai Tensuclab Instruments Manufacturing Co., Ltd., China) and operated at a constant temperature of 20°C and 180  $r \cdot min^{-1}$  for 10 h. Preliminary experiments indicated that the adsorption of TEX reached equilibrium in about 6 h. Thus, the contact time of 10 h was selected in the batch

experiments. All the adsorption experiments were conducted at least twice. The blank experiments without the addition of MWCNTs were conducted to ensure that the decrease in the concentration was actually due to the adsorption of MWCNTs, rather than by the adsorption on glass bottle wall or via volatilization. The total loss about the blank samples for five compound losses during the experiment shows no more than 10%. After equilibrium was achieved, the TEX concentration of the supernatant solutions was analyzed by gas chromatograph (GC 2010, Shinmadzu Corporation, Japan) with flame ionization detection (GC-FID) [36] and a 0.25 mm inner diameter (ID)  $\times$  30.0 m DB-FFAP column. The oven, injector and detector temperatures of this gas chromatograph were fixed at 50°C, 250°C, and 250°C, respectively.

The amount of adsorbed TEX on adsorbents ( $q_e$ ,  $mg \cdot g^{-1}$ ) was calculated as follows:

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

where  $C_0$  and  $C_e$  are the concentrations of TEX ( $mg \cdot L^{-1}$ );  $V$  is the initial solution volume (L); and  $m$  is the adsorbent weight (g). The amount of adsorbed TEX per unit weight of MWCNTs ( $mg \cdot g^{-1}$ ) was plotted versus the equilibrium concentration ( $mg \cdot L^{-1}$ ).

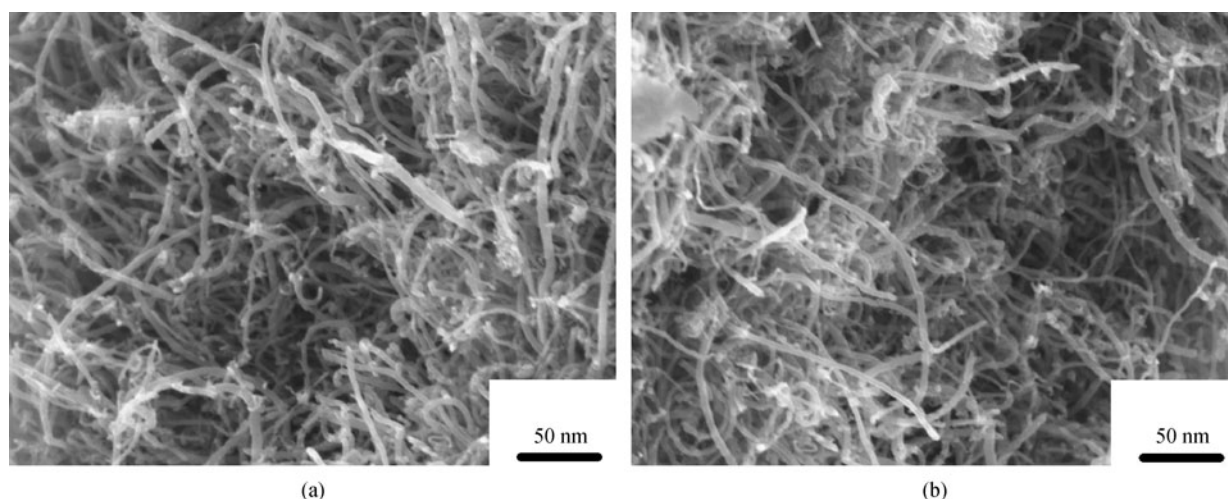
### 3 Results and discussion

#### 3.1 Surface characterization

Figure 1 exhibits the SEM images of as-grown CNTs and CNTs-30% NaOCl, which show that these samples consist of a fiber-like substance, and the fibers are tangled with each other to form a network. The size of outer diameter is less than 10 nm. After the MWCNTs were oxidized by 30% NaOCl, there is no obvious destroy of MWCNTs structure compared Fig. 1 (b) with Fig. 1 (a). After NaOCl-oxidized treatment, the carbon-containing defects could be introduced along the surface of MWCNTs, functional groups can be easily introduced to MWCNT surface and thus provide numerous chemical adsorption sites for TEX. The SEM images of other oxidized MWCNTs show similar results. Thus, their SEM images are not shown in this study.

Figure 2 presents the pore size distribution curves of as-grown and oxidized MWCNTs. The summary of physical properties of the pristine and oxidized MWCNTs are shown in Table 1, which indicates the total surface area (SA), the internal surface areas (ISA) and the external surface areas (ESA), the pore volume (PV) and the average pore diameter (APD) obtained by analyzing the nitrogen adsorption/desorption on MWCNTs at 77 K. The results show that the pristine MWCNTs have the greatest ISA, ESA, and PV. After MWCNTs was oxidized by NaOCl solutions, ISA of all the oxidized MWCNTs were sharply





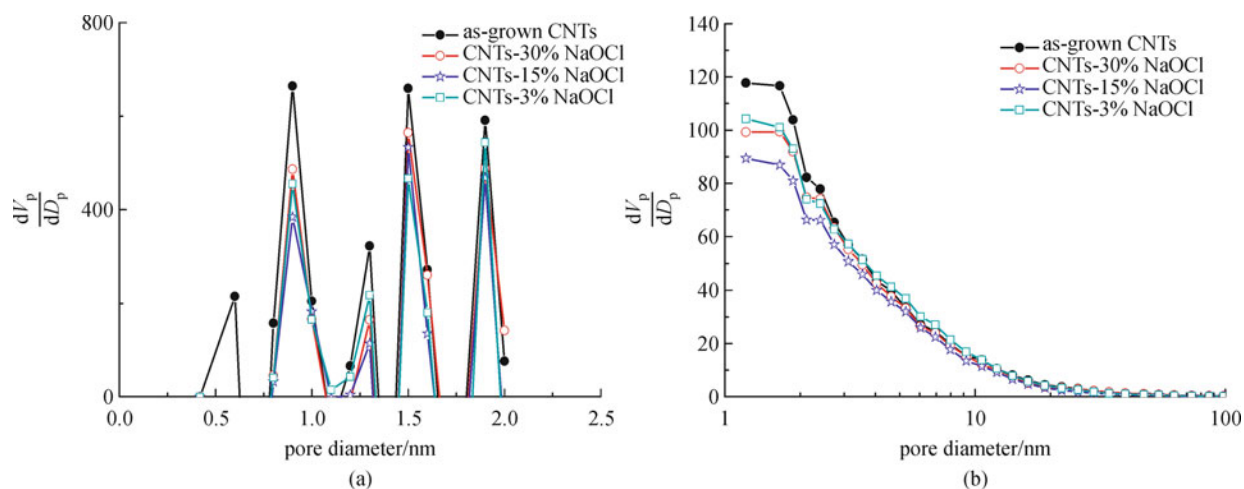
**Fig. 1** SEM of as-grown CNTs (a) and CNTs-30%NaOCl (b)

reduced, ESA and PV of those were reduced, and APD was slightly increased. Comparing CNTs-3% NaOCl with CNTs-30% NaOCl, SA, ISA, ESA, PV, and APD have similar variation trend, which show that CNTs-3% NaOCl and CNTs-30% NaOCl have the same physical properties according to Table 1 and Fig. 2. More interestingly, the total surface area of CNTs-15% NaOCl has decreased greatly than CNTs-3% NaOCl and CNTs-30% NaOCl. Some micropores of CNTs-3% NaOCl could be enlarged into mesopores or some mesopores were destroyed and disappeared, so the total surface area will decrease. 15% NaOCl solution has stronger oxidability than 3% NaOCl, and more micropores could be enlarged into mesopores or more mesopores are destroyed. Consequently, the total surface area will remarkably decrease. With the increasing of oxidability for 30% NaOCl solution, some new pores may be produced or two tips of some MWCNTs may be opened, and thus the total surface area will significantly

increase compared with CNTs-15% NaOCl.

The XRD patterns of as-grown CNTs and oxidized MWCNTs are shown in Fig. 3. It is evident that these patterns illustrate the characteristics of a typical MWCNT structure [37], which indicates a typical peak of graphite at  $2\theta = 26.1^\circ$ . After the MWCNTs were oxidized, the XRD results clearly demonstrated that the graphitic structures were still preserved in the carbon nanotubes.

To further investigate the graphitic structure during the whole NaOCl modification process, Fig. 4 shows the Raman peaks at high frequencies of as-grown CNTs and oxidized MWCNTs. The G peak at about  $1585\text{ cm}^{-1}$  is related to  $E_{2g}$  graphite mode [38–40]. The strong intensity of this peak indicates good graphitization of CNTs. The D-line at around  $1345\text{ cm}^{-1}$  is induced by defective structures. The intensity ratio of the D and G peaks ( $I_D/I_G$ ) is an indicator for estimating the structure quality of MWCNTs samples. As shown in Fig. 4, the values of  $I_D/I_G$  ratio are

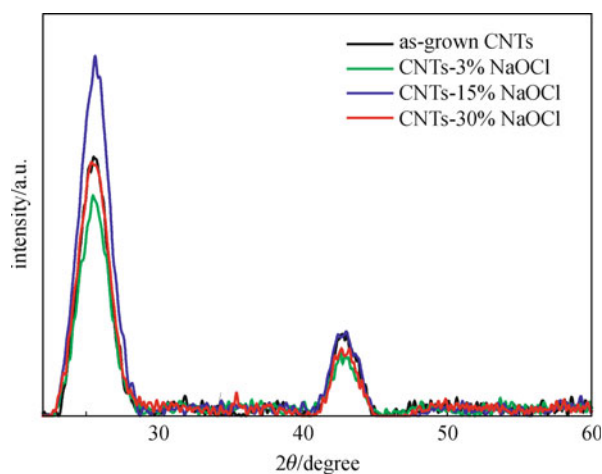


**Fig. 2** Micropore distributions (a) and Mesopore (b) of as-grown CNTs and oxidized MWCNTs

**Table 1** Physical properties of as-grown CNTs and oxidized MWCNTs

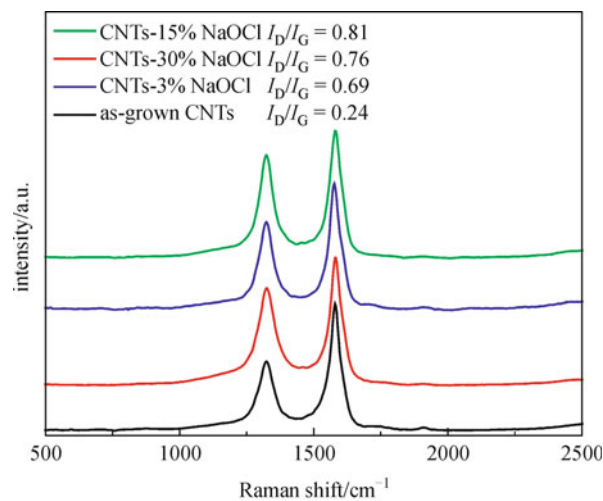
sample	as-grown CNTs	CNTs-3%NaOCl	CNTs-15%NaOCl	CNTs-30%NaOCl
SA	471	381	327	382
ISA	136	61	50	74
ESA	335	320	277	308
PV	0.64	0.58	0.49	0.58
APD	5.4	6.0	5.9	6.0

Note: SA = BET surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ ); ISA = internal surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ ); ESA = external surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ ); PV = pore volume ( $\text{cm}^3 \cdot \text{g}^{-1}$ ); APD = average pore diameter (nm)

**Fig. 3** X-ray diffraction (XRD) patterns of as-grown CNTs and oxidized MWCNTs

0.24, 0.69, 0.81, and 0.76 for as-grown CNTs, CNTs-3% NaOCl, CNTs-15% NaOCl, and CNTs-30% NaOCl, respectively. The lower  $I_D/I_G$  ratio means a higher structure quality of MWCNTs. MWCNTs structures is not greatly destroyed after modification and the results is according with the results of XRD. The results implies that the oxidized MWCNTs have less smooth carbon surface and more structure defects which may be easily introduced oxygen-containing functional groups along the surface of MWCNTs for studying the TEX adsorption performance.

Figure 5 presents the FTIR spectra of MWCNTs, the spectra of these MWCNTs display some significantly apparent bands. It is clear that the bands at about  $3433 \text{ cm}^{-1}$  are assigned to  $-\text{OH}$  stretch from carboxylic groups ( $-\text{COOH}$  and  $-\text{COH}$ ) and  $-\text{OH}$  stretch from strongly H-bonded- $\text{COOH}$ , respectively. The band at about  $1652 \text{ cm}^{-1}$  can be assigned to the stretching variations of  $\text{C}=\text{O}$  groups while the peak at about  $1430 \text{ cm}^{-1}$  is related to the carboxylate anion stretch mode [41]. The band at about  $1099 \text{ cm}^{-1}$  is associated to  $\text{C}-\text{O}$  stretching of alcoholic compounds [42], which evidenced that the carboxylic groups ( $-\text{COOH}$ ) exist in the MWCNTs samples oxidized by NaOCl. These functional groups produced via oxidation exist in the external and internal surface of oxidized MWCNTs, which increase the surface polarity and further

**Fig. 4** Micro-Raman spectra of as-grown CNTs and oxidized MWCNTs

alter the surface charges properties. For example, after NaOCl oxidation, the zeta potentials of as-grown CNTs is reduced from  $-24.9$  to  $-33.7$  mV,  $-30.8$  and  $-33.0$  mV for 3% NaOCl, 15% NaOCl, and 30% NaOCl, respectively, when the solution pH is near neutral. Thus, the introduction of these oxygen-containing functional groups to MWCNTs could provide numerous chemical absorption sites for TEX.

The samples have the same type functional groups after oxidized by 3% NaOCl and 30% NaOCl solutions, the amount of  $\text{C}=\text{O}$  groups and  $-\text{OH}$  groups of oxidized MWCNTs are more than those of untreated MWCNTs. The amount of  $\text{C}=\text{O}$  groups of CNTs-15% NaOCl decreased more than those of as-grown CNTs and  $-\text{OH}$  groups increased. The sharp peak at  $1380\text{--}1680 \text{ cm}^{-1}$  for the MWCNTs suggests that NaOCl oxidation introduces abundant carboxyl surface groups.

### 3.2 Adsorption performance

Adsorption isotherms of TEX on MWCNTs oxidized by different concentration NaOCl solutions, when the solution pH is 7, are shown in Fig. 6. All data points shown in Fig. 6 represent average values from at least duplicate measurements. This study employed the Langmuir and

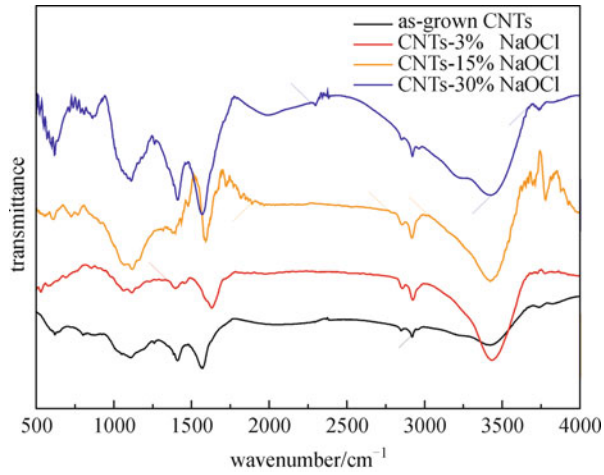


Fig. 5 FTIR spectra of as-grown CNTs and oxidized MWCNTs

Freundlich models to describe the equilibrium adsorption. The expression of the Langmuir model can be stated as follows:

$$q = q_m \frac{K_L C}{1 + K_L C}, \quad (2)$$

where  $q$  is the amount of TEX adsorbed per gram of MWCNTs ( $\text{mg} \cdot \text{g}^{-1}$ );  $C$  denotes the equilibrium concentration of TEX in solution ( $\text{mg} \cdot \text{L}^{-1}$ );  $K_L$  represents the Langmuir constant ( $\text{L} \cdot \text{mg}^{-1}$ ) that relates to the affinity of binding sites; and  $q_m$  is the theoretical saturation capacity of the monolayer ( $\text{mg} \cdot \text{g}^{-1}$ ). The Freundlich equation can be given by:

$$q = K_F C^{1/n}, \quad (3)$$

where  $n$  and  $K_F$  are the Freundlich constants. The magnitude of  $1/n$  quantifies the favorability of adsorption and the degree of heterogeneity of the CNTs surface. If  $1/n$  is less than unity, indicating favorable adsorption, then the adsorption capacity increases and new adsorption sites occur. These isotherms are fitted by both Langmuir and Freundlich models and the parameters are given in Table 2. In the Langmuir model, the  $R^2$  ranges from 0.94 to 0.99. In Freundlich model, the values of  $1/n$  are all less than 1,

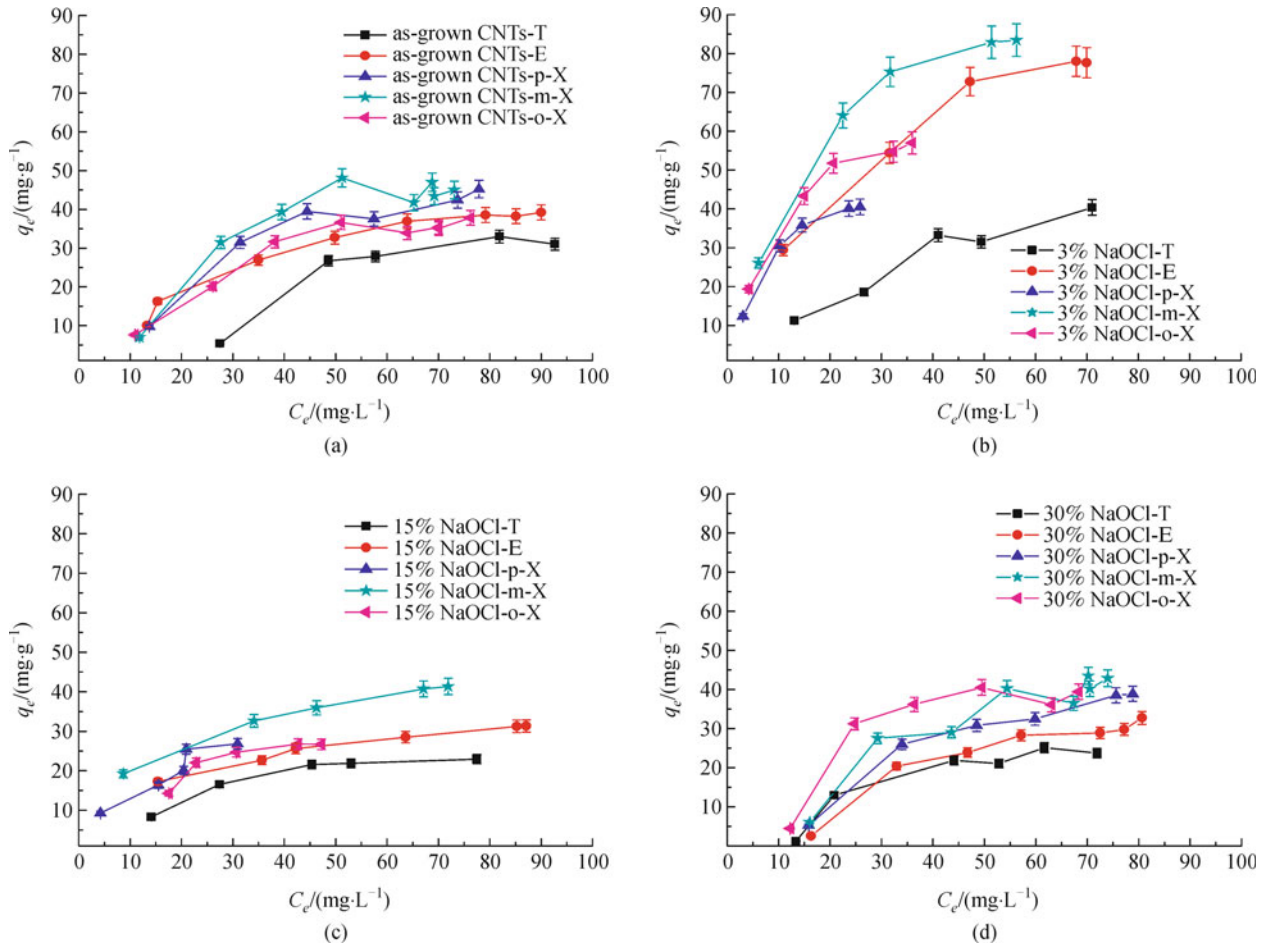


Fig. 6 Adsorption isotherms of TEX on as-grown CNTs and oxidized MWCNTs at pH 7: (a) as-grown CNTs; (b) CNTs-3% NaOCl; (c) CNTs-15% NaOCl; (d) CNTs-30% NaOCl



which suggests that the adsorption is favorable and the  $R^2$  ranges from 0.87 to 0.99. The adsorption capacities simulated by the Langmuir model better than those obtained by the Freundlich model, and the  $R^2$  values of the Langmuir model are almost higher than those of the Freundlich model.

It follows the order for different adsorbents:  $m\text{-X} > p\text{-X} > o\text{-X} > E > T$  for as-grown CNTs, CNT-30% NaOCl and CNT-15% NaOCl with different initial concentration TEX, and  $E > m\text{-X} > T > o\text{-X} > p\text{-X}$  for CNT-3% NaOCl. The nature of adsorbates plays an important role in adsorption characteristics. Favorable adsorption of that order of compounds may be attributed to the decrease in solubility ( $T$ ,  $515 \text{ mg} \cdot \text{L}^{-1} > p\text{-X}$ ,  $198 \text{ mg} \cdot \text{L}^{-1} > m\text{-X}$ ,  $175 \text{ mg} \cdot \text{L}^{-1} > E$ ,  $152 \text{ mg} \cdot \text{L}^{-1} > o\text{-X}$ ,  $130 \text{ mg} \cdot \text{L}^{-1}$ ), and the increase in molecular weight ( $T$ ,  $92.15 < E$ ,  $X$ ,  $106.18$ ) and boiling point ( $T$ ,  $110.63^\circ\text{C} < E$ ,  $136.19^\circ\text{C} < p\text{-X}$ ,  $138.35^\circ\text{C} < m\text{-X}$ ,  $139.1^\circ\text{C} < o\text{-X}$ ,  $144.42^\circ\text{C}$ ). Nonetheless, it is not completely consistent with physical property of adsorbates. Generally, the adsorption for hydrophobic organic compounds will increase, when the solubility of adsorbates decreases. Because ethylbenzene and xylene isomers have very similar nature, their characteristics of adsorption will not have the same order with the nature of adsorbates. The nature of adsorbates is one of factors influencing TEX adsorption performance. The physiochemical of adsorbents also affect the adsorption onto the MWCNTs.

It is evident that the  $q_e$  increased with  $C_0$  as shown in Fig. 6. It is also found that the  $q_e$  is significantly enhanced after the 3% NaOCl and 30% NaOCl oxidation, but is considerably reduced after the 15% NaOCl oxidation. The maximum adsorption capacity ( $q_m$ ) of CNTs-3% NaOCl, CNTs-30% NaOCl, as-grown CNTs, and CNTs-15% NaOCl, respectively, are  $95.4$ ,  $64.7$ ,  $40$ , and  $35.1 \text{ mg} \cdot \text{g}^{-1}$  for  $T$ ;  $115.6$ ,  $85.5$ ,  $61.1$ , and  $38.4 \text{ mg} \cdot \text{g}^{-1}$  for  $E$ ;  $56.17$ ,  $103.4$ ,  $76.1$ , and  $44.6 \text{ mg} \cdot \text{g}^{-1}$  for  $p\text{-X}$ ;  $112.2$ ,  $109.8$ ,  $76.8$ , and  $48.6 \text{ mg} \cdot \text{g}^{-1}$  for  $m\text{-X}$ ; and  $75.3$ ,  $97.4$ ,  $61.8$ , and  $44.4 \text{ mg} \cdot \text{g}^{-1}$  for  $o\text{-X}$ , calculated by the Langmuir model. The  $q_m$  of toluene and ethylbenzene via CNTs-3% NaOCl is about twofold and threefold of magnitude higher than those via as-grown CNTs and CNTs-15% NaOCl.

It appears that the order of  $q_e$  (CNTs-3% NaOCl > CNTs-30% NaOCl > as-grown CNTs > CNTs-15% NaOCl) is the result of combined action among surface area, pore diameter or pore volume (Table 1), and oxygen-containing surface groups of MWCNTs (Fig. 5). This implies that the adsorption of TEX onto the MWCNTs is dependent on the porosity characteristics and surface chemical nature. Chemical oxidants could damage the pore structure and introduce oxygen-containing surface functional groups on MWCNTs. The degree of damage, the total surface area and oxygen-containing functional groups are greatly influenced by the concentration of oxidant. So the concentrations of the oxidant have an important effect on the porosity characteristics and surface chemical nature

of MWCNTs, and then indirectly influence TEX adsorption Characteristics. As-grown CNTs have larger total surface area. However, it is evident that there are no significantly oxygen-containing functional groups on as-grown CNTs as shown in Fig. 5. After oxidized by 15% NaOCl solution, the porosity characteristics were changed, the total surface area significantly decreased and the amount of efficient joint-sites may also decreased for surface functional groups, so efficient oxygen-containing functional groups, such as  $\text{C}=\text{O}$ , were less introduced to the surfaces of MWCNTs. Therefore, the TEX adsorption onto CNTs-15% NaOCl is less than as-grown CNTs. The results of CNTs-15% NaOCl implied that the introduced hydroxyl groups may have reduced TEX adsorption capacities. Similar results have been reported hydrophobic organic compounds sorption by MWCNTs [43]. 30% NaOCl solution was a higher concentration for oxidizing MWCNTs, and the total surface area greatly increased compared with 15% NaOCl. CNTs-30% NaOCl also have much more the  $\text{C}=\text{O}$ ,  $\text{C}-\text{O}$  functional groups on the surface of MWCNTs, and so the adsorption greatly increased. Based on the results of SA given in Table 1 and FTIR shown in Fig. 5, it is obvious that CNTs-3% NaOCl not only have larger the total surface area than CNTs-15% NaOCl, but also introduces more oxygen-containing functional groups than as-grown CNTs. Hence, 3% NaOCl solution would be the best suitable for oxidizing MWCNTs on TEX adsorption and CNTs-3% NaOCl have the best adsorption performance for TEX.

It is of great importance to reveal the adsorption mechanism of TEX on MWCNTs even though it is not straightforward. From Fig. 6, it is obvious that toluene adsorption capacity is lower than other compounds, which may be attributed to hydrophobic interaction. However, hydrophobic interaction alone is not enough to interpret the TEX adsorption by MWCNTs.  $\pi$ - $\pi$  bonding interaction has been used to interpret the adsorption of organic molecules with a benzene ring on the surface of MWCNTs, because these organic molecules contain  $\pi$  electrons to interact with the  $\pi$  electrons of the benzene rings on MWCNTs surface through the  $\pi$ - $\pi$  electron coupling [44]. In this paper, since surface oxygen-containing functional groups of MWCNTs modified by NaOCl are observed, it is plausible that the  $\pi$ - $\pi$  electron coupling mechanism involving the carboxylic oxygen-atom of MWCNTs surface is the responsible for the uptake of TEX by modified MWCNTs. Similar conclusions have been drawn in the literature for adsorption of BTEX on CNT (NaOCl) [8]. Furthermore, the electrostatic interaction between the TEX molecules and the MWCNTs surface may also explain the observation of high TEX adsorption via the untreated MWCNTs and oxidized MWCNTs. Since the TEX molecules are positively charged, which have been reported in the literature for TEX adsorption on CNTs, adsorption of TEX is thus favored for adsorbents with a negative surface charge [3,45]. The zeta potentials of the CNTs-3% NaOCl



**Table 2** Parameters of the Langmuir and the Freundlich models for adsorption of TEX on as-grown CNTs and oxidized MWCNTs

	Langmuir constants			Freundlich constants		
	$q_m/(\text{mg} \cdot \text{g}^{-1})$	$K_L/(\text{L} \cdot \text{mg}^{-1})$	$R^2$	$K_F/(\text{mg} \cdot \text{g}^{-1})$	$1/n$	$R^2$
as-grown CNTs						
T	44.90	0.029	0.99	3.892	0.48	0.96
E	61.16	0.021	0.97	3.64	0.54	0.94
p-X	76.15	0.019	0.99	3.58	0.59	0.93
m-X	76.86	0.023	0.96	4.12	0.57	0.88
o-X	61.86	0.021	0.97	3.24	0.57	0.91
CNTs-3% NaOCl						
T	99.47	0.010	0.99	1.87	0.73	0.98
E	115.63	0.031	0.98	9.92	0.49	0.95
p-X	56.17	0.109	0.98	9.57	0.46	0.91
m-X	112.19	0.057	0.99	15.09	0.44	0.91
o-X	75.27	0.090	0.98	12.71	0.43	0.92
CNTs-15% NaOCl						
T	31.28	0.041	0.99	4.28	0.40	0.94
E	38.40	0.047	0.97	6.87	0.34	0.99
p-X	44.60	0.048	0.95	3.87	0.59	0.98
m-X	48.58	0.069	0.98	9.11	0.36	0.99
o-X	44.42	0.035	0.94	4.32	0.49	0.87
CNTs-30% NaOCl						
T	59.48	0.011	0.99	1.22	0.72	0.98
E	85.49	0.007	0.99	1.06	0.78	0.96
p-X	103.40	0.008	0.99	1.39	0.77	0.97
m-X	109.78	0.009	0.96	1.67	0.76	0.96
o-X	97.39	0.013	0.95	2.53	0.69	0.91

and CNTs-30% NaOCl at a pH of 7 are  $-33.7$  and  $-33.0$  mV, which also leads to a high TEX adsorption for the electrostatic attraction.

## 4 Conclusions

MWCNTs were fabricated by ACCVD methods and oxidized by different concentrations of NaOCl solutions. The untreated MWCNTs and oxidized MWCNTs were employed as adsorbents to study their physicochemical properties and adsorption performance of TEX in an aqueous solution. It is evident that the  $q_e$  is significantly enhanced after the 3% NaOCl and 30% NaOCl oxidation, but is reduced after the 15% NaOCl oxidation. The Langmuir model fits the experimental data better than those obtained by the Freundlich model, the  $R^2$  ranging from 0.94 to 0.99. The  $q_e$  of toluene and ethylbenzene via CNTs-3% NaOCl is about twofold and threefold of magnitude higher than those via as-grown CNTs and CNTs-15% NaOCl. The degree of damage, the pore structure and oxygen-containing functional groups are

influenced by the concentration of oxidant. 3% NaOCl solution could not only introduce much oxygen-containing functional groups on MWCNTs, but also lead to less damage for the pore structure. Therefore, 3% NaOCl solution would be the best degree for oxidizing MWCNTs on TEX adsorption. Based on the nature of TEX and the results of the total surface area, FTIR, zeta potentials of MWCNTs, the adsorption mechanism of TEX on oxidized MWCNTs is attributed to the comprehensive interactions including hydrophobic interaction,  $\pi$ - $\pi$  bonding interaction between the aromatic ring of TEX and the surface oxygen-containing functional groups of MWCNTs as well as electrostatic interaction. This suggests that the CNTs-3% NaOCl sample is an efficient TEX adsorbent and that they may possess good potential for TEX removal in wastewater treatment.

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