

Performance of raw and regenerated multi- and single-walled carbon nanotubes in xylene removal from aqueous solutions

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ABSTRACT

Aims: The ability of raw and recycled multi- and single-walled carbon nanotubes (MWCNT and SWCNT) for xylene adsorption from aqueous solutions was evaluated.

Materials and Methods: Batch adsorption experiments were conducted in 110 ml glass bottles. Gas chromatography–mass spectrometry was used for xylene measurement and the carbon nanotube characteristics were evaluated with the help of a transmission electron microscope.

Results: With a carbon nanotube dose of 1 g/l, xylene concentration of 10 mg/l, pH 7, and a contact time of 10 minutes, the equilibrium adsorption capacity (q_e (mg/g)) of SWCNT was 9.2 mg/g, which was higher than that for MWCNT (8.9 mg/g). The SWCNT revealed a better performance for xylene sorption than the MWCNT. Results of a desorption study showed that xylene adsorbed onto the SWCNT and MWCNT can be easily desorbed at $105 \pm 2^\circ\text{C}$.

Conclusions: It is concluded that recycled carbon nanotubes on heating for the first time, show a better performance for xylene adsorption than when they are raw. The SWCNT are efficient as xylene adsorbents in an environmental pollution cleanup.

Key words: Carbon nanotube, regeneration, water pollution, xylene

INTRODUCTION

Reusability of an adsorbent is an important factor for its cost-beneficiary application in environmental pollution control. Such adsorbents must not only possess higher adsorption capability, but must also show a better desorption property, which can significantly reduce the overall cost of the adsorbent. Carbon nanotubes seem to be an alternative, due to their high performance in adsorbing organic pollutants such as xylene from aqueous solutions; however, their cost-effectiveness must be taken into account.

Xylene is a volatile, monoaromatic compound, and is a common constituent in petroleum products.^[1] that is widely used in the industry as solvents for organic synthesis, equipment cleaning, and other downstream processing purposes. It is present in refinery and chemical industry effluents. Xylene compounds are frequently found in groundwater as a result of leaks in underground storage tanks and pipelines, improper waste disposal practices, inadvertent spills and leaching from landfills.^[2] These pollutants have been found to cause many serious health effects to humans (e.g., skin and sensory irritation, central nervous system depression, respiratory problems, leukemia, cancer, as well as disturbance in the kidney, liver, and blood systems).^[3]

Although carbon nanotubes (CNTs) show more xylene sorption capacities from aqueous solutions, their very high unit cost currently restricts their potential use in water treatment. Thus, testing the reversibility of sorbents that are used for pollutant removal is required, in order to reduce

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their replacement costs. For this purpose, recycling of used SWCNT and MWCNT and changes in their efficiency have been investigated.

The present study aims to determine and compare the xylene removal efficiency of single- and multi-walled carbon nanotubes. The contribution of this study is the regeneration of CNTs as adsorbents of xylene by temperature.

MATERIALS AND METHODS

Materials

Xylene with a purity of 99% was purchased from the Merck Company. A stock solution of 100 mg/l of xylene was prepared by dissolving appropriate amounts of xylene in deionized water. The mixture was mixed thoroughly by using an ultrasonic bath for 60 minutes. Then, it was stirred continuously for 24 hours at 25°C. Following that, the solution was put in an ultrasonic bath again for 30 minutes and was used to prepare the 10 mg/l concentration initial solutions of xylene. Finally, standard series and samples were made to the desired concentrations by using deionized water.

During the experimental procedure, two different nano materials were tested: (1) a single-walled carbon nanotube (SWCNT) with 1 – 2 nm diameter and a (2) multi-walled carbon nanotube (MWCNT) with a 10 nm diameter, which were purchased from the Iranian Research Institute of Petroleum Industry [Figure 1].

Experimental

Batch adsorption experiments were conducted using 110 ml glass bottles, with an addition of 1000 mg/l of adsorbents and 100 ml of 10 mg/l of the initial concentration (C_0) of xylene solution. This initial concentration of 10 mg/l was chosen to be representative of the low xylene levels in water polluted with gasoline. The glass bottles were sealed with a 20 mm stopper. The headspace within each sample container was minimized to exclude any contaminant volatilization phenomena. The glass bottles of the batch experiments were placed on a shaker (Orbital Shaker Model OS625), and were stirred at 240 rpm^[2,4] at room temperature for 10 minutes. The solution samples were then settled for two minutes. The supernatant was used to determine the xylene in the

liquid phase using the GC/MS chromatography model 7890A. All the experiments were repeated thrice and only the mean values and standard deviations were reported. Blank experiments, without the addition of adsorbents, were also conducted to ensure the xylene concentration decrease that had actually been adsorbed onto the glass bottle walls or via volatilization. The initial pH (pH_{in}) was adjusted at neutral range using 0.05 M HCl or 0.05 M NaOH. The amount of adsorbed xylene on the adsorbents (q_e , mg/g) was measured and the percent removal (%R) was calculated as follows:

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

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

Where C_0 and C_t , are the xylene concentrations at the beginning and after a certain period of time (mg/l); V , is the initial solution volume (lit); and m , is the adsorbent weight (g).

The reversibility of sorbents that were used for xylene removal from the aqueous solution was evaluated via two sequential adsorptions, followed by two successive desorptions. Recycling was also conducted at $105 \pm 2^\circ\text{C}$ and 24 hours in the oven (Memmert D-91126, Schwabach FRG). All samples were performed at least in triplicate and only the mean and standard deviation were reported.

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 xylene concentration. A fused silica column, HP-5 ms (5% phenyl-95% dimethylpolysiloxane; 30 m \times 0.25 mm I.D, 0.25 μm film thickness), 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: 36°C for 10 minutes, increasing to 150°C at 10°C/min and holding for two minutes. The injector port was maintained at 250°C and 1 ml volume of headspace was injected into the splitless mode (2 minute). 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 scan mode. The data were acquired and processed by the data analysis software.

Static headspace analysis was performed using a CTC PAL-Compi PAL headspace sampler. The experimental optimum parameters of the headspace sampler were: Incubation time, 25 minutes; incubation temperature, 70°C; sample loop volume, 1 ml; syringe/transfer line temperature, 110°C; flash time, two minutes with N_2 ; loop fill time, 0.03 minutes; injection time, one minute, and sample volume, 10 ml in 20 ml vials. No NaCl was added to the samples.

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

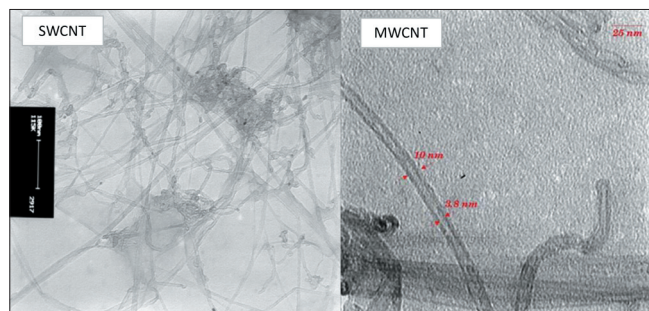


Figure 1: TEM image of SWCNT and MWCNT

Analysis of data

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

RESULTS

Adsorption performance

Table 1 shows the xylene removal percent by MWCNT and SWCNT, under an initial xylene concentration of 10 mg/l, adsorbent concentration of 1000 mg/l during 10 minutes contact time, and shaking at 240 rpm. It has revealed that SWCNT shows better xylene adsorption efficiency than MWCNT.

Figure 2 indicates the equilibrium capacity of xylene adsorbed on MWCNT and SWCNT (q_e (mg/g)) with a C_0 of 10 mg/l and contact time of 10 minutes.

Carbon nanotube recycling

Figures 3 and 4, compare raw SWCNT and MWCNT with their recycle types in cycles of 1 and 2.

DISCUSSION

Based on the DOE analysis, there is a significant difference between MWCNT and SWCNT in xylene removal ($\text{Prob} > |t| \leq 0.05$). In this study it is seen that SWCNT has better xylene removal than MWCNT.

Based on Table 1, it is evident that the q_e by SWCNT is higher than by MWCNT. In a C_0 of 10 mg/l, the SWCNT shows the greatest $q_e = 9.2$ mg/g. This makes one speculate on the presence of chemically inherited groups that lead to such direction of affinity to xylene removal, irrespective of the texture characteristics. The adsorption of xylene to the CNT is dependent on the nature of the surface chemical and the porosity characteristics.^[5] Similar findings have been reported in literature for the adsorption of xylene on activated carbon.^[6]

It is of great importance to disclose the adsorption mechanism of xylene via CNTs. As no significant pH variation during adsorption is observed, it has been suggested that the π - π electron-donor-acceptor mechanism involving the carboxylic oxygen-atom on the CNT surface, as the electron-donor, and the aromatic ring of xylene, as the electron-acceptor, are responsible for the uptake of xylene by CNTs.^[2] Similar conclusions have been drawn in literature for adsorption of ethylbenzene and toluene on MWCNT.^[4,5] Furthermore, the electrostatic interaction between the xylene molecules and the CNT surface may also explain its high xylene adsorption capacity. As the xylene molecules are positively charged,^[7] adsorption of xylene is favored for adsorbents with a negative surface charge. This results in more electrostatic attraction, and thus leads to higher xylene adsorption.

Table 1: Xylene removal by MWCNT and SWCNT at $C_0 = 10$ mg/l and contact time of 10 minutes

Adsorbent	Xylene		
	C_0 (mg/l)	C_t (mg/l)	Removal percent
MWCNT	10 ± 0.2	1.05 ± 0.05	89.5 ± 0.65
SWCNT	10 ± 0.1	0.84 ± 0.06	91.7 ± 0.43

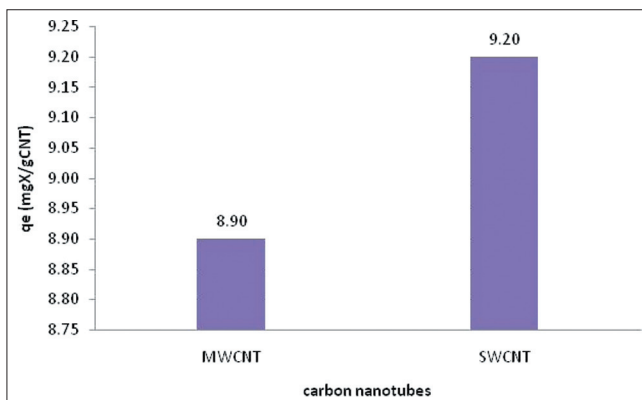


Figure 2: Equilibrium amount of xylene adsorbed on CNTs with a C_0 of 10 mg/l

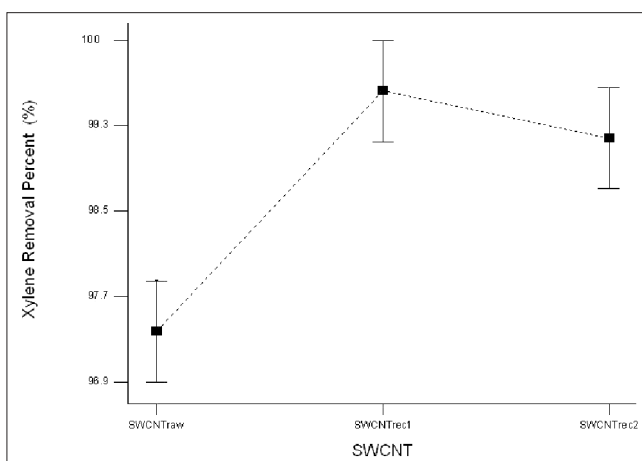


Figure 3: Comparison of raw and recycled SWCNT in xylene adsorption

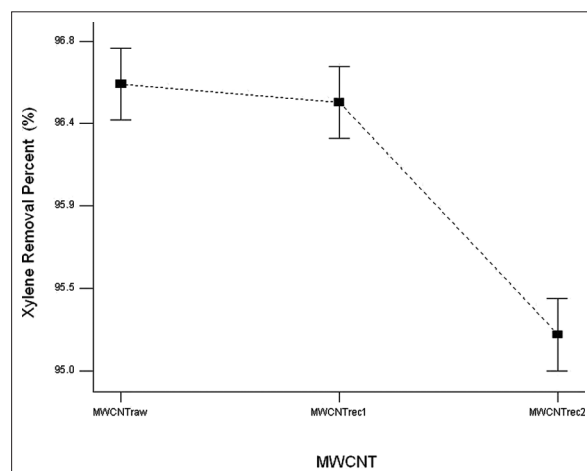


Figure 4: Comparison of raw and recycled MWCNT in xylene adsorption

At present, the very high unit cost of CNTs restricts their potential use in water treatment. Thus, testing the reversibility of sorbents that are used for xylene removal is required, in order to reduce their replacement cost.

Based on Figures 3 and 4, it is apparent that SWCNT and MWCNT can be reused for the removal of xylene through a large number of water and wastewater treatments and regeneration cycles. The presence of metal catalysts in raw SWCNT that could have remained through the chemical process to functionalize it may be removed due to heating and cause a better adsorption performance for recycled SWCNT than raw SWCNT. Also the structure and nature of the carbon surface is changed after thermal treatment, including an increase in the graphitized structure and a decrease in the surface functional groups and negative charges.^[8] Thus, SWCNT can adsorb more xylene. Results show that the xylene adsorbed by the SWCNT can be easily desorbed by temperature, and thereby SWCNT can be employed repeatedly in water and wastewater management. This is the key factor to knowing whether a novel, but expensive, sorbent can be accepted by the field or not. It is expected that the unit cost of CNTs can be further reduced in the future by recycling heat processes. Thus, SWCNTs and MWCNTs appear to be cost-effective sorbents in water and wastewater treatment. The desorption difference between CNT and other carbonaceous materials may be due to their distinct geometric structure.^[2] The carbonaceous materials exhibit a high degree of porosity and an extended interparticulate surface area, whereas, CNTs are one-dimensional hollow, nano-sized tubes, as well as aggregates. CNTs easily adhere to each other and form bundles due to the strong Van der Waals interactions. The adsorption sites are therefore defined for the entire bundles instead of individual nanotubes. There are four possible groups of adsorption sites on the bundles: The interiors of the individual tubes, interstitial channels between the nanotubes, external groove sites, and the outer surface sites of the individual tubes, on the peripheral surface of the bundles. The interiors of the individual tubes are only available in open-ended tubes; the interstitial channels are applied for large tube diameters, while grooves and the external surface are most important for adsorption.^[9]

Therefore, it is inferred that most of the xylene is located on the external adsorption sites. Moreover, CNTs cannot form closed interstitial spaces in their aggregates. Hence, the xylene adsorbed is released due to temperature.

The sorbent weight loss was neglected in the recycling processes. The weight loss could be attributed to the

evaporation of adsorbed water and the elimination of the carboxylic groups and hydroxyl groups on the CNT wall.^[7]

It is concluded that SWCNT shows a higher adsorption capacity than MWCNT for xylene removal. It appears that xylene isomers are the components with a high adsorption tendency onto CNT. The sequence of equilibrium amount (q_e) is SWCNT > MWCNT. After recycling of the carbon nanotubes via two cycles, SWCNT and MWCNT are still efficient xylene sorbents. Therefore, they can be regenerated and reused in water and wastewater treatment. Furthermore, heating could upgrade the adsorption capacity of recycled SWCNT more than raw SWCNT.

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