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Using of a New Carbon Nano Tube Version in Sheet Shape for Water and Wastewater Treatment

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Removal of xylene (a toxic compound) from aqueous solution by modified multi wall carbon nano tubes (MWCNT) via silica as sheeted carbon nanotube (SCNT) was evaluated. The physicochemical properties of MWCNT such as structure and availability surface were improved due to convert tubes into sheets that cause significantly increase in xylene adsorption. The equilibrium amount (qe (mg/g)) in nano material's dose of 1g/l, xylene concentration of 10mg/l, contact time of 10min, and pH 7, for SCNT (qe = 9.8 mg/g) was higher than single wall carbon nano tubes (SWCNT) (qe = 9.2 mg/g) and MWCNT (qe = 8.9 mg/g). It is concluded that sheeted carbon nanotube due to their large surface area improve performance of xylene adsorption. Also carbon nano tube (CNT) recycling by heating, showed better adsorption performance for recycled SCNT. A comparison study on xylene adsorption revealed that sheeted carbon nanotube has better xylene adsorption performance as compared to CNT, carbon and silica adsorbents. This suggests that the SCNT is an efficient adsorbent for xylene removal in environmental pollutions cleanup.

Keywords: Sheeted carbon nanotube, Regeneration, Xylene, Wastewater pollution.

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1. . INTRODUCTION

Xylene is an aromatic compound that is found in air, surface and ground water due to introducing petroleum product or wastewater polluted by its products in environment [1, 2]. Every year, large amounts of xylene discharge into the aqueous environment via manufacturing, transportation and disposal sites wastewater [3]. Such contamination in water sources making them unsuitable for many uses (spatially for drinking) due to their toxic properties [4]. Environmental protection agency (EPA) has classified the xylene as a priority compound due to its toxic effect on human health and environmental [5]. Previous studies show that various kinds of technologies used for xylene removal. Physicochemical process was preferred because of easy to use and cost-effectiveness [6-9]. These studies show that CNT have more potentially for removal of organic pollutant in environmental filed. The nanomaterials have been used for removing many kinds of organic pollutants such as BTEX from aqueous solutions [3, 4, 7]. The modified carbon nanotubes as the tube opening to achieve higher levels of adsorption surface area, can improve the performance of their absorption. So in this study, multi wall carbon nanotubes was converted to sheets by silica and employed as adsorbent for xylene removal from aqueous solution. The main objective of this paper is to investigate the performance of sheeted multi wall carbon nanotube in xylene removal from aqueous solution.

2. MATERIALS AND METHODS

2.1 Materials

Xylene (purity 99%) purged from Merck and three different nano materials were tested: (1) SWCNT with 1-2nm diameters (figure 1). (2) MWCNT with 10nm diameter (figure 2). (3) sheeted carbon nanotube (SCNT) that made by MWCNT in hybrid with silica. SWCNT and MWCNT were purchased form Iranian Research Institute of Petroleum Industry and SCNT was made in this industry. The morphology of adsorbents was analyzed by transmission electron microscopy (TEM) Philips CM10-100KV.

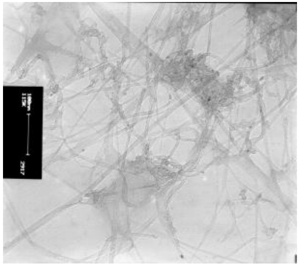

Fig. 1 – TEM image of SWCNT

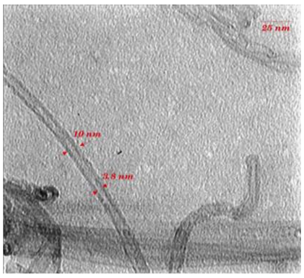

Fig. 2 – TEM image of MWCNT

The surface area, pore volume and pore size distribution were measured by nitrogen adsorption at 77K using an ASAP-2010 porosimeter from the Micromeritics Corporation GA. The pore size distribution (PSD) was evaluated from the adsorption isotherms using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) available as a built-in software from Micromeritics. The surface area, average pore size diameter, and pore volume of the SWCNT and MWCNT are presented in table 1.

Table 1 – N2 adsorption data of SWCNT and MWNT

Adsorbents	BET surface area (m^2/g)	Average pore diameter-by BET (nm)	BJH adsorption cumulative surface area of pores (m^2/g)	BJH adsorption average pore diameter (nm)	BJH adsorption cumulative pore volume of pores (cm^3/g)
SWCNT	198.93	11.87	253.12	12.02	0.62
MWCNT	132.42	13.21	175.74	13.57	0.58

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2.2 Experimental

Batch adsorption experiments were conducted using 110ml glass bottles with addition of 100mg of adsorbents and 100ml of xylene solution with concentrations (C_0) 10mg/l. The glass bottles were sealed with 20mm stopper. Headspace within each beaker 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 240rpm for 10min in room temperature. The solution samples were then settled for 2min. The supernatant was used to determining xylene in the liquid phase using GC/MS chromatography. All the experiments were repeated three times and only the mean values were reported.

The reversibility of sorbents that used for xylene removal from aqueous solution was evaluated via 2 adsorptions followed by 2 desorption. Recycling was also conducted at 105±2°C in 24h by oven (Memmert D-91126, Schwabach FRG). All samples were performed at least in triplicate.

Xylene concentrations were analyzed by Agilent Technologies system consisting of a 5975C Inert MSD with Triple Axis Detector equipped with a 7890A gas chromatograph with a split/splitless injector. A HP-5 ms column (30m×0.25mm Id, 0.25μm), was employed with helium (purity 99.995%) as carrier gas at flow rate of 1ml/min. Static headspace analysis was performed using a CTC PAL- Combi PAL headspace sampler.

In order to compare adsorption performance of employed carbon nanotubes in this study, design of experiments (DOE) software (design expert 6) was used.

Isotherm study was evaluated for xylene adsorption by SCNT with initial concentration of zero to 100mg/l (interval 10mg/l), CNT dose 2g/l, contact time 14min, and pH = 7. Water solubility (S_w) of xylene was estimated 50mg/l at pH 7 [2].

3. RESULTS

Figure 3 shows TEM image of carbon tubes that sheeted in contact with silica. The results obtained for SCNT include surface area, average pore size diameter, adsorption cumulative surface area of pores, adsorption average pore diameter and adsorption cumulative pore volume of pores was 273.6m²/g, 12.9nm, 258.6m²/g, 12.1nm, 0.78cm³/g respectively.

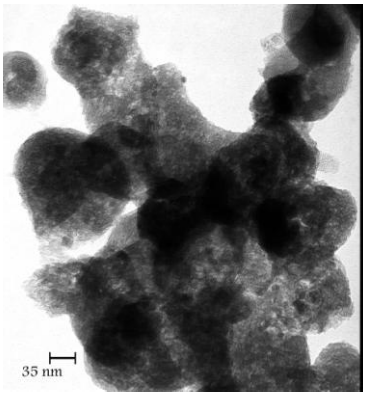

Fig. 3 – TEM image of SCNT

Table 2 shows the xylene removal percent by SCNT, SWCNT, and MWCNT under initial xylene concentration, 10mg/l; adsorbent concentration of nano material, 1000mg/l; contact time, 10min; and shaking in 240rpm. A different way for comparison of CNTs performance in xylene removal is in terms of surface area instead of the unit weight that adsorbed by CNT.

Table 2 – Xylene removal by CNT at C_0 = 10mg/l

Adsorbent	Xylene concentration		Removal percent (%)	Xylene adsorption capacity by CNT (mg/m²)
	C_0 (mg/l)	C_t (mg/l)		
MWCNT	10±0.2	1±0.05	89.5	0.07
SWCNT	10±0.1	0.8±0.08	91.6	0.05
SCNT	10±0.2	0.2±0.05	98	0.04

Figure 4 shows the xylene removal by SCNT, SWCNT, and MWCNT and that comparison of them. It reveals that SCNT is better than SWCNT and MWCNT to remove the xylene.

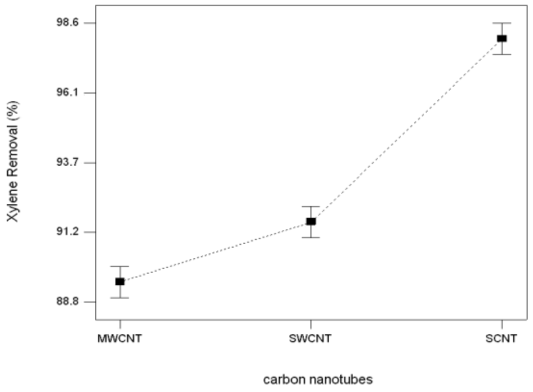

Fig. 4 – Comparison of SCNT, MWCNT, and SWCNT in xylene removal with a C_0 = 10mg/l

Figure 5 indicates the equilibrium amounts of xylene adsorbed on SCNT, MWCNT, and SWCNT (q_e (mg/g)) with a C_0 of 10mg/l and contact time, 10min.

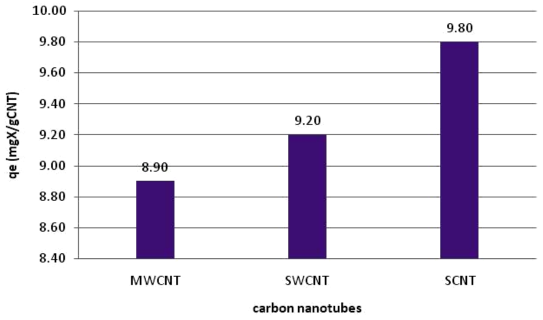

Fig. 5 – Equilibrium amount of xylene adsorbed on CNTs with a C_0 of 10mg/l

Table 3 shows the xylene removal percent by SCNT, MWCNT, and SWCNT that was recycled in the first cycle (SCNTrec1, MWCNTrec1, and SWCNTrec1) and the second cycle (SCNTrec2, MWCNTrec2, and SWCNTrec2) under initial xylene concentration of 10mg/l, carbon nanotubes concentration of 1000mg/l, contact time of 10min and shaking in 240rpm. Figure 6 compares raw SCNT, SWCNT, and MWCNT with their recycling in cycles of 1 and 2.

Table 3 – Xylene removal by raw and recycled SCNT, MWCNT, and SWCNT at $C_0 = 10$mg/l and contact time of 10min

Adsorbent	Xylene		
	C_0 (mg/l)	C_t (mg/l)	Removal percent (%)
SCNTrec1	10±0.2	1.1±0.04	98.8
MWCNTrec1	10±0.1	0.6±0.1	89.3
SWCNTrec1	10±0.2	0.1±0.01	93.6
SCNTrec2	10±0.1	1.3±0.08	96.8
MWCNTrec2	10±0.2	0.95±0.1	87.3
SWCNTrec2	10±0.1	0.32±0.06	90.5

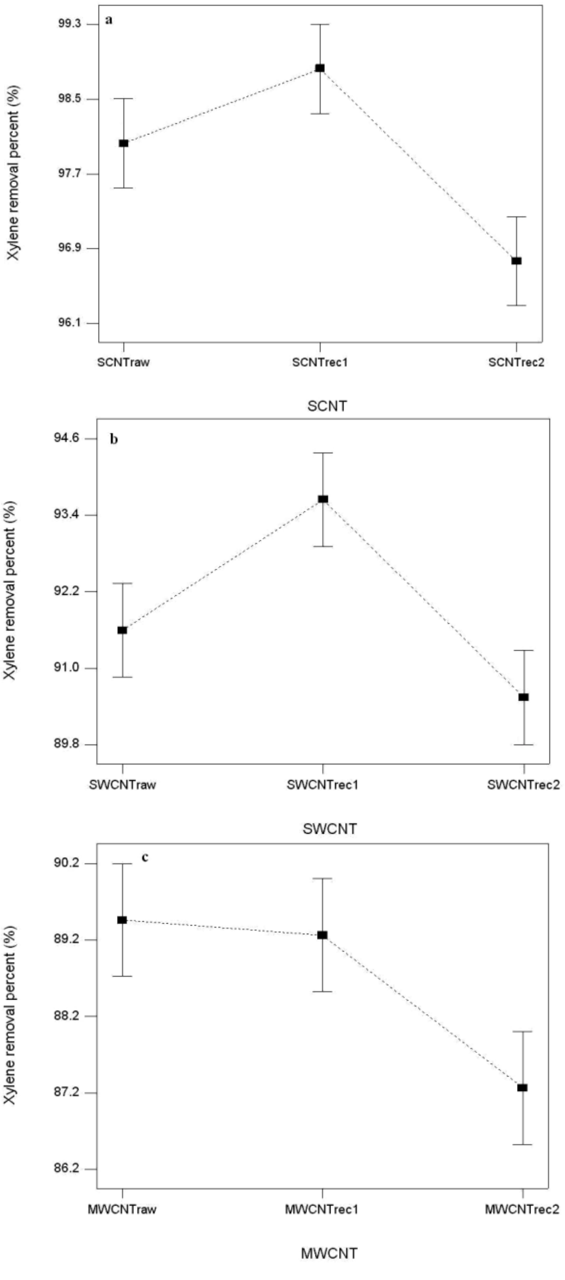

Fig. 6 – Comparison of raw and recycled: (a) SCNT, (b) SWCNT and (c) MWCNT in xylene removal with a $C_0 = 10$mg/l

Table 4 summarizes some of the diagnostic statistics computed by ISOFIT and reported in the output file for xylene removal.

Figure 7 contain plot of the fitted isotherms for xylene adsorption by SCNT, along with the observed data points.

Table 4 – Summary of selected diagnostics for xylene adsorbed by SCNT

Isotherms	Multi model ranking (AICc)	Correlation between measured and simulated observation (R_y^2)	Correlation between residual and normality (R_N^2)	linssen measure of non-linearity (M^2)	Linearity assessment
GLF	20.6	0.996	0.916	7.6×10^{1}	non-linear
P-P	24.4	0.920	0.781	2.6×10^{-1}	uncertain
Polanyi	24.5	-	0.936	4×10^{-15}	linear
Langmuir	49.3	0.983	0.923	8×10^{-10}	linear
Toth	49.4	0.953	0.931	8×10^{-10}	linear
F-P	49.4	0.953	0.913	8×10^{-10}	linear
Linear	49.4	0.953	0.913	8×10^{-10}	linear
L-P	52.6	0.903	0903	1×10^{5}	non-linear
Freundlich	52.7	0.953	0.905	3.8	non-linear
BET	74	0.305	0.923	9.4×10^{-2}	uncertain

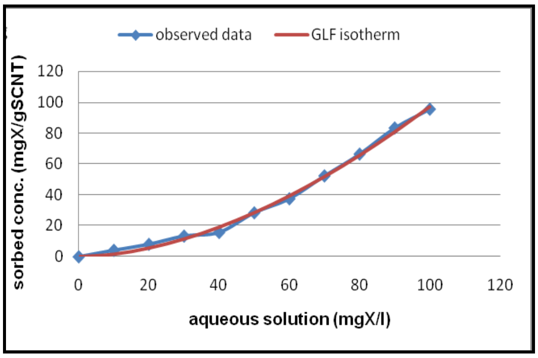

Fig. 7 – Plot of GLF isotherm and observed data for xylene adsorption

4. DISCUSSION

As can be concluded, the use of silica in MWCNT producing process causes important changes in MWCNT properties. This change in surface area and pore volume of pores are more specific. It caused an increase in surface area of about 52% as well as could increase cumulative pore volume of pores about 20%. This is attributed to modify MWCNT shape from tube to sheet due to silica operation. Silica cause destruction of tube wall and a corresponding increase in surface area and volume of pores but decrease the average pore diameter. It is evident that SCNT has greater surface area and pore volume but smaller average pore diameter than MWCNT. On the other hand, the mesopore of MWCNT have smaller pore volume than SCNT, which could be attributed to the open of tubes that produce sheet carbon nanotubes. When tubes of MWCNT were opened and converted to sheet via contact with silica, high surface area was created for xylene adsorption. Based on DOE analysis there is a significant difference between SCNT, MWCNT, and SWCNT in xylene removal (values of "Prob>|t|" less than 0.05). So that SCNT has better performance in xylene removal than SWCNT and MWCNT in this study. This is due to increasing in surface area that was 132.4 and 198.9m²/g for MWCNT and SWCNT respectively and was 273.6m²/g for SCNT. The order of xylene removal efficiency (SCNT > SWCNT > MWCNT) is consistent with the order of surface area and pore volume but is not in agreement with the pore diameter of CNTs. This indicates that the adsorption of xylene to the CNTs is dependent on the surface characteristics. Similar findings have been reported in the literature for adsorption of xylene on activated carbon and modified MWCNT [7, 8]. Also SCNT has the greatest q_e=9.8mg/g, so that is higher than SWCNT and MWCNT. Moreover, it is evident that the mass of xylene adsorbed on MWCNT was increased when used of silica in MWCNT production process. This phenomenon can be attributed to the fact that silica causes structure changing, so it effect on MWCNT surface area and increases it. This speculates the presence of chemically inherited groups that lead to such direction of affinity to xylene removal, irrespective of the texture characteristics. The results also show that sheeted MWCNT improve performance of MWCNT base on increasing adsorption site and available surface. So that it was better than SWCNT in xylene removal. It can be expected that the adsorption of xylene to the SCNT is dependent on the surface chemical nature and the porosity characteristics. Because there were not pH variation during experiments, π-π electron-donor–acceptor is main mechanism for xylene adsorption to SCNT. Carboxylic oxygen-atom of CNT surface performs as the electron-donor and the aromatic ring of xylene as the electron-acceptor. So increasing adsorption surface is due to sheet form of CNT, cause more available carboxylic oxygen atoms for electron donor and better xylene removal [7]. Furthermore, the electrostatic interaction between the xylene molecules and the CNT surface may also explain the observation of high xylene adsorption via the sheeted carbon nanotube. Since the xylene molecules are positively charged [7], adsorption of xylene is thus favored for adsorbents with a negative CNT surface charge. This results in more electrostatic attraction and thus leads to a higher xylene adsorption.

It is apparent from recycling results that SCNT, SWCNT, and MWCNT used in xylene removal can be reused through a large number of water and wastewater treatments for several regeneration cycles.

After CNTs oxidization by heating process, a large amount of metal catalysts and amorphous carbons that were used for CNT making, was removed and both ends of the nanotubes were be opened. Also the structure and nature of carbon surface were changed after thermal treatment including the increasing in graphitized structure, surface functional groups, and negative charges [1]. This is caused that SCNT and SWCNT could be adsorbed more xylene after first recycling. As regards the possibility of CNT recycling by heat processing, it is expected that the unit cost of CNTs can be further reduced.

Isotherm expressions are important for describing the partitioning of contaminants in environmental systems. The AICc values indicate that the GLF isotherm expression provides the best fit of the sorption data for xylene adsorption.

ISOFIT used by Shawn Matott for zinc adsorption by ferrihydrite, indicate that ISOFIT produced equivalent or better fits, in terms of minimum and median RMSE values. In particular, ISOFIT provided superior fits for the GLF, Toth, Polanyi and Polanyi-Partition isotherms [11]. The adsorption process of atrazine on CNTs study by Yan et al. shows the adsorption equilibrium isotherms were nonlinear and were fitted by Freundlich, Langmuir, and Polanyi–Manes models. They were found that the Polanyi–Manes model described the adsorption process better than other two isotherm models [10]. Wibowo et al. studied the adsorption of benzene and toluene from aqueous solutions onto activated carbon, there study show that the Langmuir equation can describe the experimental data fairly well than Freundlich [12].

5. CONCLUSION

The main goal of this study was CNT comparison to xylene adsorption (a certain common petroleum pollutant). Therefore SWCNT, MWCNT and a new type of CNT (SCNT) were tested for xylene removal from aqueous solution. It is concluded that SCNT shows the greatest enhancement in xylene adsorption. The sheet shape of CNT as SCNT by silica can change the available area surface for adsorption. The results appear that xylene isomers are the components with the high adsorption tendency onto CNT. The equilibrium amount (q_e) sequence is SCNT > SWCNT > MWCNT. After recycling of carbon nanotubes via 2 cycles, SCNT, SWCNT, and MWCNT are efficient xylene sorbents and can be regenerated and reused in water and wastewater treatment works. Furthermore, heating could be upgraded adsorption of recycled SCNT and SWCNT. The removal of metal catalysts by thermal treatment in raw CNTs can change the structure and nature of carbon surface and cause increasing in surface functional groups and negative

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