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REMOVAL OF TRICHLOROETHYLENE FROM WATER BY ADSORPTION ON TO MULTIWALL CARBON NANOTUBES

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ABSTRACT

Groundwater recourses may be contaminated with trichloroethylene (TCE) which is used in electronic, electric, dry cleaning and other similar industries and often treated by air stripping, which TCE in its vapor form is stripped from groundwater by air and is emitted into the atmosphere without any additional treatments. Carbon nanotubes are expected to play an important role in sensing, pollution treatment and separation techniques. In this study adsorption of trichloroethylene on multiwall carbon nanotubes has been investigated. The effect of contact time, pH, initial concentration of trichloroethylene and temperature on its adsorption were investigated. Adsorption isotherms and related constants were also determined. Results showed that contact times to reach equilibrium changed from 30 min (for 150 µg/L initial concentration) to 10 min (for 600 µg/L concentrations) at 25 °C; the equilibrium times in 40°C were 40 min and 15 min, respectively. Multi-wall carbon nanotubes showed to act as a good adsorbent for TCE in a wide range of pH=(3-9). For pH>9, adsorption decreased due to ionization of oxygen-containing groups. Adsorption test results revealed that TCE adsorption on the studied adsorbents could be better described by Freundlich isotherm.

Key words: Adsorption; Trichloroethylene; Multiwall carbon nanotube; Isotherm

INTRODUCTION

The contamination of groundwater with industrial solvents such as trichloroethylene and tetrachloroethynene (PCE) has become one of the most serious problems in water environment, especially in urban areas (Kikuchi, 2001, Dobaradaran *et al*, 2010a, Nakano *et al*., 2000). TCE is one of the major volatile chlorinated hydrocarbons which readily evaporates at room temperature, and has been used in large quantity as a solvent or detergent in frontier technological industries (Tanda *et al.,* 1992). TCE mainly affects the central nervous system (the brain), causing headache, nausea, dizziness, clumsiness, drowsiness, and other effects like those of being drunk. TCE can also damage the facial nerves, and it can cause skin rash. Heavy exposure can damage the liver and kidneys. TCE causes cancer in animals and may cause cancer in humans (factsheet, 1997).

It has been widely used as a degreasing agent for metalworking, machine and electronic industries due to its non flammability and its ability to dissolve various organic matters (Ohba, 1997; Nakano *et al*., 2000; Zendehdel *et al*, 2011).

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United states environmental protection agency (US.EPA) has set the maximum contaminant level (MCL) and maximum contaminant level goal (MCLG) of TCE at 5 µg/L and zero, respectively (EPA, 2007). In order to meet these limits, some water treatment processes have been developed and put into practice.

There are several treatment technologies for TCE removal from drinking water. Activated carbon, air stripping, photosonochemical degradation, bioremediation and advanced oxidation processes represent commonly adopted technologies used for TCE contaminated groundwater sites (Sakoda *et al.*, 1987b, Sakoda *et al.*, 1987a, Wu *et al,* 2001, Miyake and Suzuki, 1993, Dobaradaran *et al,* 2010b). Among the depuration technologies for groundwater remediation, adsorption has been widely used because it conjugates good efficiencies with a reliable and robust process configuration (Urano *et al.,* 1991, Karanfil and Dastgheib, 2004, Kilduff and Karanfil, 2002) (Ghadiri *et al*, 2010).

Carbon nanotubes (CNTs) are relatively new adsorbents that have proven very efficient for treating many kinds of trace pollutants such as dioxins from air (Long and Yang, 2001) or lead (Li *et al*., 2002a), cadmium (Li *et al.,* 2003a), fluoride (Li *et al.,* 2003b), 1,2-dichlorobenzene (Peng *et al.,* 2003) or trihalomethanes (THMs) (Lu *et al*., 2005) from water because they have large specific surface area, and small, hollow and layered structures. The comparisons of CNTs with other commercial adsorbents made by the foregoing researchers suggest that CNTs have great potential in environmental protection applications. Earlier works have suggested that CNTs may be a potential adsorbent for treating wastewater (Li *et al.*, 2007, Yin and Zhang, 2008); however, the studies on the adsorption of TCE with multiwall carbon nanotubes (MWCNTs) are still very limited in the literature.

The experimental data for TCE adsorption onto CNTs could be approximated by the isotherm models, respectively, of Langmuir and Freundlich (Wang *et al.,* 2007):

$$q = \frac{a\, b\, C_e}{1 + a\, b\, C_e} \quad (1)$$

$$q = K_f\, C_e^{1/n} \quad (2)$$

Where C_e is the equilibrium concentration of TCE (mg/L); *a* and *b* are Langmuir constants and K_f and *n* are Freundlich constants.

The linearized form of Langmuir and Freundlich isotherms are presented in equations (3) and (4):

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \quad (3)$$

$$\mathrm{Ln}q_e = (1/n)\,\mathrm{Ln}\,C_e + \mathrm{Ln}\,K_F \quad (4)$$

Where q_m is the maximum adsorption at monolayer (mg/g) and K_L is the Langmuir constant including the affinity of binding sites (L/mg). K_F and *n* are the Freundlich constants indicating adsorption capacity $[(mg/g)(L/mg)^{1/n}]$ and intensity, respectively.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) which can be defined by:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

The R_L value indicates the type of the isotherm to be either irreversible (R_L =0), favorable (0< R_L <1), linear (R_L =1) or unfavorable (R_L >1) (McKay *et al,* 1982).

The objective of this research was to investigate adsorption characteristics of TCE with MWCNTs.

MATERIALS AND METHODS

Multi-walled CNTs (provided from Research Institute of Petroleum Industry (RIPI), Tehran, Iran) was selected as adsorbents to study the adsorption characteristics of TCE

from water. On the basis of the information provided by the manufacturer, the MWCNTs were synthesized by catalytic chemical vapor deposition (CVD) method. The size of the outer diameter for the MWCNTs was more than 10 nm. The length of MWCNTs ranged from 5 to 15 µm. Furthermore, specific surface area of MWCNTs was 280m^2/g, and the mass ratio of the amorphous carbon of MWCNTs was less than 5%.

Because carbon nanotubes had the amorphous carbon and therefore the adsorption rate is very low, therefore, carbon nanotube should be purified. In order to functionalize MWCNTs, 0.3 g of the as-received MWCNTs were dispersed in 25 mL of nitric acid (65 wt %) in a 100 mL round bottom flask equipped with a condenser and the dispersion was refluxed under magnetic stirring for 48 h. After that, the resulting dispersion was diluted in water and filtered. The resulting solid was washed up to neutral pH, and the sample was dried in vacuum at 40 °C overnight.

Trichloroethylene (ρ=1.46 kg/L and 99% purity) was employed to prepare a stock solution containing 600 mg/L of TCE, which was further diluted with deionized water to the desired TCE concentrations (pH of this solution was almost 7). The initial pH was adjusted by adding either HCl or NaOH. Physico-chemical properties of trichloroethylene are presented in Table 1.

Batch adsorption experiments were performed in glass bottles with TCE solution (250 mL) of the prescribed concentration ranging from 150 to 600 µg/L and 20 mg of MWCNTs was added to each bottle. The amount of MWCNTs was fixed in all experimental steps. According to previous studies, TCE concentration range in groundwater is 100-700 µg/L. In this regard TCE concentration ranging from 150 to 600 µg/L was selected for this study.

The bottles were capped with glass stoppers, placed on a magnetic shaker (IKA® RCT basic) and were shaken at 25°C and 40°C until equilibrium. The pH of the solution was maintained at 7 with the exception of the case of studying the pH effect, in which the pH range of 3–11 was chosen. The pH was adjusted using 0.1M HNO_3 or 0.1M NaOH.

After shaking and reaching to equilibrium time, the suspension was filtered through a 0.2 µm filter and the filtrate was analyzed using gas chromatograph (VARIAN CP-3800, Australia, equipped with Compi PAL headspace). The amount of TCE adsorbed by MWCNTs was calculated from:

$$q = \frac{(C_0 - C_e)\, V}{m} \qquad (6)$$

Where q is the amount of TCE adsorbed by MWCNTs (mg/g); C_0 is the initial TCE concentration (mg/L); C_t is the final TCE concentration after a certain period of time (mg/L); V is the initial solution volume (L) and m is the MWCNTs dosage (g).

Table 1: Physico-chemical Properties of Trichloroethylene (Hugh *et al*, 1992)

Density	1.46 g/mL
Water solubility (in 25 °C)	1280 g/L
Henry's law constant (atm-m^3/mol at 20°C)	0.00892
Molecular weight	131.4
Boiling point	86.7°C
Log Octanol-Water Partition Coefficient	2.42

RESULTS

Fig.1 shows the effect of contact time on the adsorption of TCE onto purified MWCNTs at 25°C. The effect of contact time on the adsorption of TCE on to purified MWCNTs at 40°C in different initial TCE concentrations is demonstrated in Fig. 2. Adsorption Langmuir and Freundlich isotherms for TCE with CNTs could be seen in Figs. 3 and 4. Table 2 shows these Adsorption isotherm constants at 25 °C. Fig.5 shows the effect of pH on the adsorption of TCE on to CNTs.

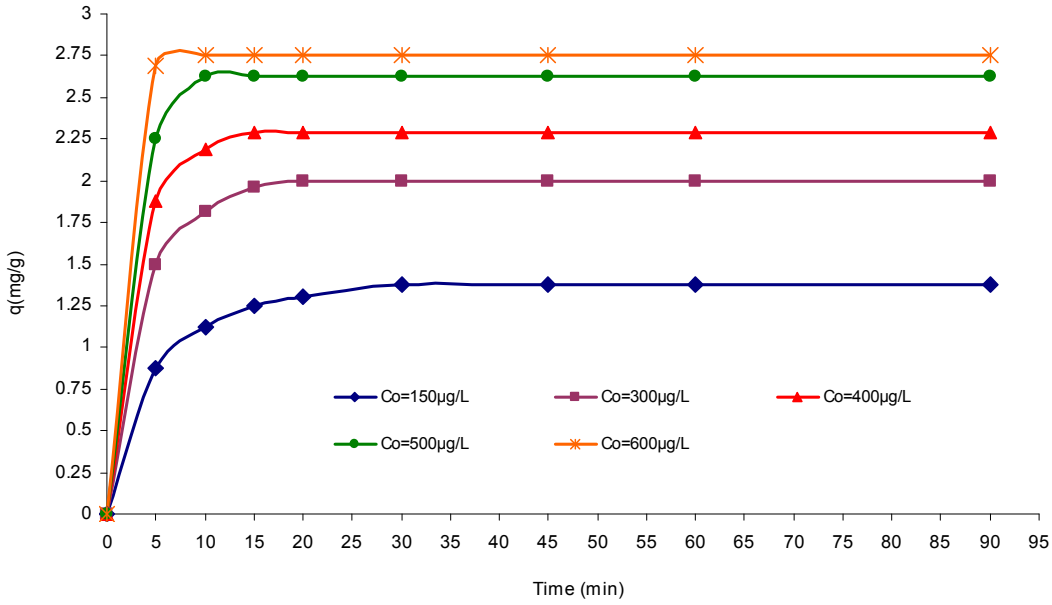

Fig.1: Effect of contact time on the adsorption of TCE with purified MWCNTs at 25°C

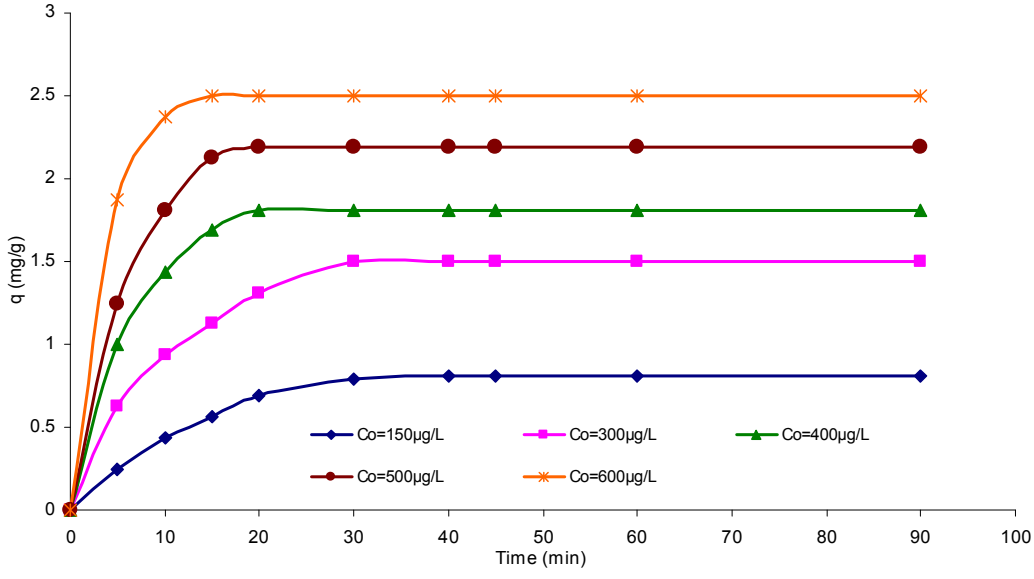

Fig.2: Effect of contact time on the adsorption of TCE with purified MWCNTs at 40°C

DISSCUSION

Effect of contact time

According to Fig.1, TCE adsorption rate increased quickly with time and then reached equilibrium. The contact times to reach equilibrium changed from 30 min for 150 µg/L concentrations to 10 min for 600 µg/L of MWCNTs. The final capacities for adsorption of TCE onto MWCNTs reached 1.38, 2, 2.3, 2.62 and 2.75 mg/g, respectively, for C_0 = 150, 300, 400, 500 and 600 mg/L.

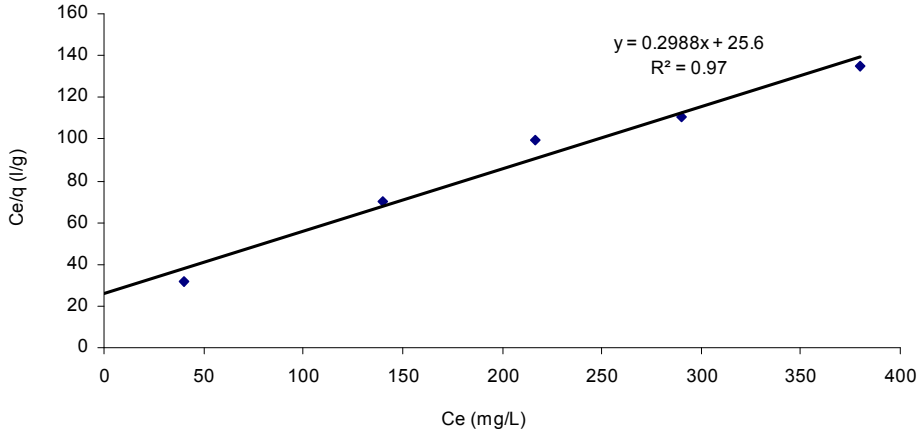

Fig. 3: Adsorption Langmuir isotherm for TCE with MWCNTs at 25°C

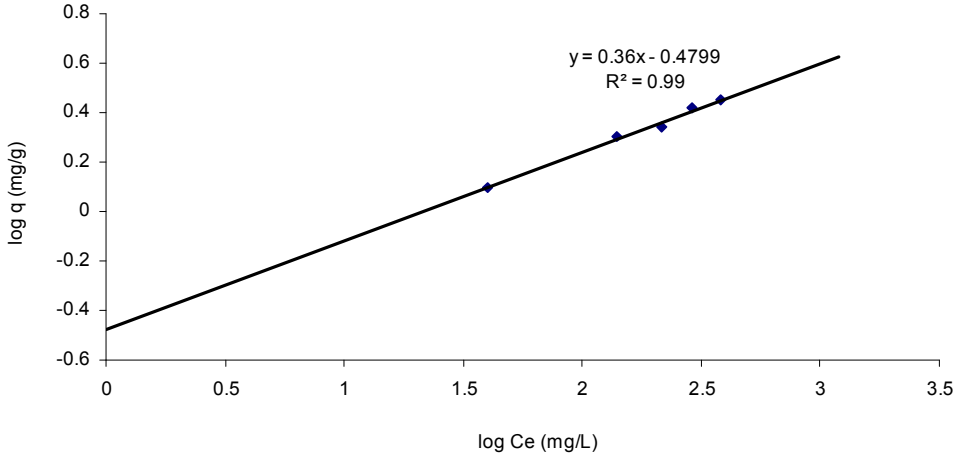

Fig. 4: Adsorption Freundlich isotherm for TCE with CNTs at 25 °C

The longer contact time to reach equilibrium for lower initial TCE concentration may be explained by the fact that diffusion mechanisms control the adsorption of TCE onto MWCNTs. Reid *et al*. indicated that the mass diffusivity decreases with decreasing concentration under very dilute solution and causes the decrease in diffusion flux of adsorbate onto the surface of the adsorbent (Reid *et al*., 1988). This can be interpreted that if we choose constant mass of adsorbent and constant volume of solution and low concentration of trichloroethylene in the solution, therefore, the time needed for the adsorbate to reach the adsorption sites is higher than when higher trichloroethylene concentration are used.

Effect of temperature

Temperature is an important parameter that can influence the equilibrium and rates of environmental processes. As shown in Fig. 2 the contact times to reach equilibrium were change from 40 min for 150 µg/L to 15 min for 600 µg/L of TCE. The final capacities for adsorption of TCE on to MWCNTs reached 0.8, 1.5, 1.8, 2.1 and 2.5 mg/g, respectively, for C_0

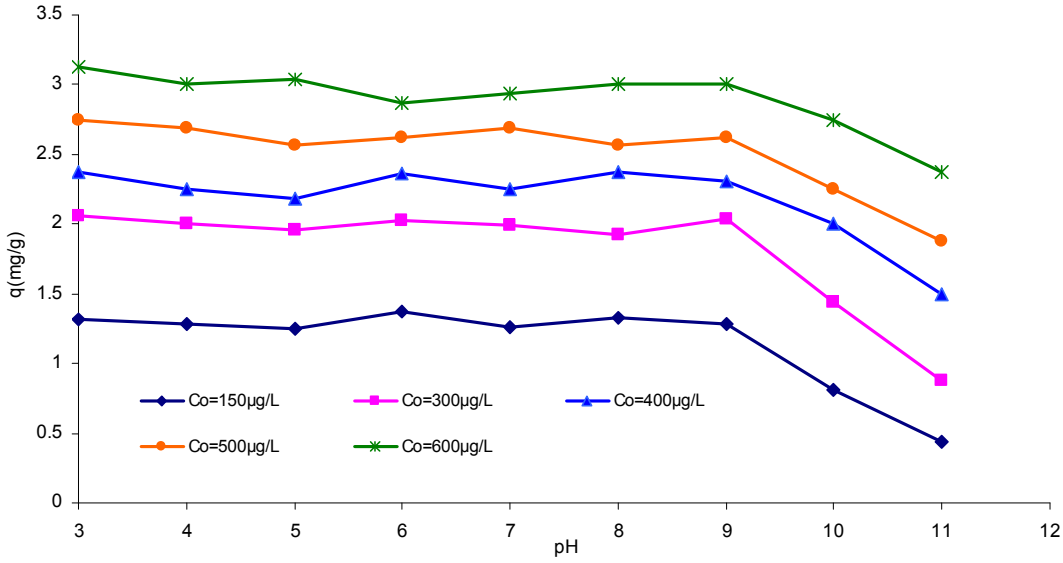

Fig. 5: Effect of pH on the adsorption of TCE on to CNTs

Table 2: Adsorption Langmuir and Freundlich isotherm constants for TCE with CNTs at 25 °C

Freundlich model			Langmuir model		
k_f	n	R^2	a	b	R^2
(mg TCE/g MWCNTs) (L water/mg TCE)$^{1/n}$	dimensionless	-	mmol/g	(dm^3/mmol)	-
0.33	2.8	0.99	83.3	0.04	0.97

= 150, 300, 400, 500 and 600 mg/L. Hence, the amount of TCE adsorbed on to MWCNTs at 25°C was higher than for 40°C, presenting the characteristic of physical adsorption. This finding were in accordance with Seiki Tanda *et al* (Tanda *et al.,* 1992) who investigated adsorption characteristic of TCE onto activated carbon fiber and reported that the amount of TCE adsorbed was higher at lower temperature. This result also was in agreement with Shih and Li (Shih and Li, 2008) studies, who surveyed the adsorption of selected volatile organic vapors on multiwall carbon nanotubes and demonstrated that the amount of TCE adsorbed onto CNTs increased when temperature decreased.

The dominant surface adsorption through ion exchange and absence of any particle diffusion may account for the decreased TCE uptake at high temperatures. This is obvious as the particle diffusion is an endothermic process favored at high temperatures (Ho and McKay, 2003). In addition, it has been reported that the higher the temperature, the lower the ion exchange adsorption capacity and the larger physical adsorption capacity (Vlasov *et al*, 1988).

Adsorption isotherms

According to Figs. 3 and 4 and Table 1 the constants of Langmuir and Freundlich models are obtained from fitting the adsorption equilibrium

data and are listed in Table 2. The correlation coefficients of Langmuir and Freundlich models were 0.97 and 0.99, respectively, indicating that the Freundlich model was more appropriate to describe the adsorption characteristics of TCE onto MWCNTs. These results were in accordance with Erto *et al* (Erto *et al*., 2010) who investigated the statistical analysis of trichloroethylene adsorption onto activated carbon and reported that the Freundlich model is the best data fitting model for TCE adsorption. Also Crittenden reported that the Freundlich model may be used to describe the data for heterogeneous adsorbent such as activated carbon (Crittenden *et al.*, 2005).

Effect of pH

The solution pH is one of the key factors that controls the adsorption process on carbon materials; it controls the electrostatic interactions between the adsorbent and the adsorbate (Anbia and Ghaffari, 2009).

The result from Fig. 5 shows the effect of pH on the adsorption of TCE on to MWCNTs with the different initial TCE concentrations. It is obvious that the adsorption of TCE onto MWCNTs fluctuates very little in the pH range of 3-9. This may be due to the fact that the employed CNTs have been purified by acid solution to improve their properties which may enhance the resistance of MWCNTs to acid environment (Lu *et al.,* 2005). However, the adsorption of TCE decreased as the pH exceeded 9. This is due to the fact that more oxygen-containing groups on the CNTs surface are ionized at higher pH values and thus they adsorb more water (Peng *et al.,* 2003). The formation of water cluster on these groups blocks the access of TCE molecules to adsorption sites and results in less adsorption of TCE.

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