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Adsorption efficiency of functionalized multi-walled carbon nanotube in sampling trichloroethylene in air

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Abstract

Introduction: Trichloroethylene (TCE) is an industrial solvent which is often used as a degreaser for metal parts. Due to adverse health effects and carcinogenic properties of this solvent, knowing its concentration in the workplace atmosphere is really crucial. Nowadays, carbon nanotubes with high efficiency are being used for sampling of this chemical.

Method: Three types of static standard atmosphere with the concentrations of 18, 35, and 53 ppm were produced. Then, sampling tubes which contained 10 mg of functionalized multi-walled carbon nanotubes were prepared. Subsequently, air standard atmosphere was made inside sampling bags. The mean adsorption efficiency was examined in three sampling flows (0.1, 0.15, and 0.2 L/minute). Finally, desorption was performed by carbon disulfide and analysis was conducted using gas chromatography coupled to mass spectrometry (GC/MS)according to the instructions of NIOSH 1022 and OSHA 1001.

Results: The highest amount of adsorption occurred in the flow of 0.1 L/minute (81.51±3.72). Furthermore, considering the three studied concentrations of trichloroethylene (18, 35, and 53 ppm); the highest efficiency was recorded at 18 ppm concentration (83.18±11.67). The highest adsorption efficiency with the lowest standard deviation (80.55±3.85) was observed in samples that were immediately injected into the GC/MS machine.

Conclusion: Given that time-lapse had no significant effect on adsorption efficiency, it is argued that the pollutant had suitable stability on the surface of the adsorbent. The results of this study show that multi-walled carbon nanotubes have better performance at lower concentrations of trichloroethylene.

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Introduction

Over the past years, volatile organic compounds (VOCs) have been regarded as the third major air pollutant following particles and sulfur dioxide (1). One of the main constituents of VOCs is chlorinated hydrocarbon, which remains in the air for a longer period of time (2). A common type of chlorinated hydrocarbon is trichloroethylene (TCE), which is an industrial solvent. It has a vapor pressure of 58 mmHg (in normal

condition) and a boiling temperature of 87.2 °C. It is colorless, slightly polar, and lipophilic and has a sweet smell. In atmosphere, TCE reacts with hydroxyl radicals (OH), which are the results of photochemical atmospheric reactions. This reaction yields phosgene, dichloroacetyl chloride, and other destructive compounds. Studies show that the concentration of TCE is 1.2 mg/m^3 in urban environments, while industrial exposures can be ten times greater than the concentration of urban environments (3,4).

TCE is a widely used industrial decolorized solvent and is often used as a degreaser for metal parts, especially in textile, leather, and wool industries. In addition, it is used in the processes for the separation of oils, resins, paints, and printing inks as well as in manufacturing clocks, adhesives, fluid silicones, ether, cellulose esters, and sulfur (3,5-7). Epidemiological studies have indicated the carcinogenic nature of TCE. That is, exposure to this commonly used solvent leads to severe forms of occupational allergy (5) and several types of cancer including kidney, liver, lymphatic system, and spinal cord cancers (8-11). These complications are caused by the chemical properties of TCE (the presence of chlorine and diphtheria) and its easy adsorption via inhalation, skin, and food. Therefore, the International Agency for Research on Cancer (IARC) has categorized TCE as definitely carcinogenic to human (7).

In order to measure VOCs in work environments, one should either use direct reading devices or collect samples from the environmental air, followed by preparing and analyzing the samples. In the second procedure, usually carbon-based adsorbents (e.g. activated carbon, chromosorb, porapak, molecular sieve, and porous polymers in granular form) are used (1,4,12,13).

Furthermore, other methods used for sampling of VOCs from air are based on ionic liquid-phase adsorbent (14). Sampling is the main step in every measurement procedure (15); thus, an ideal adsorbent should have chemical stability and the capability of adsorption and desorption of polar and non-polar compositions. It should be heat resistant and economic as well. Of course, all these properties cannot be simultaneously found in a single adsorbent. It is obvious that the combination of various types of adsorbent in a sampling tube will result in the adsorption of a huge bulk of VOCs. As a result, it is essential to have a multi-layer adsorbent, like multi-walled carbon nanotube, in order to collect air samples through reliable procedures (1). During the past decade, numerous attempts have been made to develop the use of carbon nanotube in sampling VOCs (6,13). Recent research has revealed that carbon nanotubes are efficient for the adsorption of toxins in vapor phase (16). Moreover, they are highly elastic (16-19), with appropriate chemical, electrical, and thermal properties. They also have high adsorption capacity and high adsorption surface (150-1550 m^2/g), and efficient desorption capability (18-20).

The main advantage of carbon nanotubes in the sampling process is that they are nonpolar, hence holding analyte on their surface with Van der Waals force leading to the improvement of their desorption capability (12,18). Pollutants can be adsorbed by carbon nanotubes, inline network channels between nanotubes, or external grooves available at secondary levels of bands, where two carbon nanotubes meet (19). Acidification of carbon nanotubes breaks their structure and the carboxyl group COOH is bound with nanotubes creating a better opportunity for adsorption.

Due to the quantitative and qualitative increase in the production of chemicals, it is incumbent to constantly measure and control their pollutants (21,22). In recent years, many studies have focused on the efficiency of multi-walled and single-walled carbon nanotubes to adsorb VOCs under various conditions (12,23, 24). The results of these studies are contradictory. The present study aimed at investigating the efficiency of multi-walled functionalized carbon nanotubes in adsorbing trichloroethylene.

Materials and Method

The following materials were purchased for this study: TCE with high purity (99.5%), ethanol HPLC grade and carbon disulfide GC grade manufactured by Merck (Germany), highly purified concentrated nitric acid, nanotube with a diameter of 20-40 nanometer and a length of 1-10 µm manufactured by Plasma Chem GmbH (Berlin, Germany), sampling tube manufactured by CONSCO, coconut-shell based sorbent tube, and 10-liter sample bag made by SKC (England).

Generation of static standard atmosphere

In Germany, exposure to trichloroethylene (5–15 µg/m3) is reported as the typical concentration range for urban areas. In occupational settings, the exposure levels are higher than urban areas. In the United States, metal degreasers were found to be exposed to trichloroethylene; 60% of the measured concentrations were less than 270 mg/m3 and 93% less than 540 mg/m3 (25). As a result, we decided to work at maximum concentrations.

Static standard atmosphere was generated through injecting 180, 350, and 530 µL of TCE into the 10-liter sampling bags, which had already been filled with 9.5 L of pure nitrogen as neutral gas. In order to evaporate trichloroethylene, a bain-marie at the temperature of 85 °C was used. As a result, the concentrations of 18, 35, and 53 ppm (which are standard concentrations) were obtained which is presented in Table 1.

Functionalizing or acidifying multi-walled carbon nanotubes

At first, amorphous (super fine carbon particles in between nanotubes) deposition was performed on carbon nanotube to reduce the pressure drop. More specifically, some carbon nanotubes were sieved to remove microscopic particles. The amount of amorphous carbon was determined by weighing the remaining carbon nanotube before and after the amorphous deposition.

In order to functionalize the carbon nanotube, 0.1 g of carbon nanotube was transferred to a rounded balloon placed in a metal container containing paraffin. Then, 7 mL of concentrated nitric acid and a 1cm magnet was added to it. The compound was subsequently put on a heater stirrer, which produced a heat of 110 °C, for three hours. After cooling down the acid which contained multi-walled carbon nanotube, the mixture was poured into a funnel and the pH of the carbon nanotube was neutralized by adding deionized water. The mixture was then placed inside a furnace with a temperature of 70 °C and was heated for two hours (26-30).

Producing the adsorbent tube for sampling single- and multi-walled carbon nanotube

In order to reduce laboratory errors, NIOSH and OSHA 1022 and 1001 were respectively used (31,32). For producing the finalized adsorbent tube, the purified and meshed carbon nanotube were poured into some tubes which were 11 cm long,

and had inner and outer diameters of 4 and 6 mm, respectively. The tubes were made of quartz, in which one end of them was closed by heated foam. A mechanical shaker was used to unify adsorbent surface. An appropriate amount of polyurethane foam with its retaining spring was put at the end of the tube to avoid carbon nanotube spill. In the light of the research objectives and previous studies, 10 mg of carbon nanotube was used.

Drawing the calibration curve

In order to determine the amount of trichlorethylene in the samples, the calibration curve should be plotted within the desired concentration range. To do so, particular concentrations of TCE liquid (5, 25, 50, 100, 250, 500, 800ppm) were injected to GC/MS following the standard procedure. Then the calibration curve was plotted based on the concentration and area obtained. The obtained curve regression coefficient which is shown in Fig. 1 is 0.9944.

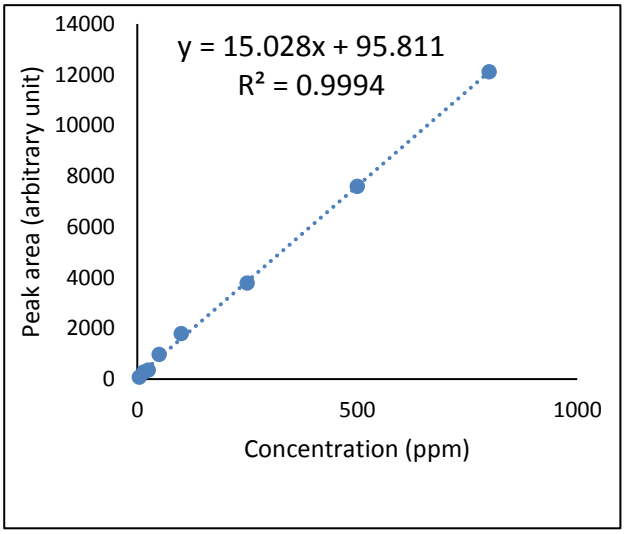

Figure 1. Calibration curve of TCE Standard solution injected into GC/MS

Adsorption and desorption

After producing the adsorbent tube for sampling, attempts were made to calibrate it. In this regard, one end of the tube was connected to a personal sampler pump, while the other end was connected to the electronic calibrator for flow rate calibration. This process was adopted to measure drop pressure inside the sampling tube caused by carbon nanotube and to regulate sampling flow.

Preparing and extracting TCE using carbon disulfide and Statistical analysis

Upon finishing the sampling process, the adsorbent was evacuated from the sampling tube. The extraction was performed based on NIOSH 1022 and OSHA 1001 and in the light of factors such as the amount of adsorbent, sampling flow, TCE concentration, and air volume sampling. According to the two above-mentioned procedures, 1 mL of carbon disulfide was first poured into a vial containing adsorbent. A piece of

glass wool that was intended to prevent adsorbent spill was also transferred to the vial along with the adsorbent. The vial was subsequently sealed. The sample was then placed in ultrasonic bath for 30 minutes. The sample was injected into GC/MS to assess the amount of adsorbed analyte. Sample was analyzed on a Agilent column (19091S-433, HP-5MS) with 30 m length, 250 µm diameter and 0.25 µm film. The column temperature was kept at 40 °C and programmed to 130 °C at a rate of 5 °C/min. The flow rate of helium as carrier gas was 6.0 mL/min with a split ratio of 5:1.

Data were fed into SPSS software version 22 and one-way ANOVA was utilized to examine the differences in the mean and standard deviation for the adsorption efficiency in various options of each variable.

Table 1. The conditions of obtained samples

Test number	Test	Test conditions				
		Amount of adsorbent (mg)	TCE concentration (ppm)	Flow (ml/min)	Time lapse before analyte (day)	Sampling time length (min)
1	Effect of low concentration and flow on adsorbent efficiency in various time periods	10	18	100	0 5 10	20
2	Effect of high flow on adsorbent efficiency in various time periods	10	18 35	200	0 5	20
3	Effect of sampling flow in various time periods	10	53	100 150 200	0 5 10	20

Results

The current study focused on the effect of two variables – concentration and time lapse between sampling and analysis – on the efficiency of multi-walled carbon nanotube in adsorbing TCE. The maximum average adsorption efficiency of this adsorbent was 81.51±3.72 with a flow of 0.1. The domains of 0.1 to 0.2 L/minute were selected for the flow in the light of the carbon nanotube sizes, pressure loss caused by them, and the adsorption opportunity of analyte molecules on the surface of the adsorbent. Out of the three flow amounts, 0.2 L/minute had the lowest mean efficiency (77.96% ± 4.06). The change of flow did not lead to any significant variations in the efficiency of adsorbent ($p>0.05$). The results are displayed in Table 2.

Table 2. Mean and standard deviation for efficiency in various sampling flows

Flow	Mean	Standard deviation	Domain
0.1	81.51	3.72	87.04-66.25
0.15	80.09	4.5	86.24-70.95
0.2	77.96	4.06	80.86-59.26

The effect of time lapse between sampling and injection to machine in the temperature of 4 °C on the efficiency of

adsorbing functionalized multi-walled carbon nanotube was investigated in order to study pollutant stability on the adsorbent surface in three time lapses of 0, 5, and 10 days.

The results indicated that the highest adsorption efficiency with the lowest standard deviation was observed in samples which were immediately injected into the GC machine (80.55%±3.85). There was no statistically significant relationship between this variable and adsorption efficiency. The results are depicted in Table 3.

Table 3. Mean and standard deviation for efficiency in various time lapses between sampling and analysis

Time lapse	Mean	Standard deviation	Domain
0	80.55	3.85	81.94-74.26
5	80.19	5.93	80.85-74.15
10	78.74	4.24	79.64-76.95

Based on the standard atmosphere structure and the minimum concentration with the lowest error, the efficiency adsorbing TCE by multi-walled carbon nanotube was investigated in three concentration ranges of TCE (18, 35, and 53 ppm of trichloroethylene). The results are demonstrated in Table 4.

Table 4. Mean and standard deviation for efficiency in different sampling concentrations

Concentration	Mean	standard deviation	Domain
18	83.18	11.67	85.86-71.15
35	79.40	9.33	81.01-70.07
53	75.53	6.82	76.24-69.78

Discussion

This experimental study aimed at examining the efficiency of removing TCE (Halogenated carcinogenic hydrocarbons) from air by the use of functionalized multi-walled carbon nanotube. The study specifically focused on the influence of time lapse, flow, and concentration on TCE adsorption efficiency. All tests were conducted in the room temperature and relative humidity of 12%.

The results indicated that time lapse between sampling and analysis and sampling flow did not statistically affect the mean efficiency of carbon nanotube in adsorbing TCE ($p>0.05$). Conversely, the mean efficiency of TCE adsorption by carbon nanotube was lower in higher concentrations, a finding that is in line with Saridara et al.'s conclusion (33). It was hypothesized that if the time lapse between sampling and sample injection into the GC/MS machine is reduced, the pollutant is less likely to leave the adsorbent surface. The results of the present study, however, indicated that variations in time lapse did not significantly affect the mean efficiency of carbon nanotube in adsorbing TCE.

It should be noted that, in our study, the samples were kept in the temperature of 5 °C before the analysis stage. Attari et al. found that the increase in time lapse led to reduction in the mean efficiency of carbon nanotube in adsorbing TCE. This might be explained in the light of the temperature in which they held the samples before analysis (25 °C) (34). Increasing the sampling flow to 0.15 L/minute did not significantly affect the adsorption efficiency. However, the highest drop in mean adsorption efficiency was recorded in the flow of 0.2 L/minute. This may be attributed to the fact that, in this sampling flow, the pollutant molecules have more time to be adsorbed and homogenously distributed in the adsorbent. In contrast, the results of the study

conducted by Rafieepour et al. indicated that the efficiency of activated carbon in adsorbing single-ring hydrocarbons is greater than that of single- and multi-walled carbon nanotubes, a claim that is not in line with the results of this study (24). This discrepancy may be explained based on the different nature and structure of single-ring hydrocarbons and TCE as well as laboratory conditions. Studying two types of MWCNT, Shih et al. showed that organic compounds are adsorbed by porosities within carbon nanotubes, the space between nanotube networks, and curved surfaces of nanotube clusters (23). The researchers concluded that adsorption does not occur inside the layers of MWCNT because VOCs are too big to be adsorbed by the space between MWCNT layers. Therefore, desorption reduction can not be attributed to encapsulation of analyte molecules among the graphenes of multi-walled carbon nanotubes. The results of the study carried out by Quon Long et al. also confirm the findings of the current research. They introduced carbon nanotubes as an alternative adsorbent which can replace the stationary phase of the GC machine column. This further supports the high efficiency of multi-walled carbon nanotube (35).

Conclusion

Like the majority of research projects, the results of this study demonstrate that carbon nanotube is an appropriate alternative to typical adsorbents. Given that the time lapse between sampling and analysis and variations in sampling flow were not significantly effective in changing adsorption efficiency, it is argued that the pollutant had suitable stability on the adsorbent surface. The results of this study demonstrate that multi-walled carbon nanotubes have better performance at lower concentrations. The findings of this study revealed that functionalized multi-walled carbon nanotube can be a suitable adsorbent for sampling TCE in the air. It is therefore necessary to conduct further studies under various laboratory conditions in order to make firm claims in this regard.

References

1. Liu J, Li L, Ning Z, Zhao P, Fan H. Multi-layer cartridges filled with multi-walled carbon nanotubes for the determination of volatile organic compounds in indoor air. Anal Sci 2008; 24(4):515-9.
2. Abedi K, Ghorbani-Shahna F, Jaleh B, Bahrami A, Yarahmadi R. Enhanced performance of non-thermal plasma coupled with TiO 2/GAC for decomposition of chlorinated organic compounds: influence of a hydrogen-rich substance. J Environ Health Sci Eng 2014; 12(1):119.
3. World Health Organization. WHO Guidelines for Indoor Air Quality: Selected Pollutants. Geneva: WHO; 2010.
4. Lash LH, Parker JC, Scott CS. Modes of action of trichloroethylene for kidney tumorigenesis. Environ Health Perspect 2000; 108(Suppl 2):225-40.
5. Kamijima M, Wang H, Yamanoshita O, Ito Y, Xia L, Yanagiba Y, et al. Occupational trichloroethylene hypersensitivity syndrome: human herpesvirus 6 reactivation and rash phenotypes. J Dermatol Sci 2013; 72(3):218-24.
6. Sone H, Fugetsu B, Tsukada T, Endo M. Affinity-based elimination of aromatic VOCs by highly crystalline multi-walled carbon nanotubes. Talanta 2008; 74(5):1265-70.

7. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. [12 June 2019] Available from:https://monographs.iarc.fr/wpcontent/uploads/2018/06/mono27.pdf

8. Brauch H, Weirich G, Klein B, Rabstein S, Bolt HM, Brüning T. VHL mutations in renal cell cancer: does occupational exposure to trichloroethylene make a difference? Toxicol Lett 2004; 151(1):301-10.

9. Brautbar N, Williams J 2nd. Industrial solvents and liver toxicity: risk assessment, risk factors and mechanisms. Int J Hyg Environ Health 2002; 205(6):479-91.

10. Huang H, Li L, Chen B, Huang J, Kuang S. New problems caused by occupational trichloroethylene exposure. Int J Immunopathol Pharmacol 2002; 15(15):30-2

11. Cooper GS, Makris SL, Nietert PJ, Jinot J. Evidence of autoimmune-related effects of trichloroethylene exposure from studies in mice and humans. Environ Health Perspect 2009; 117(5):696-702.

12. Hussain CM, Saridara C, Mitra S. Microtrapping of volatile organic compounds with carbon nanotubes. Sonklanakarin Journal of Science and Technology 2010; 32(5):505.

13. Golbabaei F, Ebrahimi A, Shirkhanloo H, Koohpaei A, Faghihi-Zarandi A. Single-Walled Carbon Nanotubes (SWCNTs), as a novel sorbent for determination of mercury in air. Glob J Health Sci 2015; 8(7):273-80.

14. Faghihi-Zarandi A, Shirkhanloo H, Jamshidzadeh C. A new method for removal of hazardous toluene vapor from air based on ionic liquid-phase adsorbent. Int J Environ Sci Technol (Tehran) 2019; 16(6):2797-2808.

15. Kumar A, Víden I. Volatile organic compounds: sampling methods and their worldwide profile in ambient air. Environ Monit Assess 2007; 131(1-3):301-21.

16. Gooding JJ. Nanostructuring electrodes with carbon nanotubes: a review of electrochemistry and applications for sensing. Electrochimica Acta 2005; 50(15):3049-60.

17. Cho HH, Smith BA, Wnuk JD, Fairbrother DH, Ball WP. Influence of surface oxides on the adsorption of naphthalene onto multiwalled carbon nanotubes. Environmental Science & Technology 2008; 42(8):2899-905.

18. Hussain CM, Mitra S. Micropreconcentration units based on carbon nanotubes (CNT). Anal Bioanal Chem 2010; 399(1):75-89.

19. Agnihotri S, Mota JP, Rostam-Abadi M, Rood MJ. Theoretical and experimental investigation of morphology and temperature effects on adsorption of organic vapors in single-walled carbon nanotubes. J Phys Chem B 2006; 110(15):7640-7.

20. Kim YJ, Shin TS, Do Choi H, Kwon JH, Chung YC, Yoon HG. Electrical conductivity of chemically modified multiwalled carbon nanotube/epoxy composites. Carbon 2005; 43(1):23-30.

21. Strelko Jr V, Malik DJ, Streat M. Characterisation of the surface of oxidised carbon adsorbents. Carbon 2002; 40(1):95-104.

22. Datsyuk V, Kalyva M, Papagelis K, Parthenios J, Tasis D, Siokou A, et al. Chemical oxidation of multiwalled carbon nanotubes. Carbon 2008; 46(6):833-40.

23. Shih YH, Li MS. Adsorption of selected volatile organic vapors on multiwall carbon nanotubes. J Hazard Mater 2008; 154(1-3):21-8.

24. Rafieepour A, Ghorbani Shahna F, Hashemi Z, Ghamari F. Measurement of benzene in air by iranian single-wall carbon nanotubes. Iranian Journal of Toxicology 2012; 5(15):535-40.

25. World Health Organization. Trichloroethylene. [16 November 2015.] Available from: http://www.euro.who.int/__data/assets/pdf_file/0003/123069/AQG2ndEd_5_15Trichloroethylene.pdf?ua=1

26. Ha B, Park J, Kim SY, Lee CJ. Investigation of field emission and photoemission properties of high-purity single-walled carbon nanotubes synthesized by hydrogen arc discharge. J Phys Chem B 2006; 110(47):23742-9.

27. Ago H, Kugler T, Cacialli F, Salaneck WR, Shaffer MS, Windle AH, et al. Work functions and surface functional groups of multiwall carbon nanotubes. J Phys Chem B 1999; 103(38):8116-21.

28. Zhang N, Xie J, Varadan VK. Functionalization of carbon nanotubes by potassium permanganate assisted with phase transfer catalyst. Smart Mater Struct 2002; 11(6):962.

29. Beker UG, Malik DJ, Strelko V, Streat M. Influence of activated carbon oxidation treatments on the selective removalof copper and lead. Chemical Engineering Communications 2003; 190(5-8):610-29.

30. Bandosz TJ, Jagiello J, Contescu CI, Schwarz JA. Characterization of the surfaces o activated carbons in terms of their acidity constant distributions. Carbon 1993; 31(7):1193-202.

31. NIOSH. NIOSH manual of analytical methods (NMAM'TM). [29 December 2015] Available from: https://www.cdc.gov/niosh/docs/96-135/pdf/96-135.pdf.

32. Coyne LS, Havalias G, Echarte MC. Vapor intrusion sampling options: performance data for canisters, badges, and sorbent tubes for vocs. [29 December 2015] Available from: https://cluin.org/download/contaminantfocus/vi/Canister%20Badges%20Sorbent%20Tubes.

33. Saridara C, Brukh R, Iqbal Z, Mitra S. Preconcentration of volatile organics on self-assembled, carbon nanotubes in a microtrap. Analytical chemistry 2005; 77(4):1183-7.

34. Attari SG, Bahrami A, Shahna FG, Heidari M. Solid-phase microextraction fiber development for sampling and analysis of volatile organohalogen compounds in air. J Environ Health Sci Eng 2014; 12(1):123.

35. Li Q, Yuan D. Evaluation of multi-walled carbon nanotubes as gas chromatographic column packing. Journal of Chromatography A 2003; 1003(1-2):203-9.