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Quantification of carbon nanotubes in different environmental matrices by a microwave induced heating method

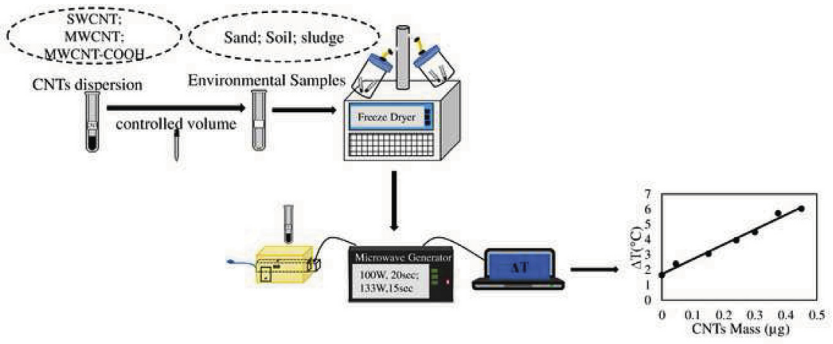
Yang He [a], Souhail R. Al-Abed [b,*], Dionysios D. Dionysiou [a]

[a] Environmental Engineering and Science program, Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, 2600 Clifton Ave., Cincinnati, OH 45221, United States
[b] National Risk Management Research Laboratory, U.S. Environmental Protection Agency, 26 W. Martin Luther King Dr., Cincinnati, OH 45268, United States

HIGHLIGHTS

- A quick microwave method was used to quantify CNTs in sand, soil and sludge.
- MWCNTs were more sensitive to microwave energy than SWCNTs and carboxylated MWCNTs.
- Other carbonaceous materials did not interfere the microwave detection of CNTs.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon nanotubes (CNTs) have been incorporated into numerous consumer products, and have also been employed in various industrial areas because of their extraordinary properties. The large scale production and wide applications of CNTs make their release into the environment a major concern. Therefore, it is crucial to determine the degree of potential CNT contamination in the environment, which requires a sensitive and accurate technique for selectively detecting and quantifying CNTs in environmental matrices. In this study, a simple device based on utilizing heat generated/temperature increase from CNTs under microwave irradiation was built to quantify single-walled CNTs (SWCNTs), multi-walled CNTs (MWCNTs) and carboxylated CNTs (MWCNT-COOH) in three environmentally relevant matrices (sand, soil and sludge). Linear temperature vs CNT mass relationships were developed for the three environmental matrices spiked with known amounts of different types of CNTs that were then irradiated in a microwave at low energies (70–149 W) for a short time (15–30 s). MWCNTs had a greater microwave response in terms of heat generated/temperature increase than SWCNTs and MWCNT-COOH. An evaluation of microwave behavior of different carbonaceous materials showed that the microwave measurements of CNTs were not affected even with an excess of other organic, inorganic carbon or carbon based nanomaterials (fullerene, granular activated carbon and graphene oxide), mainly because microwave selectively heats materials such as CNTs that have a higher dielectric loss factor. Quantification limits using this

Abbreviations: CNT (s), Carbon nanotube(s); CTAB, Hexadecyltrimethylammonium bromide; C_{60}, Fullerene; GAC, Granular activated carbon; GO, Graphene oxide; HA, Humic Acid; MDL (s), Method detection limit (s); MWCNT (s), Multi-walled carbon nanotube (s); MWCNT-COOH, Carboxylated MWCNT; SWCNT (s), Single-walled carbon nanotube (s).

* Corresponding author.
E-mail address: al-abed.souhail@epa.gov (S.R. Al-Abed).

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technique for the sand, soil and sludge were determined as low as 18.61, 27.92, 814.4 μg/g for MWCNTs at a microwave power of 133 W and exposure time of 15 s.

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1. Introduction

Carbon nanotubes (CNTs) are molecular-scale cylindrical tubes of graphitic carbon (Iijima, 1991). Their unique structures give them a large surface area, good electronic conductivity, excellent thermal stability and strength. CNTs have been successfully applied in various fields such as drug delivery system (Liu et al., 2009), aerospace (Baur and Silverman, 2007), construction (Lee et al., 2010) and incorporated into numerous consumer products (Vance et al., 2015; De Volder et al., 2013), with potential uses in everything from tennis racquets and bulletproof vests to electronic components and energy storage devices. The size of global CNTs market is estimated to reach $5.64 billion by 2020 from $2.26 billion in 2015 (www.marketsandmarkets.com). Therefore, the likelihood of CNTs being released into the environment during the manufacture, use and disposal of products containing CNT has definitely increased (Nowack et al., 2013). Despite exceptional properties that are valuable in many applications, there is a concern regarding their potential negative influence on environmental and human health (Wiesner et al., 2006; Oberdörster et al., 2005). Information on the amounts of CNTs accumulated or deposited in various environmental matrices is required before any risk or hazard assessment can be conducted. Typical methods that can be used for determining carbon content such as total organic carbon (TOC) analysis simply provide a nonspecific measurement of carbon, and are not able to distinguish CNTs from other carbon sources in environmental matrices. Therefore, a quantitative method that is specific for CNTs is needed.

Quantification of CNTs in complex environmental media remains a challenge. Nevertheless, there have been several detection techniques that focus on quantifying CNTs in real environmental and biological samples. In past studies, an ultraviolet-visible (UV–vis) spectrophotometer was used to determine the concentration of SWCNTs and MWCNTs in water and in electrophoretic suspension samples at a wavelength of 660 or 800 nm (Ye et al., 2013; Li et al., 2006), while a UV–vis-near infrared spectrometer was used to determine the concentration of SWCNTs in heavy water (Jeong et al., 2007). However, components from real water samples such as dissolved organic matter in surface water could also make contributions to the UV absorbance, leading to imprecise measurements. In addition, absorbance in CNT suspensions could be affected by several factors such as the type and concentration of surfactants, sonication and centrifugation conditions, and interactions between surfactants and CNTs (Angelikopoulos et al., 2010). Near-infrared fluorescence based techniques have been utilized in detecting SWCNTs in blackworm (Yang et al., 2011) and wastewater samples (Schierz et al., 2012), but this method was shown to be valid only for well dispersed SWCNTs, and not for the full range of CNTs (MWCNTs, functionalized CNTs, aggregates of CNTs, etc.). For solid samples, thermal oxidation methods such as thermogravimetric analysis coupled with mass spectrometry (Plata et al., 2012), chemothermal oxidation at 375 °C (Sobek and Bucheli, 2009) and programmed thermal analysis (Doudrick et al., 2012) were also used to quantify SWCNTs and MWCNTs in soil, sediments, air and cyanobacteria due to their high thermal stability, but the degradation of other natural carbon materials in environmental samples that are not as thermally stable as CNTs could potentially interfere with the quantification of CNTs in such matrices. Recently, several studies used single stranded DNA (ssDNA) with magnetic fluorescence spheres to capture CNTs in water and soil samples, which relied on a decrease in fluorescence because of quenching to quantify the CNTs in the samples (Mota et al., 2013; Jeong et al., 2015). However, the ssDNA method was quite complicated to use, and there is a lack of information on the performance and efficiency of the method. Overall, the presence of different types of carbon (e.g., natural organic matter) in environmental samples interfered with the analysis and prevented the accurate determination of CNT concentration using the methods described previously (Herrero-Latorre et al., 2015; Petersen et al., 2011). Moreover, most current methods are appropriate for the detection of pristine CNTs only; these methods have not been shown to successfully quantify functionalized CNTs. Since the ratio of SWCNTs to MWCNTs production is reported to be 1:280 (Herrero-Latorre et al., 2015), the majority of CNTs released into the environment is expected to be MWCNTs and functionalized MWCNTs rather than SWCNTs. Therefore, it is very important to develop a selective and reliable methodology to detect and quantify the different types of CNTs, including MWCNTs and functionalized CNTs in the environment.

In addition to optical and thermal properties, CNTs have other exceptional properties that could be leveraged to provide a solution to

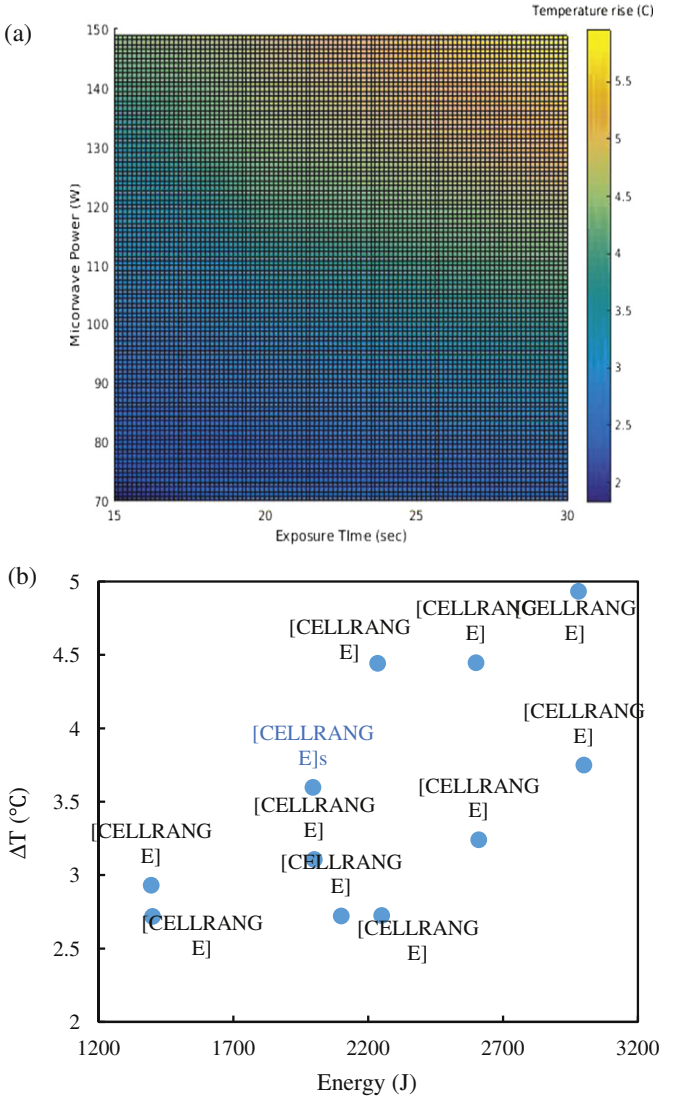

Fig. 1. Effect of (a) microwave power and exposure time on temperature rise of 0.09 mg MWCNTs in sand; (b) microwave energy on temperature rise of 0.09 mg MWCNTs in sand.

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