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Rapid and versatile pre-treatment for quantification of multi-walled carbon nanotubes in the environment using microwave-induced heating

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Abstract

The concerns regarding potential environmental release and ecological risks of multi-walled carbon nanotubes (MWCNTs) rise with their increased production and use. As a result, there is the need for an analytical method to determine the environmental concentration of MWCNTs.

Although several methods have been demonstrated for the quantification of well-characterized MWCNTs, applying these methods to field samples is still a challenge due to interferences from unknown characteristics of MWCNTs and environmental media. To bridge this gap, a recently developed microwave-induced heating method was investigated for the quantification of MWCNTs in field samples. Our results indicated that the microwave response of MWCNTs was independent of the sources, length, and diameter of MWCNTs; however, the aggregated MWCNTs were not able to convert the microwave energy to heat, making the method inapplicable. Thus, a pre-treatment process for dispersing bundled MWCNTs in field samples was crucial for the use of the microwave method. In the present paper, a two-step pre-treatment procedure was proposed: the aggregated MWCNTs loaded environmental samples were first exposed to high temperature (500 °C) and then dispersed by using an acetone-surfactant solution. A validation study was performed to evaluate the effectiveness of the pre-treatment process, showing that an 80–120% recovery range of true MWCNT loading successfully covered the microwave-measured MWCNT mass.

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Electronic supplementary material

A supplementary material file is used to present characteristics of MWCNTs used in this study and calibration curves generated in different environmental media.

Keywords

Microwave induced heating method; Quantification; MWCNTs; Aggregation; Environmental sample; Pre-treatment

Introduction

Since carbon nanotubes (CNTs) were discovered in the 1990s by Iijima (1991), they have been emerging as one of the most promising nanomaterials in various applications including sporting goods, electronic components, aircraft parts, and medicine delivery, due to their extremely large surface area, excellent electronic conductivity, and thermal stability (Garner et al. 2017). However, the growing use of CNTs will likely increase the release of CNTs to the natural environment (Garner et al. 2014). As summarized by Schlagenhauf et al., the emissions of multi-walled CNTs (MWCNTs) from CNT-polymer nanocomposites have been observed under sanding, abrasion, high temperature, and light irradiation (Schlagenhauf et al. 2014). Rhiem et al. also reported the detection of released MWCNTs from polycarbonate composite in artificial acid rain and landfill leachate (Rhiem et al. 2016). The quantity of CNTs was released from products during manufacturing, use or disposal phase has been estimated by Nowack's group using several mathematical models, and their prediction shows that the annual emission to soil will increase from approximately 8 tons in 2015 to 40 tons by 2030 (Sun et al. 2017). Another research group reported their prediction of the released CNTs to the sludge biosolids in wastewater treatment plants to be 0.5–8 mg/kg (Keller and Lazareva 2014). Considering the increasing emission of CNTs, the possibility of exposure to human and other ecosystem receptors cannot be ignored. A growing number of studies have demonstrated the potential hazards of CNTs, and such physicochemical properties of CNTs as size, shape, surface area, and agglomeration were observed as main factors in influencing toxicity of CNTs (Helland et al. 2007). However, there is still a research gap in quantitative analysis of CNTs in the environment. The lack of quantitative data yields an information gap on CNT exposure path, from CNT release to environmental transport and transformation to receptors' exposure. Therefore, one of the foremost challenges in CNT relevant studies is the development of measurement methods for quantifying CNTs in the environment.

During the last decade, several methods have been developed for CNT detection and quantification in different environmental or biological samples, such as ultraviolet–visible (UV–Vis) spectrophotometry (Jeong et al. 2007; Li et al. 2006), near-infrared fluorescence spectroscopy (Schierz et al. 2012; Yang et al. 2010), ^{14}C labeling (Zhang et al. 2012; Zhao et al. 2016, 2017), chemothermal oxidation at 375 °C (Doudrick et al. 2013), programmed thermal analysis (Doudrick et al. 2012), single-stranded DNA (ssDNA) with magnetic fluorescence spheres (Jeong et al. 2015; Mota et al. 2013), and Raman spectroscopy associated with UV–Vis spectrometer (Anoshkin et al. 2017). The advantages and limitations of these methods have been discussed in our previous papers (He et al. 2017; Petersen et al. 2011), and all these methods worked with well characterized CNTs whose diameter, length, and degree of agglomeration were clearly defined. However, the characteristic information of CNTs accumulated in field samples is usually unknown.

As demand increases, CNTs are synthesized and sold by many companies globally. In environmental samples, CNTs typically have a range of diameters and lengths due to differences in manufacturing and environmental effects. Since the characteristics of CNTs are always unknown before environmental quantification, whether different characteristics of CNTs may distort signals of the quantification instruments should be examined. Moreover, although most CNTs are used in dispersed form for a better compatibility with polymers or other materials, the CNTs can be highly aggregated when they are deposited in the environment as a result of environmental transformations. The impact of this aggregation on the performance and accuracy of quantification methods need to be clearly investigated. For example, bundled single-walled CNTs (SWCNTs) did not fluoresce, leading to a failure of fluorescence based methods. Therefore, in order to develop an effective method for determination of the environmental concentration of CNTs, a comprehensive evaluation of the proposed method with different characteristics of CNTs is very necessary.

In our previous study, a microwave-induced heating method has been successfully used to generate the microwave-induced temperature rise-mass of CNT calibration curves for different CNTs in quartz sand, soil, and sludge samples (He et al. 2017). The prior results showed that the presence of other carbonaceous materials (e.g., inorganic carbon, organic carbon, fullerene) in the environmental matrices did not affect the microwave responses of CNTs because the microwave energy selectively coupled with CNTs whose dielectric constant is much higher than that of other carbon materials (Robinson et al. 2008), and the detection thresholds of the microwave method were closer to the predicted environmental concentration of CNTs in soil and sludge (Gottschalk et al. 2009; Sun et al. 2017).

This study presents the results of further evaluation on the microwave-induced heating method for the quantification of CNTs in environmental samples. Since it has been reported that annual production ratio of SWCNTs to MWCNTs is estimated to be 1:280 (Herrero-Latorre et al. 2015), we focused on MWCNTs that are most likely to be present in the environment. In the present work, we investigated how environmental factors such as particle size and charge of solid materials, organic content in the matrices, and MWCNT characteristics, such as sources, shape, and aggregation, affected the quantification of MWCNTs. Finally, we proposed and evaluated a generalized pre-treatment process for the microwave-induced heating method for the quantitative analysis of environmental MWCNT samples.

Material and methods

Materials

MWCNTs with different diameters and length were purchased from US Research Nanomaterials Inc. (USR), Cheaptubes (CT), and Sun Innovation's Nanomaterial Store (SI). All MWCNTs had purity greater than 90% with < 1.5 wt% ash content. The length of short MWCNTs (Short-MWCNT) ranged from 0.5 to 2 μm , whereas the length of long MWCNTs (Long-MWCNT) ranged from 10 to 30 μm . The Long-MWCNT from URS was the MWCNTs used in our previous study and used for experiments on the effects of particle size, surface charge, and organic matter content of the environmental medium in present work. For the study of effect of different diameters of MWCNTs, three types of MWCNTs

with outer diameters of 50–80 (MWCNT-50–80), 20–30 (MWCNT-20–30), and less than 8 nm (MWCNT<8) were used. The characterization data of all MWCNT samples used in this study are provided by vendors and summarized in Supplementary Material, Table S1. Additionally, X-ray Photoelectron Spectroscopy analysis was performed using a Quantera II (Physical Electronics, Chanhassen, MN) equipped with an Al K α source. High-resolution C1s and O1s spectra were obtained at a pass energy of 13 eV, presented in Supplementary Material, Table S2.

Quartz sand, agricultural soil, and anaerobic sludge were used as environmental media for this study. Three different sized quartz sands with silicon dioxide content > 99.7% were obtained from US Silica Company. An average size of whole grain silica, ground silica (S-250), and fine ground silica (S-40) was approximately 0.8, 0.25, and 0.04 mm, respectively. The collection and analysis of soil and sludge samples were the same as we reported in our previous study (He et al. 2017). The organic carbon content has been measured and reported as 1.15% and 41.08% for soil and sludge samples. To obtain different sized soil samples, the bulk soil was passed through a series of sieves, resulting in size fractions of 2, 0.25, and 0.045 mm, labeled as soil#1, soil#2, and soil#3. Hexadecyltrimethylammonium bromide (CTAB, CAS#57–09-0), sodium dodecylbenzenesulfonate (SDBS, CAS# 25155–30-0), and kaolin clay (Al₂Si₂O₅(OH)₄, CAS#1332–58-7, 0.1–4 μ m) were purchased from Sigma and used without any further purification.

Microwave device setup

The detailed information of the microwave system design can be found in our previous paper (He et al. 2017). The microwave condition of 133 W–15 s was used for all experiments in this work.

Experiment design and data analysis

One of the objectives of the present study was to investigate the influences of supplier, length, diameter, and aggregation of MWCNTs on the microwave-induced heating method, because these effects were the major characteristic properties of MWCNTs that could play a role in the microwave behavior of MWCNTs. Each effect was examined separately, as indicated in Table 1. Soil was used as a representative environmental medium, all samples were prepared in triplicate, and each sample was measured three times by the microwave-induced heating method to ensure the variability within an acceptable range. The significance of the difference in temperature rise (ΔT) of each factor was determined by ANOVA at 95% confidence level in corresponding test.

The other objective of this work was to suggest an effective pre-treatment process for the quantification of the aggregated MWCNTs in field samples. The influences of particle size, surface charge, and organic carbon content of environmental media on the pre-treatment process were studied. The difference in ΔT values of pre-treated samples and dispersed samples was determined by ANOVA at 95% confidence level.

Sample preparation

Each dispersed MWCNT sample was prepared by dispersing 0.5 mg MWCNTs into a 2-ml aqueous or acetone solution containing 0.1% w/v CTAB (cationic surfactant) or SDBS (anionic surfactant) in a bath sonicator (100 W, Fisher Scientific, FS30) for 3 h. The UV–Vis spectrometer was applied to ensure maximum achievable MWCNT dispersion after the sonication procedure (the UV–Vis spectra were shown in Supplementary Material, Fig. S1). The suspended MWCNT solution was mixed with environmental media. To ensure the volume of the environmental sample that is exposed to microwave energy the same, whole grain sand of 0.130 g, S-250 of 0.085 g, S-40 of 0.055 g, soil of 0.100 g, and sludge of 5 ml (dry weight 15.3 mg) were used. Undispersed MWCNT samples were simply prepared by mixing 0.5 mg MWCNT powder with the environmental medium. In addition to dispersed and undispersed MWCNT samples, post-dispersed MWCNT samples were prepared by using CTAB or SDBS surfactant solution to suspend the bundled MWCNTs that have been deposited in environmental matrices. In other words, the post-dispersion means that the dispersion of MWCNTs happens after a mixture of aggregated MWCNTs and environmental samples. To post-disperse 0.5 mg bundled MWCNTs embedded in sand, soil, or sludge samples, 2 ml surfactant solution (0.1 wt% CTAB or SDBS aqueous solution or 0.1 wt% CTAB or SDBS acetone solution) was added prior to 3-h sonication. All MWCNT-loaded environmental samples were dried in an oven at 105 °C overnight to remove water or organic solvent before the microwave exposure. The dried environmental samples containing MWCNTs were exposed to 133 W microwave energy for 15 s, and the temperature change after the microwave irradiation (ΔT , °C) was computed by subtracting the initial temperature from final temperature.

Results and discussion

Microwave behavior of MWCNTs from different suppliers and with different shapes

As seen in Table S1 (in Supplementary Material), the MWCNTs sold by USR, SI, and CT were synthesized by the chemical vapor deposition (CVD) method. This is a commonly used synthesis method for large scale production due to its low cost. Therefore, most MWCNTs entering the environment may be prepared by CVD method. Figure 1a shows that the average ΔT of MWCNTs from three companies (USR, SI and CT) was 17.11, 16.93, and 16.75 °C, respectively. They were not significantly different from each other indicated by the p value greater than 0.05 at a 95% confidence level. The ΔT reading for 0.5 mg MWCNTs was 17.52 °C from the calibration curve developed for MWCNTs spiked soil samples in our previous study (Fig. S2, Supplementary Material). The match of the observed ΔT of MWCNTs from different suppliers and the ΔT reading from the calibration curve suggests the microwave responses of MWCNTs are not affected by the material suppliers. From Fig. 1b, the ΔT value of Long-MWCNTs (17.13 °C) was not statistically different from that of Short-MWCNTs (16.85 °C), confirmed by the nonsignificant difference test result of $p > 0.05$. Moreover, Fig. 1c indicates that the ΔT values of MWCNTs with different diameters were statistically equal (17.05, 17.07, and 16.76 °C). The similar ΔT values across different shapes demonstrate that length and diameter do not play a role in the microwave measurements of MWCNTs, which is consistent with the mechanism of the microwave-induced heating, dielectric heating. The structural imperfections of CNTs decay ballistic

transport of electrons, resulting in intense heating independent of length and diameter of CNTs as long as the defect density of CNTs is similar (Vázquez and Prato 2009). Thus, the microwave responses of MWCNTs are independent of the sources, length, and diameter of MWCNTs. The results validated the capacity of the microwave-induced heating method for determination of the MWCNTs whose production information is unidentified.

Microwave behavior of aggregated MWCNTs

The microwave performance of aggregated MWCNTs in different environmental media was examined. In Fig. 2, the average T values of bundled MWCNTs in the whole grain quartz sand, soil, and sludge (0.03 °C, 1.37 °C, and 2.86 °C) were almost equal to the T values of respective environmental media (0.03 °C, 1.34 °C, and 1.98 °C), much smaller than those of the dispersed MWCNTs in the medium (17.79 °C, 17.11 °C, and 12.80 °C). The result indicates that the aggregated MWCNTs did not release heat when exposed to the microwave irradiation. Deering et al. also found very slight temperature rises of bundled CNTs, and they provided an explanation: microwave-induced heating originates from the conversion of electromagnetic energy into mechanical vibrations, but CNTs do not vibrate in a dense and viscous local environment (Vázquez and Prato 2009; Ye et al. 2006). If the aggregated MWCNTs are not able to convert the microwave energy to heat, the microwave-induced heating method will not work for quantification of MWCNTs. Therefore, a pre-treatment process to post-disperse the bundled MWCNTs embedded in the environmental medium is desirable, making the microwave method applicable for quantifying bundled MWCNTs in field samples. Post-dispersion process is to suspend undispersed MWCNTs that have been deposited in environmental matrices by adding surfactant solutions followed by a sonication process. If the T of the post-dispersed MWCNTs in a medium could statistically match the T of the dispersed MWCNTs in the medium, the calibration curve generated through the microwave method with the dispersed MWCNTs can be used to determine the mass of MWCNTs.

Figure 3a shows that the T of 0.5 mg post-dispersed MWCNTs using 2 ml of 0.1 wt% CTAB aqueous solution was $17.13\text{ }^{\circ}\text{C} \pm 0.71\text{ }^{\circ}\text{C}$ in the whole grain quartz sand, which is not significantly different from the T of dispersed MWCNTs ($17.79\text{ }^{\circ}\text{C} \pm 1.04\text{ }^{\circ}\text{C}$) in the sand. The matched T values of dispersed and post-dispersed MWCNTs in sand indicate that post-dispersion using CTAB may be a good pre-treatment procedure for determination of bundled MWCNTs with the microwave method. However, the same surfactant solution did not work for post-dispersing MWCNTs in soil and sludge samples, as shown in Fig. 3b, c. The texture and composition of soil and sludge are much more complex than quartz sand, probably hindering the post-dispersion process of MWCNTs. Therefore, a modified post-dispersion process has to be proposed for complex environmental media. Since earlier studies showed the adsorption of surfactants to soils or other environmental matrices (Ishiguro and Koopal 2016), the potential reason why the post-dispersion with 0.1% CTAB failed was that the components of soil or sludge, such as clay minerals or organic matter, may absorb most surfactants, leaving insufficient surfactant available to suspend undispersed MWCNTs. To improve the post-dispersion, 2 ml of concentrated CTAB solutions (1 and 2 wt%) was introduced, which exceeded the reported maximum adsorption capacity of soil at room temperature (Gürses et al. 2009). Additionally, the negatively charged surfactant SDBS

was used with respect to the surface charge of the medium. The quantities of CTAB and SDBS added here were larger than the reported maximum adsorption amount of the surfactants on soil to ensure an excess of surfactants (Xingchao Qi et al. 2016). As illustrated in Fig. 3b, c, the T values of post-dispersed MWCNTs were still not comparable to the T of the dispersed MWCNTs no matter what type of surfactants were used, even the concentration of surfactant solutions went up to 2 wt%. One possible reason for the failure is the large heat capacities of CTAB and SDBS (Chew et al. 2015). The high heat capacity of the surfactant molecules could prevent temperature increase from being detected in the surrounding sample. Therefore, simply increasing the concentration of surfactant solution could not improve the post-dispersion. To propose an effective pre-treatment process, it is extremely important to investigate which factors affect the post-dispersion of MWCNTs.

Effects of particle size and surface charge of the environmental matrices on post-dispersion of MWCNTs

In this section, different sized quartz sands (whole grain sand, S-250, and S-40) and soil (soil#1, soil#2, and soil#3) were used as media to investigate whether particle size and surface charge of the medium impact the post-dispersion and microwave responses of MWCNTs. Figure 4a shows the T of dispersed and post-dispersed MWCNTs in different sized quartz sands. As discussed in the above section, the average T values of post-dispersed MWCNTs in whole grain sand were close to those of the dispersed MWCNTs irrespective of the type of the surfactant (14.72 °C vs. 14.46 °C for 0.1% SDBS assisted MWCNT). However, the average T of post-dispersed MWCNT in S-250 and S-40 did not reach the T of the dispersed MWCNTs in these two media. As particle size of the sand decreases, the T of the post-dispersed MWCNT decreases. Since quartz sands, even different sizes, are transparent to microwave energy (Haque 1999) and no organic carbon or surface charges exist within samples, the discrepancies among sand samples with different grain sizes is most likely attributed to the surface area. The S-40 sand has the largest surface area, offering more accessible sites for the adsorption of surfactants. As a result, it was more difficult to post-disperse MWCNTs. A similar trend for T of the post-dispersed MWCNTs was found in varying sized soils (Fig. 4b).

In addition to particle sizes, surface charge of the environmental medium could play an important role in the post-dispersion process. Kaolin, negatively charged clay mineral, was chosen to study the effect of the surface charges on the post-dispersion of MWCNTs, and all results are presented in Fig. 5. In a pure kaolin medium, the T of post-dispersed MWCNT using SDBS (15.37 °C) was almost the same as T of the dispersed MWCNT (15.54 °C), whereas the T of post-dispersed MWCNT using CTAB (2.21 °C) was less than T of the dispersed MWCNT (5.53 °C). The results show that surface charge of the environmental medium interferes with the interaction between MWCNTs and surfactants. The electrostatic repulsion between the negatively charged surface of kaolin and SDB⁻ anion could be the reason for the success of SDBS for dispersing and post-suspending MWCNTs. The affinity of SDB⁻ anion and kaolin was weak, resulting in most SDBS suspending bundled MWCNTs. The results are consistent with findings published by Han et al. that the presence of negatively charged clay destabilized the CTAB-suspended MWCNT dispersion, but the introduction of clay did not change the stability of SDBS suspended MWCNTs (Han et al.

2008). The same research group also reported that the capacity of MWCNTs in sorption of SDBS was much stronger than that of kaolin, while the sorption of CTAB was similar by MWCNTs and kaolin (Han et al. 2008). For the further investigation, a mixture of kaolin and soil (50:50 by weight) was used as medium. The T of post-dispersed MWCNTs in the mixture was 85.80% of the T of dispersed MWCNT with the assistance of SDBS. The ratio was smaller than the ratio in the pure kaolin medium (98.9%), but larger than the ratio in a pure soil sample (29.7%) using SDBS. Compared with the T of post-dispersed MWCNT using CTAB in kaolin, the T in the mixture did not increase significantly. Thus, an appropriate surfactant needs to be selected considering the surface charge of the environmental medium. Although soil samples are usually negatively charged, the performance of SDBS in post-dispersing MWCNTs in soil was not as good as the performance of CTAB. The reason could be that the presence of other components within samples, like organic carbon, may capture some surfactants, leading to less efficient performance of SDBS in soil samples. Therefore, the effect of the organic carbon on the post-dispersion was discussed in the next section.

Effect of organic carbon on post-dispersion of MWCNTs

Organic carbon content may interfere with post-dispersion of MWCNTs because the adsorption of surfactants by environmental media is governed by the organic carbon fraction of media. The media with higher organic carbon content will adsorb more surfactant molecules, and less surfactant will be left to disperse bundled MWCNTs. Thus, the removal of the organic content from the environmental matrices is essential to offer sufficient surfactants for MWCNTs. In this section, the undispersed MWCNT-loaded soil and sludge samples were treated at an elevated temperature (500 °C) for 2 h and then post-dispersed by adding 2 ml of 0.1 wt% surfactant solutions and sonicating for 3 h. This process would not damage MWCNTs due to their excellent thermal stability. Figure 6a indicates that the removal of the organic content at high temperature effectively increased the T ratio of post-dispersed MWCNTs to dispersed MWCNTs in soil from 28.40 to 48.99% by using 0.1 wt% CTAB solution and 29.70 to 61.46% by using 0.1 wt% SDBS solution, respectively. The improvement in the T ratio demonstrates that the high-temperature treatment has a positive influence on the post-dispersion of MWCNT from the soil. For the MWCNTs in the sludge sample (Fig. 6b), the average T of post-dispersed MWCNT with 0.1 wt% CTAB solution after the high-temperature treatment increased to 24.87 °C, not significantly different from the average T of CTAB-dispersed MWCNT, 25.22 °C. And the average T of post-dispersed MWCNT using SDBS solution increased to 17.81 °C, close to the average T of dispersed sample (18.30 °C). The high T ratio of post-dispersed to dispersed MWCNT in sludge samples, 98.61% and 97.32% using CTAB and SDBS solutions, indicated that the high-temperature treatment improved the performance of post-dispersing aggregated MWCNTs from sludge samples. As mentioned in “Material and methods,” the organic carbon content of the sludge sample is as high as 41%, so removing the organic carbon may eliminate a major limiting factor for the post-dispersion of MWCNTs from the sludge, making the post-dispersion effective. On the other hand, the organic carbon content (1.15%) is not a principle constituent of soil, so the removal of the organics was not able to completely improve the post-dispersion of MWCNTs. The post-dispersion in soil may be affected by compound effects of the surface area, surface charge, and organic carbon content

of the medium. The surface area of soil only sample, as measured by Brunauer–Emmett–Teller (BET) analysis, increased from 7.25 to 11.70 m²/g after exposure to 500 °C. A larger surface area of ashed soil counteracted the improvement of the post-dispersion of MWCNTs from the high-temperature exposure. This partly explained why the removal of the organic carbon did not work well for soil samples.

The high-temperature treatment was also applied prior to the post-dispersion of MWCNTs in the mixture of kaolin and soil sample. As expected, the ratio of the *T* of the post-dispersed MWCNT to the dispersed MWCNTs using SDBS slightly increased from 85.81 to 92.21% after the exposure to 500 °C (Fig. 6c). However, the ratio of the *T* using CTAB was only 22.83% with the treatment, indicating that the interaction between CTAB and the medium was the main factor restricting the post-dispersion of MWCNTs. Thus, another pre-treatment step is required to further enhance the interaction of the surfactant and MWCNT.

Pre-treatment process for field samples

Based on the above discussion, all the particle size, surface charge, and organic carbon content of the environment medium are important variables influencing the post-dispersion of aggregated MWCNTs in the environmental matrix. It has been proved that the use of high-temperature treatment and surfactant effectively made the bundled MWCNTs dispersed in sludge samples but failed to post-disperse MWCNTs in soil. To overcome the effects of particle size and surface charge of the medium, another step is proposed to allow the surfactants to more effectively disperse MWCNTs from the ashed media. Essentially, the process of the post-dispersion of MWCNT using surfactant is similar to the extraction of some hydrophobic organic contaminants (HOC) from environmental matrix using a surfactant aided washing process. It has been reported that the mechanism of removing HOC from soil is that a hydrocarbon-like interior core of the surfactant micelle is formed in aqueous solution and acts as an organic pseudo-phase where HOC are partitioned (Laha et al. 2009). Compared with aqueous surfactant solution, Chu and Kwan observed that the use of the organic solvent based (acetone, triethylamine, and squalene) surfactant solutions considerably improved the removal efficiency of HOC from the soil (Chu and Kwan 2003). The enhancement likely originated from the formation of solvent-incorporated surfactant micelles, which increased both the capacity and affinity of micelles for contaminants because of the much smaller size of the solvent molecules. Inspired by the extraction of HOC from soil, the organic solvent-surfactant solution was used to post-disperse MWCNTs, instead of aqueous surfactant solution.

Surfactant solutions (0.1 wt% CTAB and 0.1 wt% SDBS) prepared in acetone were used to post-disperse MWCNTs from the environmental media, and Fig. 7 illustrates the performances of acetone-based surfactant solutions on post-dispersing MWCNTs. Comparing Fig. 7a with Fig. 6a, the use of the acetone solvent increased *T* ratio of the post-dispersed MWCNTs to the dispersed MWCNTs in original soil (without high-temperature treatment) from 29.67 to 80.66% and 29.70 to 66.05% using CTAB and SDBS, respectively. For ashed soil samples, the *T* of the post-dispersed MWCNTs (20.23 °C and 20.13 °C for using CTAB and SDBS acetone-based solution) were not significantly different from those of the dispersed MWCNTs (20.26 °C and 19.91 °C), indicating that the high-

temperature treatment with the acetone/CTAB or SDBS system might be a very helpful way to post-disperse MWCNT from the environmental media. For the sludge samples (Fig. 7b), the acetone-based surfactant solution was effective in post-dispersing bundled MWCNTs, minimizing the effect of organic carbon presence and making the values of T of dispersed and post-dispersed MWCNT about the same. The combination of high-temperature and acetone-based surfactants also yielded positive results for the post-dispersion of MWCNTs in the different sized soil samples: T values of the post-dispersed MWCNTs statistically matched the T of dispersed MWCNTs (Fig. 7c). For mixture of kaolin and soil, similar improvement of T of post-dispersed MWCNTs was observed. According to results in Fig. 7c, d, the pre-treatment process involving high-temperature treatment and acetone-based surfactant solution can overcome the constraints on the post-dispersion of MWCNTs caused by surface area and charges of the environmental medium.

Therefore, in this study, the proposed two-step pre-treatment process for MWCNTs contaminated field samples included a high-temperature treatment (500 °C for 2 h), followed by a post-dispersion of undispersed MWCNT using 2 ml of 0.1% acetone-based surfactant solution. Since the performance of CTAB was slightly better than that of SDBS based on the above results, the acetone-based CTAB solution is appropriate to be the primary surfactant solution when surface charge is not a concern. The pre-treatment procedure here suggested was based on the thermal stability of MWCNTs. However, the thermal stability of the nanotubes usually relies on characteristics of CNTs, such as inner/outer diameter, length, and structure defects. Some SWCNTs were observed to be not stable at low temperature (e.g., 600–651 °C) (Doudrick et al. 2012). The temperature of 500 °C used in our study may partially damage particular CNTs. Therefore, the pre-treatment procedure can be adjusted and modified to balancing removal of interfering carbon and preservation of “weak” CNTs.

Validation test

To test the reliability and effectiveness of the proposed pre-treatment process, a validation analysis was conducted with six MWCNTs contaminated soil and sludge samples. Two types of soil were chosen as matrices. Soil type I and sludge samples were collected from the same location as the samples used for constructing calibration curves and microwave tests in this study. Soil type II was collected from Center Hill Facility, Environmental Protection Agency, Cincinnati, Ohio, USA. All samples were exposed to 500 °C for 2 h first and then dispersed by acetone based CTAB solution (0.1 wt%) in a sonicator for 3 h. After drying, the samples were exposed to the microwave field at 133 W–15 s. Each sample was prepared in triplicate and measured three times. To avoid operator bias, all validation samples were prepared by another lab staff who did not work on this study. The T values were recorded for each sample, and the average T was used to compute mass of the MWCNTs from the calibration curves generated with acetone-based CTAB solution assisted MWCNTs in ashed environmental medium (Fig. S3, Supplementary Material). The calibration curve was generated based on type I soil with acetone/CTAB dispersed MWCNTs. Table 2 summarizes the MWCNT mass readings from the calibration curves and the actual amount of MWCNT added into the sample. According to the validation test results, the recovery of each measured MWCNT mass was within the 80–120%,

demonstrating the utility of the two-step pre-treatment process and the microwave method for environmental samples.

Conclusions

The use of the microwave-induced heating method on field samples is very promising and practical, thus addressing an obstacle in the environmental quantification of MWCNTs. The versatility of the microwave method is not limited to specific MWCNTs synthesized by certain commercial companies and the quantification of MWCNTs is not influenced by length or diameter of the nanomaterials. The results demonstrated support in the option of not needing to prepare calibration curves for MWCNTs from different suppliers or different morphologies. Additionally, interference factors for MWCNTs quantification in field samples, such as the particle size, surface charge and organic carbon content of environmental media, and aggregation of MWCNTs, can be overcome by applying a high-temperature treatment process and acetone-based surfactant solution to effectively suspend nanomaterials that have been deposited in the medium. This proposed pre-treatment process is adaptable for different characteristics of environmental matrices. Thus, the pre-treatment process proposed in this study will be useful to a broad range of readers, from environmental engineers to ecotoxicity scientists who have interest in environmental detection of MWCNTs.

Supplementary Material

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Fig. 1. Temperature rises of 0.5 mg dispersed MWCNTs **a** from different suppliers, **b** with different lengths, and **c** with different outer diameters in soil at 133 W–15 s microwave irradiation

Fig. 2. Comparison of temperature rises of environmental medium only, 0.5 mg undispersed MWCNT and 0.5 mg dispersed MWCNTs (by 0.1% CTAB) at 133 W–15 s microwave irradiation

Fig. 3. Effects of post-dispersion on the microwave measurement of 0.5 mg MWCNT in **a** whole grain sand, **b** soil, and **c** sludge at 133 W–15 s microwave irradiation

Fig. 4. Effect of particle sizes of environmental media on the post-dispersion of 0.5 mg MWCNT in **a** different sized sands and **b** different sized soils at 133 W–15 s microwave irradiation

Fig. 5.

The microwave response of 0.5 mg MWCNT in kaolin and mixture of kaolin and soil at 133 W-15 s microwave irradiation

Fig. 6.

Temperature rises of 0.5 mg dispersed and post-dispersed MWCNTs after high-temperature treatment in **a** soil, **b** sludge, and **c** mixture of kaolin and soil at 133 W–15 s microwave irradiation

Fig. 7.

Temperature rises of 0.5 mg acetone-aided dispersed and post-dispersed MWCNTs in **a** soil, **b** sludge, and **c** different sized soils; **d** the mixture of kaolin and soil at 133 W–15 s microwave irradiation

Table 1

Description of the properties of MWCNTs used in different tests

Experiment	Supplier	Length (μm)	Diameter	Aggregation
Supplier of MWCNT	USR	10–30	20–30 μm	Dispersed
	CT			
	SI			
Length of MWCNT	USR	10–30	20–30 μm	Dispersed
		0.5–2		
Diameter of MWCNT	CT	10–30	50–80 nm	Dispersed
			20–30 nm	
			< 8 nm	
Aggregation of MWCNT	USR	10–30	20–30 μm	Dispersed
				Aggregated

Table 2

Validation test results

Medium	Sample	T (°C)		Measured mass (mg)		Recovery (%)	Actual mass (mg)
		Avg.	Std.	Avg.	Std.		
Soil (type I)	A	4.05	0.38	0.09	0.01	90	0.1
	B	9.56	0.33	0.21	0.00	105	0.2
Soil (type II)	C	4.26	0.14	0.09	0.00	90	0.1
	D	16.11	0.55	0.35	0.01	88	0.4
Sludge	E	17.81	1.26	0.36	0.01	90	0.4
	F	30.22	1.55	0.62	0.01	103	0.6