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Short communication

Degradation of multiwall carbon nanotubes by bacteria

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ABSTRACT

Understanding the environmental transformation of multiwall carbon nanotubes (MWCNTs) is important to their life cycle assessment and potential environmental impacts. We report that a bacterial community is capable of degrading ^{14}C-labeled MWCNTs into $^{14}CO_2$ in the presence of an external carbon source via co-metabolism. Multiple intermediate products were detected, and genotypic characterization revealed three possible microbial degraders: *Burkholderia kururiensis*, *Delftia acidovorans*, and *Stenotrophomonas maltophilia*. This result suggests that microbe/MWCNTs interaction may impact the long-term fate of MWCNTs.

1. Introduction

Carbon nanotubes (CNTs) are one type of carbon-based nanomaterial formed by rolling graphene sheet(s) into a cylindrical shape. Multiwall carbon nanotubes (MWCNTs) are a series of coaxially-arranged graphene sheets. Due to their unique physicochemical, optical, and mechanical properties, CNTs can be applied to many fields such as reinforced composites, conductive materials, sensors, drug delivery vessels, and sorbents (Popov, 2004). Research on their ecotoxicity, aggregation and transport has been conducted in recent years to provide information on their impact to and fate in the environment (Chen et al., 2009; Kennedy et al., 2008; Petersen et al., 2011). One critical question is the extent and rate of CNT biodegradation to CO_2, which has not yet been fully investigated due to their high chemical stability and challenges with CNT quantification.

The basic structure of MWCNTs is aromatic rings fused by sp^2-hybridized carbon which are analogous to polycyclic aromatic hydrocarbons (PAHs) and considered to be stable. However, defects such as pentagon–heptagon pairs (Stone–Wales defects), sp^3-hybridized carbon atoms, vacancies in the nanotube lattice, and open ends are always associated with CNTs (Hirsch, 2002; Niyogi et al., 2002; Tasis et al., 2006; Yao et al., 1998). These defects are expected to make CNTs more reactive (Li et al., 2005; Niyogi et al., 2002), and thus may serve as sites that enzymes can attack. Researchers have shown that fullerols can be degraded by two types of white rot fungi (Schreiner et al., 2009), and carbon nanotubes can be degraded by two enzymes, horseradish peroxidase (HRP) (Allen et al., 2008, 2009; Russier et al., 2011; Zhao et al., 2011) and by neutrophil myeloperoxidase (Kagan et al., 2010) in the presence of H_2O_2. However, the extent to which MWCNTs can be degraded by microbes under natural conditions is unknown. In this study, we used ^{14}C-labeling to trace the end product of MWCNTs microbial degradation by measuring the released $^{14}CO_2$, and report a bacterial community that is capable of degrading MWCNTs into CO_2.

2. Materials and methods

2.1. ^{14}C-labeled multiwall carbon nanotubes (MWCNTs) synthesis and characterization

The ^{14}C-labeled MWCNTs were synthesized using a modified chemical vapor deposition technique (Petersen et al., 2008), purified, and treated with a 3:1 (volume fraction) mixture of sulfuric to nitric acid as described in our previous study (Petersen et al., 2010) (see Supplementary Material I for details). The ^{14}C accounts for ca. 0.002% of the total MWCNT carbon. These MWCNTs were dispersed stably in water with a concentration of 9.5 mg L^{-1} by ultrasonication for 2 h and were previously thoroughly characterized (Zhang et al., 2011). The obtained MWCNTs have a surface oxygen content of 8.6% determined by X-ray photoelectron spectroscopy (XPS) (Kratos Analytical Axis Ultra X-ray photoelectron spectrometer). See Supplementary Material I for additional characterization information.

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2.2. MWCNTs degradation experiments

The experimental set-up is briefly summarized as follow (see Supplementary Material II for details). In the treatment flasks, a 5-mL dispersion of unsterilized ^{14}C-labeled MWCNTs were added to 45 mL of a defined culture medium (composition listed in Table S1) containing all common nutrients required for microbial growth and incubated at 39 °C for 7 d. No additional microbe source was added to the medium. The different concentrations of the 5-mL MWCNTs were achieved by diluting the stock dispersion using sterilized de-ionized water. The flask was connected to a test tube containing NaOH solution (10 mL, 0.5 mol L^{-1}) to capture CO_2 if any evolved from the incubation. The system was aerated daily with O_2 (34 KPa) via the gas inlet for 30 min. Control flasks contained the same substances except 1) with sterilized MWCNTs, or 2) without MWCNTs but with the MWCNTs degrading bacteria from treatment flasks. After 7 d, the NaOH solution was mixed with 10 mL of scintillation cocktail (Insta-Gel Plus, PerkinElmer, MA), and its radioactivity was measured by a Beckman LS 5801 liquid scintillation counter (CA, U.S.). The radioactivity readings of the two controls were not significantly different from solutions with de-ionized water or the NaOH solution mixed with Insta-Gel cocktail. The degradation mass or percentage was obtained by subtracting the radioactivity of the treatment samples by the background radioactivity from the control samples. The bacteria concentration after 7-d incubation was determined using light absorbance at 650 nm to be approximately $9.8 \pm 4.7 \times 10^8$ cells mL^{-1} ($n = 3$, uncertainty value represents the standard deviation) for treatment flasks; no significant microbial population was observed in control 1. Microorganisms were identified as described in the Supplementary Material V.

2.3. Intermediate product identification

The detection of possible intermediate products was performed by liquid chromatography–tandem mass spectrometry (LC–MS/MS, Waters Micromass Quattro) and gas chromatography–mass spectrometry (GC–MS, Hewlett Packard 5971). Detailed sample preparation methods and instrument set-up were included in Supplementary Material III. The structures of the detected intermediate product were deduced according to their MS/MS spectra (example shown in Supplementary Material III).

3. Results and discussions

3.1. ^{14}C-labeled MWCNTs microbial degradation

The ^{14}C-labeled MWCNTs were incubated in various cultures under different conditions in an attempt to screen MWCNT-degrading microorganisms (see Supplementary Material II). The incubation was conducted in a setup that allowed the capture of the released end product, $^{14}CO_2$. Among the different systems tested, we observed microbial activity and significant MWCNTs degradation in the system that had unsterilized MWCNTs in a sterilized culture medium. Fig. 1 shows the quantity and percentage of MWCNTs that were released as $^{14}CO_2$ (radioactivity values are provided in Table S2) after 7 d of incubation with different initial MWCNTs concentrations (0.06–1.0 mg L^{-1}). In each case, a significant fraction of MWCNTs, ranging from 2.0% to 6.8%, was transformed into $^{14}CO_2$. Scanning electron microscope (SEM, FEI Inspect F50 FEG) and transmission electron microscope (TEM, FEI Technai 20) were used to characterize any morphological changes of the MWCNTs after incubation (see Supplementary Material VI Fig. S6 and S7). The remaining MWCNTs showed different degrees of oxidation, but most retained a tubular shape.

3.2. Degradation pathway

Although the ultimate end product of the microbial degradation of MWCNTs is CO_2, degradation products other than or as precursors of CO_2 are likely to exist. We extracted the culture media after 7-d incubation using ethyl acetate or dichloromethane and analyzed the extracts by HPLC–MS or GC/MS (Supplementary Material III). Fig. 2 shows selected ion chromatograms of LC–MS for two intermediate products and those of additional four products are shown in Fig. S3, as well as the original LC chromatographs. All figures were obtained by subtracting the chromatograms of the treatment by the chromatograms of two controls: one was incubation without bacteria and the other was without MWCNTs.

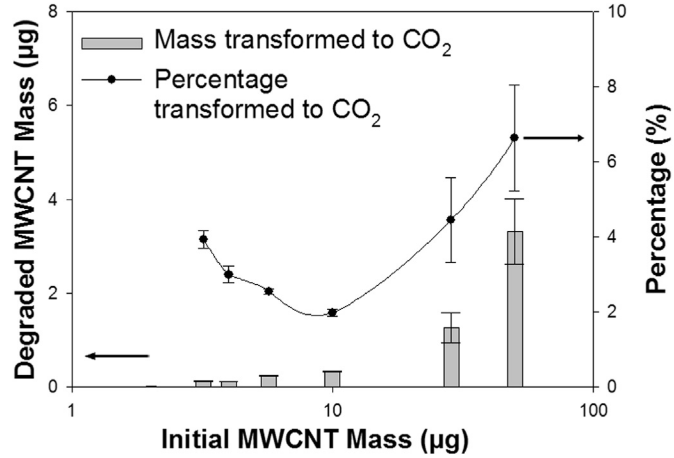


Fig. 1. Biodegradation of ^{14}C-MWCNTs after 7-d incubation at different initial dosages. Left *y*-axis shows the mass of MWCNTs that has been fully degraded (calculated based on the amount of $^{14}CO_2$, values shown in Table S2). Right *y*-axis shows the percentage (by mass) of biodegraded MWCNTs. Error bars of the two highest initial concentration show the propagated standard deviation of uncertainty from the scintillation counter and two replicates. Single measurements were performed at the lower concentrations and thus the error bars only include instrument variability.

Table 1 summarizes the products identified by LC–MS/MS as well as their deduced molecular formulas and structures, including 2-naphthol, 2-methoxy naphthalene, isophthalic acid, and cinnamaldehyde. These intermediate products were confirmed by comparing their LC–MS/MS spectra to those of high purity (>99%, Sigma Aldrich) chemical standards. The LC–MS/MS spectra comparison for isophthalic acid is shown in Fig. 2 and those for other products are given in Fig. S5. Some of the same molecular ions, such as $m/z = 165$, were also detected by GC–MS. These various oxidized organic compounds residing in the degrading mixture are similar to those found during microbial degradation of PAHs under aerobic conditions (Haritash and Kaushik, 2009), and HRP degradation of single-walled carbon nanotubes (Allen et al., 2009). The multiple intermediate products are likely due to the complexity of the degradation process, in that they came either from different steps in pathways or from parallel steps mediated by different enzymes/microbes. The presence of intermediate products indicates that small molecules were first flaked off from MWCNTs and then subjected to further degradation. This is similar to the depolymerization step in the microbial degradation of biopolymers which is also the rate-limiting step (Killham, 1994).

Given the large size of MWCNTs, the first degradation step is most likely to occur extracellularly through enzymatic reaction. Three types of extracellular enzymes were tested: horseradish peroxidase (HRP type I, Sigma–Aldrich), which has been reported to degrade MWCNTs (Allen et al., 2009; Russier et al., 2011; Zhao et al., 2011), laccase (Sigma–Aldrich) and tyrosinase (Sigma–Aldrich), which are from representative PAH-degrading enzyme categories (Haritash and Kaushik, 2009); a detailed experimental method is provided in Supplementary Material IV. However, none of the enzymes resulted in significant production of $^{14}CO_2$, which shows that these enzymes alone cannot degrade the MWCNTs into CO_2. Interestingly, previous studies showed significant removal of MWCNTs by HRP (Russier et al., 2011; Zhao et al., 2011). These different results may be due to the different properties of MWCNTs used, such as the surface functional groups and/or defects. For example, the catalytic pathway of HRP and laccase often involves radicals formed by phenol groups (Baldrian, 2006; Veitch, 2004), and thus the hydroxyl groups on MWCNTs surface are very likely to be sites attacked by these enzymes. On the contrary, the MWCNTs

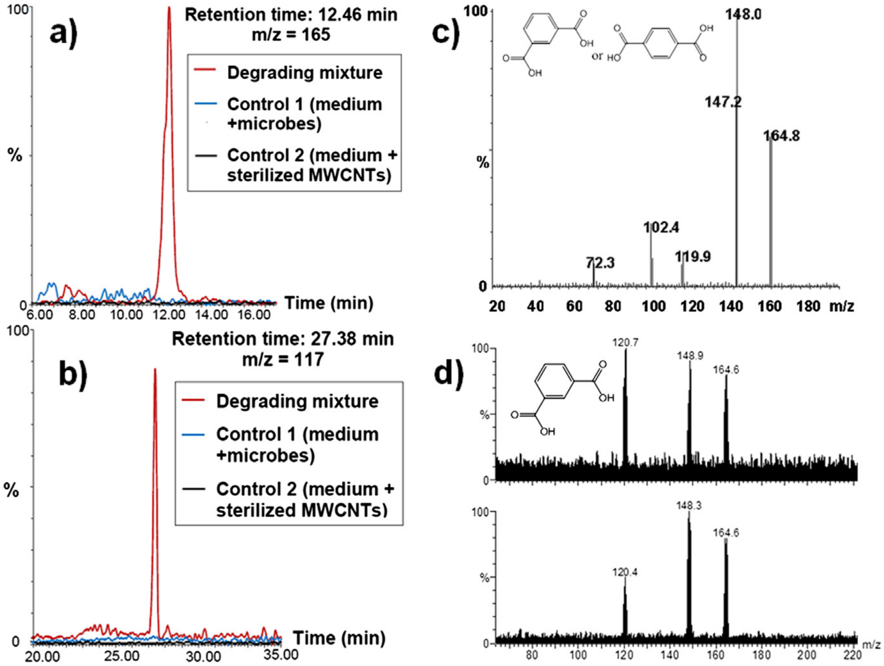
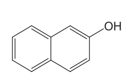
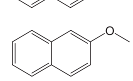
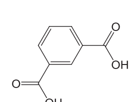
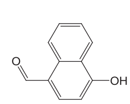
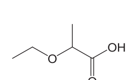
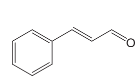


Fig. 2. Selected ion chromatograms of LC–MS and spectra of LC–MS/MS for two intermediate products. **a)** Molecular ion mass of 165, extracted by ethyl acetate; **b)** molecular ion mass of 117, extracted by dichloromethane. The red lines relate to the samples degraded by microbes, while the blue lines and black lines are the controls incubated with culture medium but without MWCNTs or without microbes, respectively. The secondary MS spectra of: **c)** the intermediate products with m/z value in the primary MS as 165; **d)** comparison between intermediate product (up) and high purity chemicals purchased from Sigma–Aldrich (down) with $m/z = 165$; The structures of the intermediate product are shown in the upper-left corner. Structures of the other products are listed in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with large numbers of carboxyl groups may not be vulnerable to these enzymes. This is an interesting area for further investigation and would have strong potential implications in environmental risk assessment (Fairbrother et al., 2010; Smith et al., 2009; Zhao et al., 2011).

Table 1
Summary of intermediate products identified by LC–MS/MS.

Extraction solvent	m/z	Formula	Structures
Ethyl acetate	143	$C_{10}H_8O$	
	157	$C_{11}H_{10}O$	
	165	$C_8H_6O_4$	
	171	$C_{11}H_8O_2$	
Dichloromethane	117	$C_5H_{10}O_3$	
	131	C_9H_8O	

3.3. Microorganism identification

Since the medium that resulted in MWCNTs biodegradation described above had other carbon sources in it (*e.g.*, glucose, veratryl alcohol), we repeated the biodegradation study in which MWCNTs were the sole carbon source to selectively enrich the microorganisms that specifically degrade MWCNTs. However, after incubation for two months, no $^{14}CO_2$ release was detected, indicating that the need for additional carbon source for the MWCNTs biodegradation to proceed via co-metabolism.

Because selective enrichment of MWCNTs degrader(s) in the sole carbon source medium was not possible, we used polymerase chain reaction (PCR)-based technique to survey the microbial pool in the culture. The genomic DNA of the microorganisms was extracted, purified, and then subjected to PCR by targeting the 16S-rDNA with a universal bacterial primer pair (Bouchez et al., 1996). The fungi universal primer pair nu-SSU-0817F and nu-SSU-1196R (Haritash and Kaushik, 2009) was also used but no product was detected, which indicated that the potential degraders were all bacteria. The PCR amplicons were then separated using cloning, sequenced, and compared with sequences in the GenBank database of the National Center for Biotechnology Information (NCBI) by BLAST search. Three bacteria species were identified: *Burkholderia kururiensis, Delftia acidovorans*, and *Stenotrophomonas maltophilia*. These bacteria are commonly found in the natural environment (*e.g.*, ground water, surface water, soil rhizosphere, *etc.*), and previous studies have shown their capability to degrade various persistent organic contaminants. *D. acidovorans* has been shown to degrade sulfophenylcarboxylates and herbicides such as linuron, phenoxypropionate, and phenoxyacetate (Bastida et al., 2010; Muller et al., 2001; Murphy, 2010), either individually or in community. *S. maltophilia* is known to metabolize phenols, benzoic acids and complex compounds like PAHs and oil refinery residuals

(Boonchan et al., 2000; de Morais and Tauk-Tornisielo, 2009; Gren et al., 2010). In addition, the combinations of strains from these species were able to degrade more compounds than when they are present individually. For example, *S. maltophilia* in combination with other species in *Burkholderia* genus were found to degrade chemicals such as PAHs, 2,4-DNT, and dodecyldimethylamine (Kroon and van Ginkel, 2001; Snellinx et al., 2003).

In order to confirm their ability to degrade MWCNTs, we made an attempt to isolate the individual bacteria and incubated them with MWCNTs. To this end, the mixed culture was diluted (10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6}) and spread-plated on a TGY (tryptone/glucose/yeast) medium (1% tryptone, 0.5% yeast extract, 0.1% glucose, and 2.0% agar). Fifteen well isolated colonies from the plates were selected and identified using the PCR-based technique described above. The results showed that they belonged to two of the three previously identified isolates, *Burkholderia kururiensis* and *Stenotrophomonas maltophilia*. The pure cultures of *B. kururiensis* and *S. maltophilia* (100 μl, cell concentration approximately 10^8 cell mL^{-1}) were then inoculated either individually or together into the medium containing MWCNTs (51.5 μg MWCNTs in 50 mL medium) and glucose (the same as MWCNTs degradation study, Table S1) to test their ability to degrade MWCNTs. No production of $^{14}CO_2$ was detected with *B. kururiensis*. Inoculation of *S. maltophilia*, however, resulted in some production of $^{14}CO_2$, *i.e.*, 0.57% ± 0.20% ($n = 3$; uncertainty indicates standard deviation) at an initial MWCNT concentration of 0.6 mg L^{-1}. This was ten times lower than that of the original bacteria community in the mixed culture, and could not be significantly enhanced by varying incubating conditions, including addition of the isolated *B. kururiensis*. This suggests that a community of microorganisms containing more than the two isolated strains is required to effectively degrade MWCNTs; and the missing species could not probably be isolated under the culture conditions we have used.

4. Conclusion

In this study, we demonstrated the ability of some bacteria to degrade acid-treated MWCNTs under environmentally relevant conditions, which would decrease their environmental persistence. This degradation appears to require external carbon source involving co-metabolism and the cooperation of several microorganisms. Additional research is needed to further explore the degradation potential of the MWCNTs in the natural environment, and to elucidate possible dependence of MWCNTs biodegradation on their surface chemistry.

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Appendix A. Supplementary material

Material associated with this article can be found, in the online version, at http://www.sciencedirect.com/ or http://dx.doi.org/10.1016/j.envpol.2013.05.058.

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