Journal of Nanotoxicology and Nanomedicine
Volume 1 • Issue 1 • January-June 2016

Transformation of Nanomaterials in Environment:

Surface Activation of SWCNTs during Disinfection of Water with Chlorine

Corneliu Bogatu, Institute of Industrial Ecology, Timisoara, Romania

Danuta Leszczynska, Department of Civil and Environmental Engineering, Interdisciplinary Center of Nanotoxicity, Jackson State University, Jackson, MS, USA

ABSTRACT

Carbon nanotubes are new class of active environmental pollutants. The authors report interactions between chlorine used as disinfectant/oxidant during typical water treatment and single-wall carbon nanotubes (SWCNTs). Alterations in SWCNT morphology were determined by TEM, while FT-IR spectra helped to determine chemical changes before, during and after chlorination. The analysis of original FT-IR spectra, and their second order derivatives revealed the formation of new, oxygen-bearing groups, namely quinones, ethers, and additional carboxyl groups on the surface of SWCNTs. The two-step reaction mechanism: (1) initial adsorption of mixture of hypochlorous acid and hypochlorite anions on the surface of carbon nanotubes, and (2) oxidation of surface and formation of new functional groups, was suggested. It was found that standard disinfection has activated previously inert carbon nanotubes and turn them into active species able to participate in further cross-contamination reactions. Interestingly, the oxygen-bearing groups were formed as a product of reaction with chlorine.

KEYWORDS

Chlorine, Disinfection, Hypochlorite Anions, Hypochlorous Acid, Oxidation, Oxygen-Bearing Groups, SWCNTs

1. INTRODUCTION

Specific physicochemical properties of carbon nanotubes with or without coating and functionalization make them pertinent in many fields, such as design of nano-composites (Nastase et all., 2013), nano-batteries (Lowy and Patrut, 2013), new catalysts development (Qui, et al. 2011, Wang and Zhang, 2011, Abate, et al. 2010, Frank, et al., 2009), hydrogen storage (Yürüm, et al. 2009), sensors (Li, et al. 2007, Zakaria, et al. 2015), but also imaging agents in medicine (A. Servant, et al. 2016), or sorbents in remediation engineering (Zare, et al. 2015). Current mass production of carbon nanotubes makes them obvious candidates to be a new class environmental pollution found in the air, water and soil.

One of the analytical tools adapted for the determination of nanocarbon's properties, could be FT-IR spectroscopy. Klein et al. (2008) reported that FT-IR spectra might assist in the analysis of surfaces of bulk particles. For example, after activated carbon was treated with mixture of hydrogen peroxide, ammonium persulfate and nitric acid, the C-O stretching vibrations were identified at 1100-1200 cm^{-1} due to carboxylic and phenolic groups, along with peaks around 1600 cm^{-1}, which were identified as

DOI: 10.4018/JNN.2016010104

carbonyl groups (Vasu, 2008). Mawhinney and Yates (2001) reported that after ozonation of activated carbon in a gas phase, the carboxyl groups were determined on carbon surface due to the formation of ozonide followed by its decomposition. Also, Mawhinney et al. (2000) reported the formation of esters and quinones on the surface of single-walled nanotubes after oxidation by ozone in gas phase.

The use of FT IR spectroscopy was successful in monitoring of oxidation of single-wall carbon nanotubes with three different oxidants, namely nitric acid, mixture of sulfuric acid with nitric acid, and potassium permanganate. Spectra recorded after treatment with potassium permanganate have shown two new bands with maxima at 1740 and 1640 cm^{-1}, which were assigned to C=O group from COOH and quinone, respectively (Zhang, et al. 2003). Kim, et al. (2005) reported that after treatment of SWCNTs with 30% hydrogen peroxide, the FT-IR spectra revealed new bands: at 1035, 1100 cm^{-} due to C-O stretching in ethers, esters, alcohols and phenols; at 1500-1660 cm^{-1} assigned to conjugation of C=O with C=C bonds; and at 1710-1734 cm^{-1} corresponded with C=O from ketone or carboxylic acid. The oxidation of multi-walled carbon nanotubes with nitric acid led to formation of carboxylated carbonaceous fragments Stéfani, et al. 2011). It is important to note that in all cited studies, the oxidation was accomplished with only oxygen-bearing reagents, and formed groups were oxygen-bearing as well.

Objective of this study was to understand the role of chlorine in altering SWCNT surfaces. The choice of chlorine was dictated by its routine use in water and wastewater treatment plants as the most common disinfectant and/or oxidant. The assumption was that chlorine might modify surfaces of SWCNT to the level thet altered surface would support, or induct new reactions or interactions between carbon nanotubes and other organic molecules found in water. Tests were conducted on the model solutions containing known concentrations of SWCNTs (functionalized with carboxyl groups) mixed with different concentrations of sodium hypochlorite solutions, source of chlorine.

2. MATERIAL AND METHODS

The SWCNTs functionalized with COOH group (2.7%) were purchased from Cheap Tubes, with purity more than 90%, OD 1-2 nm, length 5-30 μm, and they were used as received. Stock sample was prepared by adding 5.0 mg SWCNTs to 50.0 mL deionized water with conductivity less than 1 μScm^{-1}. Each mixture was sonicated for 5 minutes.

For chlorination experiments, we used commercial sodium hypochlorite (6%) (Fisher Scientific), and determination of chlorine was done by standard iodometric method (Standard Methods, 22nd Ed., 2012). Tests were conducted at pH=7.2±0.15 and temperature 20.0±0.5^{o}C. The stability of pH was confirmed minimum five times during span of 24 hours after experiments were completed. For testing, we prepared several mixtures of nanocarbons and chlorine, with ratios of mg *SWCNTs*: mg *chlorine* (per 1.0 L) as follows: 2.5:5 (R1), 5:5 (R2), 5:20 (R3), 20:5 (R4) and 20:20.

Homogeneity of solutions were maintained by continuous slow stirring for 10 hours, then the solutions containing initial concentration of 5.0 mg/L chlorine were kept at room temperature for 24 h, and those with 20 mg/L of Cl_2 for 72 h, until residual chlorine have had minimum values of 0.15-0.25 mg/L. Finally, carbon nanoparticles were separated from solutions by centrifugation.

FT-IR spectra were recorded using spectrometer Nicolet Nexus 670 FT-IR on samples prepared in potassium bromide pellets. Absorption spectra were collected in single beam mode with 32 scans at 4 cm^{-1} resolution. In addition, the Spekwin23 for optical spectroscopy, version 1.71.5 was used for the supplementary analysis (Menges F. "Spekwin32−free optical spectroscopy software", Version 1.71.5). Transmission electron microscopy (TEM) images of SWCNT were recorded with JEOL, JEM–1011 instrument.