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Degradation of oxidized multi-walled carbon nanotubes in water *via* photo-Fenton method and its degradation mechanism

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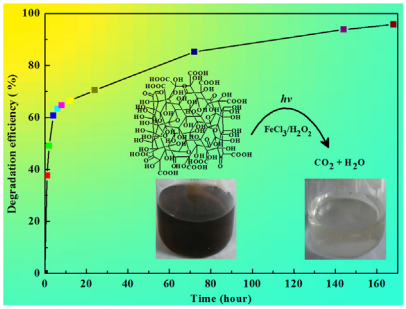
HIGHLIGHTS

- An efficient method for degrading oxidized multi-walled carbon nanotube in water.
- 95.8% of total organic carbon of degradation samples being eliminated.
- Photo-Fenton degradation mechanism of oxidized multi-walled carbon nanotube.

GRAPHICAL ABSTRACT



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ABSTRACT

With popular application of multi-walled carbon nanotubes (MWCNTs), they have been discharged into water. MWCNTs and their derivatives may harm organs, cells and organisms. Therefore, development of an efficient method for removing MWCNTs and their derivatives from water is important. Under UV–light irradiation, MWCNTs can be oxidized by oxygen in air to give oxidized MWCNTs (O-MWCNTs), therefore, degradation of O-MWCNTs is a vital step for removal of MWCNTs and their derivatives from water. In this paper, O-MWCNTs were degraded *via* photo-Fenton method to give CO_2 and water after 168 h. Degradation process was detected by total organic carbon and ultraviolet–visible absorption spectra. Degradation intermediates were supposed based on nuclear magnetic resonance, liquid chromatography-tandem mass, Raman, fourier transform infrared spectra and elemental analysis data. In order to develop an efficient degradation method for removing O-MWCNTs from water, photodegradation mechanism of O-MWCNTs was suggested.

1. Introduction

Multi-walled carbon nanotubes (MWCNTs) have been widely applied in functional materials, such as photocatalytic materials [1–3], adsorbent [4,5], drug carriers [6] and electronic materials [7]. Hundred tons of carbon nanotubes (CNTs) were produced in 2012 [8]. In process of production and application, lots of MWCNTs and their derivatives have been discharged into water. MWCNTs and their derivatives would harm organisms [9–12]. Yu et al. [9] and Kim et al. [10] reported that MWCNTs might kill Daphnia magna. Chen et al. [11] reported that MWCNTs would harm pulmonary of rats. Visalli et al. [12] reported that MWCNTs and acid-treated MWCNTs would damage A549 human lung epithelial cells. Therefore, it is urgent to remove MWCNTs and their derivatives from water.

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Allen et al. [13,14], Russier et al. [15], Zhao et al. [16] and Bhattacharya et al. [17] reported that single- and multi-walled carbon nanotubes were degraded *via* enzymatic method. However, these enzymes couldn't be popularly applied in degradation of MWCNTs and their derivatives in water due to their expensive prices. Moreover, Zhang et al. [18] reported that MWCNTs would not be completely degraded with enzymes alone.

Grujicic et al. [19] studied oxide process of MWCNTs. Under UV-light irradiation, MWCNTs can be oxidized by oxygen in air to give oxidized MWCNTs (O-MWCNTs) [19], therefore, MWCNTs in water would be oxidized by oxygen in air under sunlight to give O-MWCNTs. Study of degradation of O-MWCNTs would be important for removal of MWCNTs and their derivatives from water.

Photodegradation is an efficient technique for degrading organic pollutants [20]. Renewable solar light has been utilized in photodegradation processes [21–23]. Therefore, photodegradation is a promising and environment-friendly technology. It has popularly been applied in the removal of organic pollutants in wastewater [24–27]. Hydroxyl radical (·OH) with strong oxidation potential (2.8 eV) can be efficiently generated *via* Fenton reaction [28]. Organic pollutants react with ·OH in wastewater to produce CO_2 and H_2O [28].

The rate of Fenton reaction can be enhanced *via* UV irradiation [29], because UV irradiation can improve concentration of ·OH radicals by two following reactions (Eqs. (1) and (2)) [30].

$$Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + {\cdot}OH(\lambda < 580\ nm) \quad (1)$$

$$H_2O_2 + h\upsilon \rightarrow 2{\cdot}OH(\lambda < 310\ nm) \quad (2)$$

Therefore, photo-Fenton method is recognized as an effective method for degrading organic pollutants [31,32]. However, mechanism of O-MWCNTs degraded by photo-Fenton method hasn't been reported.

In this paper, O-MWCNTs were effectively degraded *via* photo-Fenton method. $FeCl_3$ (1 mL, 3.7 mM) and H_2O_2 (4 mL, 35 mM) were added into a suspension containing O-MWCNTs. After UV lights (Wavelength 185 nm) irradiated suspension containing O-MWCNTs for 168 h, 95.8% of TOC of O-MWCNTs was eliminated. Degradation process and structures of degradation intermediates were studied by total organic carbon (TOC), ultraviolet–visible (UV–vis) and fourier transform infrared (FT-IR) spectra, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) elemental analysis (EA), potentiometric titration. Degradation mechanism of O-MWCNTs in water was proposed based on these experimental data.

2. Experimental

2.1. Materials and equipments

MWCNTs (96 wt%), hydrogen peroxide (30 wt%, AR grade), ferric chloride (99 wt%, AR grade), hydrochloric acid (37 wt%, AR grade), nitric acid (68 wt%, AR grade) and sulphuric acid (98 wt%, AR grade) were purchased from Sigma-Aldrich. Digital light incubator with six UV lights (λ = 185 nm, E = 647.2 kJ · mol^{-1}, 8 W, F8T5, Hitachi Co. Ltd., Tokyo, Japan) was purchased from Jintan Kejie Equipment Company, China. UV–vis absorption spectra of the O-MWCNTs and degradation samples were recorded using a Lambda 25 Perkin-Elmer spectrophotometer. The spectrophotometer worked at a wavelength range from 190 to 800 nm. The TOC was measured with a Lique TOC-analyzer (ELEMENTAR, Germany). A 794 Basic Titrino (Metrohm, Switzerland) combined with a Metrohm exchange unit (Metrohm, Switzerland) were used for titrations. An aqueous solution of NaOH (0.1 mol/L) was used to titrate samples. Surface morphological images of the degradation samples were taken by a HITACHI SU1510 scanning electronic microscopy (SEM, Hitachi Co. Ltd., Tokyo, Japan). The microstructure images of samples (10 mg) was taken by a transmission electron microscopy (TEM, JEOL 2100F, 200 kV). Raman spectra of samples (30 mg) were recorded on a Renishaw inVia plus Raman microscope with an excitation wavelength of 632.8 nm. At 80 °C, samples were dried for 12 h. The dried solid was employed as a sample for XRD, FT-IR and EA. Powder X-ray diffraction (XRD-6100, Shimadzu, Japan) was performed at room temperature using Ni-filtered Cu Kα radiation (λ = 1.541 Å). The step speed was 5 deg/min. The scan range was 5–50°. FT-IR spectra were recorded on a Thermo Fisher Nicolet IS 5 spectrometer (USA) in KBr pellets. Elemental analysis (EA) was carried out on a Vario EL III element analyzer (Germany). The degraded sample was analyzed by LC-MS/MS (TSQ QUANTUM ACCESS MAX, Thermo Scientific, USA). A solution (10 μL) containing degraded sample was injected to a column (ZORBAX SB-C18, Agilent, USA). A mixture of methanol and water (7: 3, v/v) was used as mobile phase. Flow rate was 0.3 mL/min. The negative mode was used in the ESI-MS/MS analysis. Solid-state cross-polarization magic angle spinning (CP/MAS) ^{1}H and ^{13}C NMR spectra of samples (100 mg) were recorded on Bruker AM 400 (Germany, 400 MHz). δ Values in these ^{13}C NMR spectra were given in ppm and adamantane (δ = 38.56 ppm) was used as an internal standard compound. ^{1}H NMR spectra were recorded on Bruker AM 400 (Germany), and δ values were given in ppm (relative to TMS). DMSO-d_6 was used as solvent.

2.2. Oxidation of MWCNTs

O-MWCNTs were synthesized by an oxidation reaction of MWCNTs with HNO_3 and H_2SO_4 [33]. MWCNTs (96 wt%, 0.1 g) was added into a mixture of HNO_3 (68 wt%, 15 mL, 0.45 mol) and H_2SO_4 (98 wt%, 45 mL, 1.10 mol) at 0–10 °C. After the reaction mixture was stirred for 15 min, it was heated to 60 °C and stirred continuously for 24 h. Water (100 mL) was added into above reaction mixture. The reaction mixture was neutralized by $NaHCO_3$ and filtered to give crude product. The crude product was dialyzed to give O-MWCNTs suspension. Water in the O-MWCNTs suspension (100 mL) was evaporated at 65 °C to give O-MWCNTs, a dark brown solid (80 mg).

2.3. Degradation of O-MWCNTs by UV, Fenton and photo-Fenton

O-MWCNTs (80 mg) in water (200 mL) were ultrasonicated with power 100 W for 30 min to give a suspension containing O-MWCNTs. HCl solution (5 wt%) was added into the suspension to adjust pH to 3. The sample was irradiated with UV light (λ = 185 nm, E = 647.2 kJ · mol^{-1}) at 20 °C for 0, 1, 2, 4, 6, 8, 12, 24, 72, 144 and 168 h.

Similarly, a solution of $FeCl_3$ (1 mL, 3.7 mM) was added into above suspension before H_2O_2 (4 mL, 35 mM) was added. The sample was degraded without irradiation under UV light at 20 °C for 0, 1, 2, 4, 6, 8, 12, 24, 72, 144 and 168 h.

After H_2O_2 (4 mL, 35 mM) was added into above suspension, the suspension was irradiated with UV light (λ = 185 nm, E = 647.2 kJ · mol^{-1}) at 20 °C for 0, 1, 2, 4, 6, 8, 12, 24, 72, 144 and 168 h. The suspension (5 mL) of O-MWCNTs or degraded sample was used for potentiometric titration.

The suspension (1 mL) of O-MWCNTs or degraded sample was added into water (50 mL). Diluted suspension was employed as a sample for determining UV–vis absorption spectra and TOC.