Chemical Engineering Journal 334 (2018) 587–597

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Experimental and theoretical study on degradation of oxidized C_{60} in water *via* photo-Fenton method

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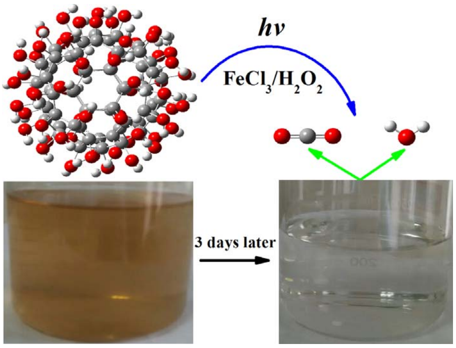
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Oxidized C_{60}
Degradation mechanism
Photo-Fenton
Degradation intermediate

ABSTRACT

With popular application of fullerene (C_{60}) and its derivative in functional materials, they have been discharged into water. Therefore, it is urgent to develop an effective and environmentally friendly method for removing C_{60} and its derivative from water. However, an efficient method of degradation of C_{60} and its derivative in water hasn't been reported. C_{60} in water can be oxidized by light to give oxidized C_{60} ($O{-}C_{60}$), therefore, degradation of $O{-}C_{60}$ plays a key role in removal of C_{60} and its derivative in water. In this paper, $O{-}C_{60}$ was effectively degraded *via* photo-Fenton method to give carbon dioxide and H_2O. The degradation process was monitored by ultraviolet–visible absorption spectroscopy, X-ray diffraction and scanning electron microscopy. Degradation intermediates were determined by Fourier transform infrared spectroscopy, liquid chromatography-tandem mass spectrometry, and elemental analysis. Density functional theory calculations were used to study the mechanism of hydroxyl radical reaction. Based on experimental data and Gaussian calculations, degradation mechanism of $O{-}C_{60}$ in water was proposed.

1. Introduction

Fullerene (C_{60}) and its derivative have been released into water due to their wide application in cosmetics [1], biomedicine [2–5], photocatalysts [6], optical and electronic devices [7]. Farré et al. [8], Wang et al. [9] and Xiao et al. [10] reported that concentration of C_{60} in wastewater and seawater was 1.5, 20–200 and 300 µg/L, respectively. Investigations show that C_{60} and its derivative would harm organisms [11–15]. Therefore, C_{60} and its derivative have to be removed from water.

Zhang et al. [16] reported that Al^{3+} was used as a flocculant to remove C_{60}. Wang et al. [17] reported removal of C_{60} from wastewater

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http://dx.doi.org/10.1016/j.cej.2017.10.062
Received 27 July 2017; Received in revised form 7 October 2017; Accepted 13 October 2017

by alum-enhanced primary treatment. Floris et al. [18] reported removal of C_{60} from water or wastewater by membrane filtration. Schreiner et al. [19] employed two species of white rot basidiomycete fungi to degrade C_{60} fullerols (C_{60} $(OH)_{19–27}$). After 32 weeks, C_{60} fullerols were partly degraded to give CO_2. However, these methods either result in secondary environmental pollution during the treatment processes or present low removal efficiency.

In recent years, advanced oxidation processes (AOPs) have popularly been applied in the removal of organic pollutants in wastewater due to high removal efficiency [20]. Photo-Fenton oxidation process is one of outstanding AOPs approaches. Photo-Fenton method has widely been applied in degradation of organic pollutants [21,22]. Under UV light irradiation, Fe^{3+} reacted with H_2O_2 to give a lot of hydroxyl radicals (·OH) with strong oxidation potential (2.8 eV) (Eqs. (1), (2) and (3)) [23,24].

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

$$Fe^{2+} + H_2O_2 \rightarrow OH^- + \cdot OH + Fe^{3+} \quad (2)$$

$$H_2O_2 + h\nu \rightarrow 2\ \cdot OH\ (\lambda < 310\ nm) \quad (3)$$

Under light irradiation, C_{60} in water can be oxidized to give oxidized C_{60} ($O{-}C_{60}$) [25,26]. Therefore, C_{60} and its derivatives in water can be removed by a method of degradation of $O{-}C_{60}$. H_2O was irradiated under UV light ($\lambda = 185$ nm) to give ·OH radicals by following reaction [27]:

$$H_2O + h\nu \rightarrow \cdot OH + \cdot H\ (\lambda = 185\ nm) \quad (4)$$

Therefore, if suspensions of $O{-}C_{60}$ were irradiated by UV light ($\lambda = 185$ nm) in a photo-Fenton process, a dosage of added hydrogen peroxide should be less than that in the irradiation process with UV light ($\lambda > 300$ nm). Therefore, the photo-Fenton method would be an economical and convenient method for degradation of $O{-}C_{60}$ in wastewater.

In this paper, the photo-Fenton method was used to degrade $O{-}C_{60}$ in water. $FeCl_3$ (3.7 mmol/L, 1 mL) and H_2O_2 (35 mM, 4 mL) were added into a suspension containing $O{-}C_{60}$ before UV lights ($\lambda = 185$ nm, $E = 647.2$ kJ·mol^{-1}) irradiated suspension for 72 h. Intermediates in the degradation process were characterized by ultraviolet–visible (UV–vis), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectra, scanning electron microscopy (SEM), liquid chromatography-tandem mass spectrometry (LC-MS/MS) and elemental analysis (EA). Experimental results show that $O{-}C_{60}$ was effectively degraded *via* the photo-Fenton method to give CO_2 and water. To study degradation mechanism, reactions of $O{-}C_{60}$ or the intermediates with hydroxyl radicals in water were calculated by density functional theory (DFT) method [28] using Gaussian09 software at the B3LYP/6-31G level [29]. Degradation mechanism of $O{-}C_{60}$ was suggested based on theory calculations and experimental data.

2. Experimental

2.1. Materials and equipments

C_{60} (99 wt%), potassium permanganate (99 wt%, AR grade), 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. $O{-}C_{60}$ was synthesized in our laboratory. The ultrasonic cleaner (KQ2200E) was purchased from Kunshan Ultrasonic Equipment Company, China. A digital light incubator (KW-1000BT) with six UV lights ($\lambda = 185$ nm, $E = 647.2$ kJ·mol^{-1}, 8 W, F8T5, Hitachi Co. Ltd., Tokyo, Japan) was customized from Jintan Kejie Equipment Company, China. UV–vis spectra of the solution containing degradation samples were recorded using a UV3600 Perkin-Elmer spectrophotometer. The spectrophotometer worked at a wavelength range from 220 to 700 nm. Samples were dried at 80 °C for 12 h. Dried solid was characterized by SEM, X-ray diffraction, FT-IR and elemental analysis (EA). Surface morphological images were taken by a HITACHI SU1510 scanning electronic microscopy (SEM, Hitachi Co. Ltd., Tokyo, Japan). The size distribution (SD) and average diameters of $O{-}C_{60}$ particles or degraded samples were measured by laser light scattering (Zetasizer Nano zs90, Malvern Instruments, Malvern, UK). Powder X-ray diffraction (XRD-6100, Shimadzu, Japan) were recorded by a XRD-6100 diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 1.541$ Å) and scintillator detector (40 kV, 30 mA) at room temperature. 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 was carried out on a Vario EL III element analyzer (Germany). Degradation intermediates were determined by LC-MS/MS (TSQ QUANTUM ACCESS MAX, Thermo Scientific, USA). A column (ZORBAX SB-C18, Agilent, USA) was eluted with isocratic solvent for 30 min before it was used. The column temperature was kept at 25 °C during the runs. Mobile phase was a mixture of acetonitrile and water (7:3, v/v). Flow rate was 0.3 mL/min. The negative and positive ion mode was used in the ESI-MS/MS analysis.

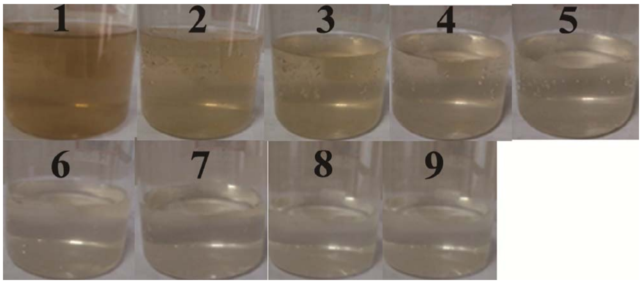

Fig. 1. Degradation process of $O{-}C_{60}$ samples.

2.2. Oxidation of C_{60}

C_{60} was oxidized by a modified method similar to that in a literature [30]. C_{60} (99 wt%, 0.5 g) was added into a solution of HNO_3 (68 wt%, 30 mL, 0.45 mol) and H_2SO_4 (98 wt%, 60 mL, 1.10 mol) at 0–5 °C. The reactive mixture was stirred for 10 min. Then, $KMnO_4$ (6 g, 38 mmol) was slowly added into the mixture within 3 h at 0–10 °C. The reaction mixture was heated to 50 °C and stirred for 15 h. Water (100 mL) and H_2O_2 (30 wt%, 5 mL, 44 mmol) were added into above reaction mixture. The reaction mixture was neutralized by $NaHCO_3$ and filtered to give crude product. The crude product was added into methanol (100 mL) to give a suspension. The suspension was filtered to remove insoluble solid. The methanol was evaporated to give $O{-}C_{60}$ (0.49 g). $O{-}C_{60}$ was characterized by FT-IR, UV–vis and elemental analysis (EA). FT-IR spectrum of the synthesized $O{-}C_{60}$ is in accord with that in literature [25]. FT-IR (KBr): $\upsilon = 3428$ (−OH), 1734 (C=O), 1635 (C=O), 1446 (O−H), 1401 (O−H), 1165 (C−O−C), 1119 (C−O−C), 1080 (C−O−C) cm^{-1}. UV–vis: $\lambda_{max} = 298$ nm. EA (%): N, 0; C, 64.03; H, 0.22; O, 35.75. The sum of C wt%, H wt% and O wt% are 100%.

2.3. Degradation of $O{-}C_{60}$ in water via photo-Fenton

$O{-}C_{60}$ (80 mg) in water (200 mL) was ultrasonicated with an ultrasonic cleaner (100 W) for 10 min to give a suspension. The pH value of suspension was adjusted to 3 *via* HCl (5 wt%). A solution of $FeCl_3$ (3.7 mmol/L, 1 mL) was added into the suspension containing $O{-}C_{60}$, before H_2O_2 (30 wt%, 4 mL, 35 mM) was added. At last, the sample was irradiated under ultraviolet light ($\lambda = 185$ nm, $E = 647.2$ kJ mol^{-1}) for 2, 4, 6, 8, 12, 24, 48 and 72 h at 20 °C. The distance between an ultraviolet lamp and sample was 5 cm. The suspension (1 mL) of $O{-}C_{60}$ or degraded sample was added into water (50 mL). The diluted samples were determined by UV–vis absorption spectra. The solution (5 mL) of