



Degradation of octafluorodibenzo-*p*-dioxin by UV/Fe(II)/potassium monopersulfate system: Kinetics, influence of coexisting chemicals, degradation products and pathways

Xiaolan Zeng^{a,b}, Jing Chen^a, Ruijuan Qu^{a,*}, Mingbao Feng^a, Zunyao Wang^{a,*}

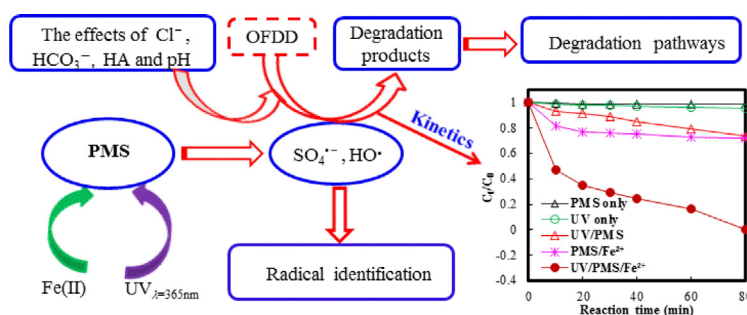
^a State Key Laboratory of Pollution Control and Resources Reuse, School of Environment, Nanjing University, Nanjing, Jiangsu 210023, PR China

^b College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang, Henan 464000, PR China

HIGHLIGHTS

- Photodegradation of OFDD was investigated using the combined UV/Fe(II)/PMS process.
- The effects of co-existing matrix components on OFDD photodegradation were evaluated.
- The photodegradation pathway of OFDD was proposed and verified theoretically.
- The combined UV/Fe(II)/PMS process is effective for OFDD photodegradation.
- Three possible routes exist for OFDD photodegradation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 October 2016

Received in revised form 26 February 2017

Accepted 27 February 2017

Available online 3 March 2017

Keywords:

Octafluorodibenzo-*p*-dioxin (OFDD)

UV

Fe(II)

PMS

Kinetics

Degradation pathways

ABSTRACT

The photodegradation of octafluorodibenzo-*p*-dioxin (OFDD) in a water/acetonitrile (*v/v* = 4:1) mixture was here investigated for the first time in the presence of Fe(II) and potassium monopersulfate (PMS) under UV ($\lambda = 365$ nm) irradiation. The degradation efficiency was found to depend on the presence of UV irradiation, and on the initial concentrations of PMS and Fe(II). OFDD with an initial dosage of 1 mg L^{-1} was successfully removed by UV/Fe(II)/PMS with OFDD:PMS:Fe(II) = 1:30:5 M ratio within 10 min irradiation. The effects of humic acid, bicarbonate, chloride and solution pH were also evaluated. The degradation process of OFDD by UV/Fe(II)/PMS can be initiated by an oxidative attack of hydroxy radical on carbon atoms in the aromatic ring, the electron transfer reaction of sulfate radical with OFDD and a direct C–O bond homolysis of OFDD. The intermediates and products of OFDD photodegradation were analyzed by using LC/MS technique and the associated photochemical pathway was proposed. The combined process with Fe(II), PMS and UV could be a useful technology for the treatment of wastewater containing OFDD.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are highly toxic, thermally stable, refractory and bioaccumulative compounds that undergo difficult degradation in the environment, and therefore they were listed as persistent organic pollutants (POPs) [1,2]. The

* Corresponding authors.

E-mail addresses: quruijuan0404@126.com (R. Qu), wangzy@nju.edu.cn (Z. Wang).

fully fluorinated organic compounds such as perfluorooctanesulfonates (PFOSs) and perfluorooctanoates (PFOAs) have also remarkable stability, bioaccumulation potential and persistence in the environment, and they were widely found in environment media, animal tissues and human serum [3–5]. Therefore, these compounds are also classified as POPs [6]. Polyfluorinated dibenzo-*p*-dioxins (PFDDs) are dioxin-like compounds because of their structural similarity to PCDDs. Since PFDDs, especially octafluorodibenzo-*p*-dioxin (OFDD), contain fluorine atoms with high electronegativity, they may be ascribed to the class of fluorinated organic compounds. Therefore, PFDDs share properties with both PCDDs and fluorinated organic compounds such as toxicity and high stability [7–9]. A good deal of information concerning the fate of PCDDs and PFOSs or PFOAs in the environment such as photodegradation and biodegradation is available [10–14]. Up to now, however, very few researchers have reported on PFDDs photochemistry. The tropospheric photochemistry of 2,3,7,8-tetrafluorinated dibenzo-*p*-dioxin (TFDD) was theoretically investigated by Zhang and Sun [15]. Photodegradation of some PFDDs in organic solvents was studied by us [16]. In this study, because all of its H atoms are replaced by fluorine atoms, we selected OFDD as a representative of PFDDs to study photolysis kinetics and possible degradation pathways in water-organic mixture systems. The results obtained can fill in the knowledge gap concerning the transformation of PFDDs in water environments.

Being similar to other fluorinated organic compounds, OFDD has peculiar physicochemical characteristics compared to PCDDs because of the high electronegativity of the F atom and of the presence of C–F bonds with large bond energies [17]. Therefore, OFDD is difficult to be decomposed in the environment. Developing rapid, effective and economically feasible methods of treating wastewater containing OFDD is thus required. These methods may include ozonolysis [18], catalytic destruction [19–21], photodegradation [14,22,23], photocatalysis [24,25], biodegradation [26], oxidative degradation [27,28] and so on. By comparing these methods, photolysis and photocatalytic methods can be thought of as promisingly effective and economically feasible techniques because of their ability to operate at ambient pressure and temperature, requiring no expensive chemical reagents and utilizing natural sunlight.

Many studies have shown that most persistent organic pollutants can be degraded effectively by hydroxyl radicals ($\text{HO}\cdot$) and/or sulfate radicals ($\text{SO}_4\cdot^-$) [29–32] because of their high redox potentials (1.9–2.7 V for $\text{HO}\cdot$ and 2.5–3.1 V for $\text{SO}_4\cdot^-$) [33,34]. Both radical species can be generated by activation of oxidants such as potassium persulfate (PS), potassium monopersulfate (PMS) and hydrogen peroxide (H_2O_2) using UV, heat or transition metals activation [13,35–37]. Therefore, UV combined with H_2O_2 [35], PS [13,38], or PMS [39] was successfully used by researchers for the removal of organic pollutants in water treatment.

PMS is a triple salt of potassium monopersulfate ($2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$), which is used because single peroxymonosulfate salts such as KHSO_5 are difficult to prepare. The active ingredient of PMS in aqueous solution is HSO_5^- . The HSO_5^- ion is regarded as a monosubstituted derivative of H_2O_2 , but it is often more powerful in reaction kinetics than H_2O_2 itself [40]. In addition, some studies showed that UV combined with PS (UV/PS) technology is a promising wastewater treatment option [41,42]. However, we found that the UV/PS process cannot effectively degrade OFDD by carrying out comparative pre-experiments on OFDD degradation using UV/PS and UV/PMS systems respectively. Hence, in this study, we employed the UV/PMS technology to photodegrade OFDD. Some studies have demonstrated that the catalytic decomposition of PMS assisted by transition metals such as Fe, Co, Ni and Cu can improve greatly the degradation rate of model compounds [43–46]. Therefore, we selected an optimal transition metal ion com-

bined with UV/PMS as an advanced oxidation technology (AOT) to decompose OFDD in water-acetonitrile solutions.

The objectives of this study were: (1) compare the photodegradation kinetics of OFDD by the use of UV ($\lambda = 365 \text{ nm}$) irradiation alone, UV/PMS and UV/PMS in combination with transition metals at natural pH and room temperature; (2) examine the influences of various experimental parameters including the water matrix components (Cl^- , HCO_3^- and humic acid HA) on OFDD photodegradation; (3) analyze and identify the intermediates and the photoproducts by LC/MS/MS; and (4) propose photodegradation pathways of OFDD in the UV/Fe(II)/PMS system, and further support the proposed degradation mechanism by theoretical calculations.

2. Materials and methods

2.1. Chemicals

OFDD was synthesized in our laboratory and was characterized by GC/MS and $^1\text{H-NMR}$ [16]. PMS (purity $\geq 99\%$, the relative amount of KHSO_5 in PMS is $\geq 47\%$) and PS (purity $\geq 99.5\%$) were obtained from Nanjing Reagent Co., Ltd. (Nanjing, China). Methanol (MeOH), tert-butyl-alcohol (TBA), formic acid and acetonitrile were of HPLC grade and supplied from Merck (Darmstadt, Germany). All the other reagents used in this study were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Millipore water ($>18.2 \text{ M}\Omega \text{ cm}^{-1}$) was prepared with a Milli-Q Plus water system (Millipore, Bedford, USA), and employed throughout the studies.

2.2. Photodegradation experiments

The photolysis experiments were performed in an XPA-7 photoreactor (Xu jiang technology Co., Nanjing) with a merry-go-around apparatus ensuring uniform light exposure (the detailed schematic diagram and real photograph of the photochemical reactor are provided in Supporting Data Fig. A0). A 500 W Hg lamp was used as the UV light source and six filters ($\lambda = 365 \text{ nm}$) were placed around it. Since the solubility of OFDD in water is very low, a water/acetonitrile ($v/v = 4:1$) mixture was used as solvent to increase the solubility of OFDD. The average light intensity was about 8.03 mW cm^{-2} , measured by a UV radio meter. OFDD stock solution (100 mg L^{-1}) was prepared in acetonitrile and stored in the dark. A fixed 30 mL volume of OFDD (1 mg L^{-1}) water/acetonitrile ($v/v = 4:1$) solution was placed in a 50-mL quartz reaction tube with a Teflon cap. During the illumination process, a Teflon-coated magnetic stirrer system was used to mix the reaction solution. At specific time intervals, a 1 mL sample aliquot was withdrawn, and an excess sodium nitrite solution (0.01 M) was immediately added to terminate the reaction for subsequent HPLC analysis. Since NO_2^- can be oxidized by $\text{HO}\cdot$ and $\text{SO}_4\cdot^-$ to NO_2 which is a nitrating agent, nitration might occur in the reaction system [47]. So the subsequent HPLC analysis was performed as soon as possible. The temperature during the photolysis experiment process was kept at $20 \pm 2 \text{ }^\circ\text{C}$ by a circulating water system. The corresponding control experiments were carried out with the quartz reaction tube covered by aluminum foil to resist light penetration. All the experiments were carried out at the natural pH of the reaction mixture (unless otherwise stated) in duplicate, and the corresponding observed values were averaged.

In order to identify the transformation products of OFDD in water/acetonitrile mixture using the UV/Fe(II)/PMS process, the initial concentration of OFDD was increased to 10 mg L^{-1} , and the reaction solution volume was changed to 20 mL. In addition, the same concentration of OFDD was packed in different quartz

Download English Version:

<https://daneshyari.com/en/article/4763100>

Download Persian Version:

<https://daneshyari.com/article/4763100>

[Daneshyari.com](https://daneshyari.com)