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Degradation of herbicide 2,4-dichlorophenoxybutanoic acid in the photolysis of $[FeOH]^{2+}$ and $[Fe(Ox)_3]^{3-}$ complexes: A mechanistic study

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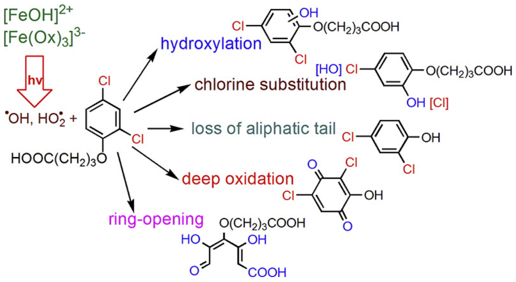
HIGHLIGHTS

- 2,4-DB undergoes extensive degradation during the photolysis of $[FeOH]^{2+}$ and $[Fe(Ox)_3]^{3-}$ complexes.
- ROS species (mainly •OH radical) are responsible for the photodecomposition of herbicide.
- Detailed scheme of 2,4-DB photodegradation including 30 photoproducts was proposed.
- Both complexes can greatly accelerate the photodegradation of 2,4-DB in natural water systems.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work the Fe(III)-assisted photodegradation of the herbicide 2,4-dichlorophenoxybutanoic acid (2,4-DB) has been studied by means of stationary (308 nm) and laser flash (355 nm) photolysis. The initial quantum yield of 2,4-DB photodegradation in $[FeOH]^{2+}$ and $[Fe(Ox)_3]^{3-}$ systems was evaluated to be 0.11 and 0.17 upon 308 nm exposure, respectively. The prolonged photolysis of $[FeOH]^{2+}$ and $[Fe(Ox)_3]^{3-}$ systems results in the complete degradation of 2,4-DB with almost complete mineralization of herbicide and its aromatic products in the case of $[FeOH]^{2+}$ photolysis and the accumulation of some persistent aromatic products in the case of $[Fe(Ox)_3]^{3-}$ photolysis. For both systems the main primary products of 2,4-DB photolysis determined by liquid chromatography – mass spectrometry are products of the hydroxylation, the substitution of chlorine atom to OH group, the loss of aliphatic tail and the opening of benzene ring. The obtained results indicate ROS species (mainly •OH radical) to be responsible for the herbicide photodegradation.

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1. Introduction

Organic pesticides are among the wide-spread environmental pollutants of natural waters due to their active usage in agriculture, chemical stability, low biodegradability and relatively good water solubility (Cohen et al., 1986; Muszkat et al., 1994). Need of purification of the drinking, ground and waste waters

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from pesticides and products of their transformations leads to the search and the development of different treatment approaches including coagulation, biodegradation and photochemical techniques. Chlorine containing herbicides such as 2,4,5-T, 2,4-D, 2,4-DB, Dicamba, Triclopyr, etc. are rather stable to biodegradation and they are sensitive to sun UV light. Maximum permissible concentrations of these compounds in natural waters are of about 0.1 ppm and the characteristic lifetimes vary from a few days to several months (Kegley et al., 2014; Guidelines for drinking-w, 1996).

Low stability of chlorine containing herbicides under UV light and short lifetimes in natural waters allow to draw a conclusion that photochemical reactions play an important role in the degradation and transformations of these compounds in the environment that could be used for the development of new water purification techniques. The proposed photochemical approaches of the removal of chlorine containing herbicides from aqueous solutions are based on three main strategies: (1) direct photolysis (Yurkova et al., 2013; Chamarro and Esplugas, 1993; Aguer et al., 2000), (2) heterogeneous photocatalysis using semiconductor materials (mainly TiO_2) (Tanaka and Reddy, 2002; Herrmann et al., 1998; Chu and Wong, 2004; Qamar et al., 2006; Devipriya and Yesodharan, 2005) and (3) homogeneous (photo)catalysis with different Fe(III) complexes and peroxides (mainly H_2O_2) (Kwan and Chu, 2003; Sun and Pignatello, 1993; Huston and Pignatello, 1999). Two last approaches have shown the highest efficiency of herbicide degradation leading to the fast oxidation and even to the complete mineralization of chlorine containing herbicides due to the generation of reactive oxygen species (ROS).

The majority of works mentioned above is focused at the determination of the herbicide mineralization, the final photochemical products and the integral kinetic characteristics of photodegradation process. Only few studies report about the quantum yields, the rate constants of elementary processes and the possible mechanisms of photochemical reactions. It should be noted that only recently the time-resolved techniques (for instance, laser flash photolysis) were applied to study the photodegradation of herbicides (Yurkova et al., 2013; Rafqah et al., 2004; Catastini et al., 2004; Da Silva et al., 2009). The fragmented information about different photochemical approaches makes it difficult to compare them with each other, to draw reliable conclusions about mechanisms of photodegradation and to systematic search of optimal conditions and methods for the photochemical degradation of chlorine containing herbicides.

The aim of the present work is to study the kinetics, mechanisms and products of the photodegradation of 2,4-dichlorophenoxybutanoic acid (2,4-DB) during the UV photolysis of $[FeOH]^{2+}$ and $[Fe(Ox)_3]^{3-}$ complexes. 2,4-DB is a close analogue of commonly used 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide. The study is carried out by means of laser flash and steady-state photolysis combined with high performance liquid chromatography – mass spectrometry (HPLC-MS) analysis. The photodegradation of target compounds in the UV photolysis of $[FeOH]^{2+}$ and $[Fe(Ox)_3]^{3-}$ complexes is typically used in advanced oxidation processes. Main attention was paid to the identification of reactive intermediates and photoproducts, the determination of quantum yields of photodegradation, the construction of detailed scheme of 2,4-DB photodegradation and the comparison of efficiency of both systems towards the complete mineralization of the herbicide. To the best of our knowledge this is a first work concerned to the study of 2,4-DB photodegradation in aqueous solution.

2. Materials and methods

2,4-dichlorophenoxybutanoic acid (2,4-DB, Fluka, 99.9%), Fe(III) perchlorate hydrate (Aldrich) and potassium oxalate (chemically pure) were used without further purification. $HClO_4$ (chemically pure) and $NaHCO_3$ (chemically pure) were used for the pH adjustment. Acetonitrile was of HPLC grade (Panreac, Spain). The reaction solutions were prepared with the deionized water (18 MΩ). In all experiments the concentration of 2,4-DB was 10^{-4} M and the total concentration of Fe(III) was 6.5×10^{-4} M and 10^{-4} M in time-resolved and steady-state experiments, respectively. The complex of $[Fe(Ox)_3]^{3-}$ was prepared by an addition to Fe(III) solution of small amounts of the stock aqueous solution of $K_2C_2O_4$ (0.12 M) to reach the total oxalate concentration at the level of 10^{-3} M. Absorption spectra of aqueous solutions of 2,4-DB, $[FeOH]^{2+}$ and $[Fe(Ox)_3]^{3-}$ are presented at Fig. 1S. All photochemical experiments were performed in a 1 cm quartz cell in air-equilibrated solutions at room temperature and under atmospheric pressure. The Fe(II) concentration in a sample was measured spectrophotometrically by the formation of the colored *o*-phenanthroline complex (Calvert and Pitts, 1966).

UV absorption spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies, USA). The transient absorption (TA) dynamics of 2,4-DB was studied with the laser flash photolysis (LFP) setup described in details earlier (Pozdnyakov et al., 2006). Briefly, LPF experiments were carried out using the third harmonic (355 nm) of a Nd:YAG laser (LS-2137U, Solar, Belarus) as an excitation source (pulse duration 6 ns, pulse energy 0.5–10 mJ/pulse). The time resolution of the setup is 50 ns. XeCl excimer lamp (Institute of High Current Electronics, Russia) with the excitation wavelength of 308 nm was used for the steady-state photolysis. The intensities of laser and lamp irradiation were measured with a SOLO 2 power meter (Gentec EO, Canada). The obtained values were used for calculations of quantum yields of photo-induced degradation (mean errors ± 20%).

The photodegradation yield of 2,4-DB was measured with a HPLC system Agilent LC 1200 system, equipped with the diode array detector. The separations were performed using Zorbax Eclipse XBD-C18 column (4.6 × 150 mm, 80 Å, 5 μm) with a flow rate 0.5 mL/min using the following mixture of mobile phase A (0.05% (v/v) trifluoroacetic acid in water) and B (acetonitrile): 0% B (0–4 min), 0–20% B (4–5 min), 20–80% B (5–25 min), 80–100% B (25–26 min), 100% B (26–33 min), 100-0% B (33–34 min), 0% B (34–48 min). The injection volume was 80 μl. The chromatograms were recorded at 250, 280, 320, 360 nm; the analysis of the obtained results was performed by Agilent ChemStation software. Before HPLC analysis all irradiated solutions were kept in fridge (4 °C). The HPLC tests had shown good reproducibility of results using this way of storage.

The photodegradation products were analyzed with HPLC electrospray ionization MS (HPLC-ESI-MS) system: ultra-HPLC system UltiMate 3000RS (Dionex, Germany) connected with high-resolution ESI time-of-flight mass spectrometer maXis 4G (Bruker Daltonics, Germany). HPLC separations were made using the same column, flow rate, gradient of mobile phases A (0.1% formic acid in water) and B (0.1% formic acid in acetonitrile) and the injection volume as it was described above. Mass spectra were acquired in the negative mode in the m/z range of 30–350. The instrument parameters were set as: end plate offset −500 V; capillary voltage 3500 V; nebulizer pressure 3 bar; dry gas flow 8 l/min; dry gas temperature 200 °C. The MS calibration was performed with an injection of the sodium formate cluster calibration solution. The obtained data were analyzed with DataAnalysis software 4.0, build 275 and QuantAnalysis software 2.0, build 275 (Bruker Daltonics, Germany).

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