



Contents lists available at ScienceDirect

## Chemical Engineering Journal

journal homepage: [www.elsevier.com/locate/cej](http://www.elsevier.com/locate/cej)Chemical  
Engineering  
Journal

## Investigations of diatrizoate degradation by photo-activated persulfate

Lei Zhou<sup>a</sup>, Corinne Ferronato<sup>a</sup>, Jean-Marc Chovelon<sup>a,\*</sup>, Mohamad Sleiman<sup>b,c</sup>, Claire Richard<sup>c,d,\*</sup><sup>a</sup> Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626 Villeurbanne, France<sup>b</sup> Université Clermont Auvergne, Sigma-Clermont, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France<sup>c</sup> CNRS, UMR 6296, ICCF, F-63178 Aubière, France<sup>d</sup> Université Clermont Auvergne, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France

## HIGHLIGHTS

- Efficient oxidation of diatrizoate could be achieved by photo-activated persulfate.
- UV/PS was found to be more efficient than UV/H<sub>2</sub>O<sub>2</sub> for DTZ removal under irradiation.
- Rate constant of DTZ with SO<sub>4</sub><sup>-</sup> was determined by laser flash photolysis.
- Pathways included deiodination/decarboxylation-hydroxylation and side chain cleavage.
- Light-absorbing photoproducts contain hydroquinone and benzoquinone moieties.

## ARTICLE INFO

## Article history:

Received 28 July 2016

Received in revised form 2 November 2016

Accepted 8 November 2016

Available online xxxxx

## Keywords:

X-ray contrast media

Sunlight activated persulfate

Sulfate radicals

Deiodination

Light-absorbing intermediates

## ABSTRACT

The widespread occurrence of iodinated X-ray contrast media (ICMs) in aquatic systems poses potential risks to ecologic system and human health. The present study investigated the degradation kinetics and mechanisms of a typical ICMs, diatrizoate (DTZ), by using simulated sunlight (from a solar simulator Suntest CPS+) activated persulfate (PS) oxidation process. The influence of key kinetic factors, such as PS concentrations, pH, dissolved organic matter (DOM), bicarbonate and chloride ions was evaluated. The reaction pathways and mechanisms were proposed based on photoproducts identification using HPLC-MS. UV/PS was found to be more efficient than UV/H<sub>2</sub>O<sub>2</sub>. Sulfate radicals (SO<sub>4</sub><sup>-</sup>) was the dominant reactive species in the oxidation process, and the second-order rate constant of sulfate radical with DTZ was calculated as  $1.90 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  based on laser flash photolysis (LFP) experiments. The results indicated that increasing initial PS concentration favored the decomposition of DTZ; whereas, degradation of DTZ was not affected by pH change ranging from 4.5 to 8.5. DOM inhibited DTZ removal rate, while, bicarbonate enhanced it, and chloride ions induced a negative effect above 500 mM. Major oxidation pathways including deiodination-hydroxylation, decarboxylation-hydroxylation and side chain cleavage were proposed, and detailed underlying mechanisms were also discussed. We suggest a direct photodegradation of primary intermediates generated by SO<sub>4</sub><sup>-</sup> attack. These findings demonstrate that halogenated pollutants can readily react with SO<sub>4</sub><sup>-</sup> to form light-absorbing intermediates (ranging from 350 to 500 nm). Thus, this activation method could be a promising approach in the removal of ICMs.

© 2016 Published by Elsevier B.V.

## 1. Introduction

In recent decades, a growing number of studies have documented the widespread occurrence of pharmaceuticals in aquatic environment, raising serious concerns about their influence on aquatic ecosystems and human health [1–4]. Many pharmaceuticals were found to be recalcitrant to conventional drinking water

and wastewater treatment processes (WWTPs) [5,6]. As a consequence, pharmaceuticals are frequently detected in natural waters, and in drinking waters and constitute a potential risk for human health [7–11].

Iodinated X-ray contrast media (ICMs), a class of medical diagnostic agents routinely prescribed for imaging tissues and internal, are among the most recalcitrant and highly persistent pharmaceuticals [5]. Large quantities of ICM are administered to individual patients undergoing tests (>100 g dose<sup>-1</sup>), and the annual worldwide consumption of ICMs was reported as approximately  $3.5 \times 10^6 \text{ kg}$  [12]. ICMs are designed to be resistant to metabolism and thus are generally excreted unchanged within 24 h [13].

\* Corresponding authors.

E-mail addresses: [lei.zhou@ircelyon.univ-lyon1.fr](mailto:lei.zhou@ircelyon.univ-lyon1.fr) (L. Zhou), [jean-marc.chovelon@ircelyon.univ-lyon1.fr](mailto:jean-marc.chovelon@ircelyon.univ-lyon1.fr) (J.-M. Chovelon), [claire.richard@univ-bpclermont.fr](mailto:claire.richard@univ-bpclermont.fr) (C. Richard).

<http://dx.doi.org/10.1016/j.cej.2016.11.066>

1385–8947/© 2016 Published by Elsevier B.V.

Conventional WWTPs could not remove ICMs effectively, leading to their occurrence in surface water and ground water at concentration ranging from  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$  [14–17]. The ICMs contribute substantially to the organic halogen levels in municipal and hospital effluents, which has raised additional concerns [18]. The published information about the environmental risk of ICMs is not abundant, however, some research has shown that DTZ may have nephrotoxic effects in animals and humans [19,20]. Although there is lack of information about their impact on health, drinking water should be free of ICMs to minimize the potential risk of long-term adverse health effects. Therefore, it is essential to develop an effective treatment technology to remove these compounds from waters.

Advanced oxidation processes (AOPs) are promising alternatives capable of removing these pharmaceuticals from WWTPs. The AOPs technology is mainly based on the generation of reactive species arising from the decomposition of oxidants such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and persulfate (PS,  $\text{S}_2\text{O}_8^{2-}$ ). Among the commonly used oxidants, PS received wide attention due to its high redox potential ( $E^0 \sim 2.1 \text{ V}$ ) [21,22]. PS is a relatively stable oxidant in water, however, it can be activated by UV, heat, base, or transition metals to generate a stronger oxidant, sulfate radical ( $\text{SO}_4^-$ ,  $E^0 \sim 2.6 \text{ V}$ ) [23–27]. It has been demonstrated that,  $\text{SO}_4^-$ , in general, could react with organic compounds with a second-order rate constant in the range  $10^6$ – $10^9 \text{ M}^{-1} \text{ s}^{-1}$  [28]. Unlike the well-known hydroxyl radical ( $\cdot\text{OH}$ ),  $\text{SO}_4^-$  is believed to react with organic compounds mainly via electron transfer mechanism, which makes it more selective [29]. Moreover, by comparison with  $\cdot\text{OH}$ ,  $\text{SO}_4^-$  is less likely scavenged by dissolved organic matter (DOM), such as humic and fulvic acids, that are ubiquitously present in natural waters [30]. Therefore,  $\text{SO}_4^-$ -based oxidation processes show advantageous relative to conventional HO-based AOPs in certain water treatment and remediation scenarios [31].

Various AOPs processes have been utilized to degrade ICMs, such as UV/ $\text{H}_2\text{O}_2$ , UV/ $\text{TiO}_2$ ,  $\text{O}_3$  [32–34]. While treatment feasibility of ICMs was examined, previous studies did not provide mechanistic details and did not explore the effects of naturally occurring substances (e.g., DOM, bicarbonate), which are essential for optimizing the treatment process. Moreover, studies reporting the treatment of ICMs by  $\text{SO}_4^-$ -based oxidation process, especially ionic ICM like diatrizoate (DTZ) that was remarkably resistant to biodegradation, are scarce [35,36]. Velo-Gala *et al.* undertook a comparative study on different AOPs processes for the degradation of DTZ, and found that  $\text{SO}_4^-$ -based oxidation process could be an effective choice [37]. However, a detailed kinetic and mechanistic map describing the degradation of DTZ by  $\text{SO}_4^-$  is still lacking.

In the present study, we attempted to elucidate the underlying mechanisms and oxidation pathways of the reaction between DTZ and  $\text{SO}_4^-$ .  $\text{SO}_4^-$  was generated by simulated sunlight activated PS process. Kinetic studies were conducted for a better understanding of the influence of factors including pH and natural water constituents. The identification of DTZ transformation intermediates and products was also performed by using HPLC-MS method. Based on the HPLC-MS data, the reaction mechanisms and detailed transformation pathways were proposed. Our study provides useful information about using sulfate radical-based technologies for remediation of the groundwater contaminated by DTZ and structurally related X-ray contrast agent.

## 2. Materials and methods

### 2.1. Chemicals

Sodium diatrizoate hydrate (DTZ, 98%), nitrobenzene (NB, 99%), *para*-nitroaniline (PNA, 99%), hydrogen peroxide (30% w/w) and

potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ , 99%) were purchased from Sigma-Aldrich. Suwannee River fulvic acid (SRFA, 1R101F) of reference grade was obtained from International Humic Substance Society (IHSS). HPLC or LC-MS grade acetonitrile (ACN), methanol (MeOH), ethanol (EtOH) and *t*-butanol (TBA) were supplied by Fisher Chemical. Other reagents were of analytical grade and used as received without further purification. Milli-Q water ( $18 \text{ M}\Omega \text{ cm}$ ) was prepared from a Millipore Milli-Q system. All solutions were prepared by dissolving the chemical agents into Milli-Q water without further purification.

### 2.2. Experiments setup

$\text{SO}_4^-$  radicals were generated by activation of persulfate under simulated solar irradiation, and the irradiation experiments were conducted in a solar simulator Suntest CPS+, (HERAEUS, Hanau, France) equipped with a 1.5 kW xenon arc and an ultraviolet filter allowing a simulation of the solar spectrum between 290 nm and 400 nm. The reaction was carried out in a cylindrical Pyrex reactor (i.d. = 5 cm, H = 15 cm, V = 150 mL) and the temperature was maintained at 20 °C using a circulating water system. A scheme of the applied reactor is present in Fig. S1 (Supplementary Material). Specific aliquot of substrate (DTZ) and appropriate volumes of persulfate stock solution were added to achieve 50 mL reaction solution. Control experiments with substrates alone and dark experiments with substrate-persulfate were carried out under identical conditions. Except for buffered solutions (achieved using 10 mM  $\text{Na}_2\text{HPO}_4$  and 10 mM  $\text{NaH}_2\text{PO}_4$  in the experiments with bicarbonate), the initial pH of other reaction solutions were adjusted using 0.01 M  $\text{H}_2\text{SO}_4$  and 0.01 M NaOH. Aliquots of 0.3 mL were withdrawn at selected time intervals and quenched immediately with the same volume of methanol, a well-known scavenger for  $\text{SO}_4^-$  and  $\cdot\text{OH}$ , to stop the chemical oxidation reactions. All experiments were performed at least in duplicate.

### 2.3. Analytical procedures

The concentrations of DTZ, NB and PNA were analyzed using a Shimadzu 10A series high performance liquid chromatography (HPLC, Shimadzu) system equipped with a Model 7725i injector with a 20  $\mu\text{L}$  sample loop and coupled with a LC-10AT binary pump and a SPD-M10ADAD. Samples were separated using an Yperspher BDS  $\text{C}_{18}$  column (5  $\mu\text{m}$ , 125 mm \* 4.0 mm, i.d.) (Interchim, France) at 40 °C. The mobile phase was a mixture of acetonitrile and acidified-water (3% formic acid by volume, pH 3.0). An overview of the HPLC parameters is given together in Table S1, Supplementary Material.

Concentrations of SRFA were expressed as total organic carbon (TOC,  $\text{mg C L}^{-1}$ ) and determined using a Shimadzu 5000A analyzer (Japan).

The UV-vis spectra of the selected chemicals were recorded using a Lambda 950 UV-vis spectrophotometer (PerkinElmer, USA) and quartz cuvettes.

Identification of the degradation products of DTZ were carried out using HPLC-MS method. The HPLC-MS data were recorded using an Agilent Chromatograph equipped with a 996-photodiode array detector, an atmospheric-pressure chemical ionization device (APCI), and a reverse Zorbax eclipse XDDC<sub>18</sub> column (5  $\mu\text{m}$ , 150 mm \* 4.6 mm, i.d.).

The pH of the solutions was measured using a combined glass electrode connected to a PHM 210 Standard pH meter (Radiometer, Copenhagen).

The second order rate constant of DTZ with  $\text{SO}_4^-$  was determined by means of laser flash photolysis (LFP) by recording the  $\text{SO}_4^-$  decay rates under different conditions. The rate constants of

Download English Version:

<https://daneshyari.com/en/article/4763402>

Download Persian Version:

<https://daneshyari.com/article/4763402>

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