Degradation of selected emerging contaminants by UV-activated persulfate: Kinetics and influence of matrix constituents

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ABSTRACT

The degradation of five selected emerging contaminants (ECs) including 1H-benzotriazole (BZ), N,N-diethyl-m-toluamide or DEET (DT), chlorophene (CP), 3-methylindole (ML), and nortriptyline hydrochloride (NH) in aqueous solutions by UV-activated persulfate (UV/PS) has been investigated. Selected ECs were not effectively degraded by direct UV photolysis or dark PS. However, their photodegradation efficiency significantly increased with addition of PS due to the generation of $SO_4^{\cdot-}$ and $HO^{\cdot}$. Second order rate constants for the reaction between $SO_4^{\cdot-}$ and each EC were determined by competition kinetics, being the values at pH 7 2.0×10^{10}, 1.2×10^{10}, 1.8×10^9, 1.1×10^9 and $9.5 \times 10^8 \, M^{-1} \, s^{-1}$ for NH, ML, CP, BZ and DT, respectively. While the dose of PS exerted a positive influence on the degradation of ECs, the highest degradation rate was observed at near neutral pH. With respect to the influence of background water matrix constituents, bicarbonate showed an inhibition effect on the removal of DT, BZ and NH and promoted the degradation of CP and especially of ML, which can be explained by their high reaction rate with carbonate radicals. The presence of humic acids inhibited the degradation of selected ECs, probably due to light screening and radical scavenging. Both radical species $SO_4^{\cdot-}$ and $HO^{\cdot}$ exert an important role on the oxidation of the ECs investigated by the UV/PS system, being the contribution of $SO_4^{\cdot-}$ predominant for those compounds that present high reactivity with this radical. Although the presence of inorganic and organic matter in real water matrices decreased the degradation rate of selected ECs, UV/PS process is an efficient option for their removal from contaminated waters.

1. Introduction

The occurrence and treatment of emerging contaminants (ECs) in water, wastewater, and water reuse scenarios has become a growing concern during the last decade. These ECs include, among others, pharmaceuticals, personal care products, endocrine disrupting chemicals, per- and poly-fluorinated alkyl substances, disinfection by-products, pesticides, and flame retardants, [1,2]. The term EC is generally used to cover not only new developed compounds, but also compounds discovered in the environment, often due to analytical developments [3]. As the list of environmentally-relevant ECs continues to grow, incorporating advanced techniques into practice is a challenge in water treatment. Several technologies have been assayed successfully with the aim of reaching high levels of elimination of these ECs, including activated carbon adsorption [4], membrane technologies [5,6] and oxidation processes [7]. Among them, advanced oxidation processes (AOPs) have shown to be very effective for the removal of these compounds from natural waters and wastewaters, even in the cases of ECs that were very refractory to conventional treatments, such as

oxidation processes by using single chlorine or ozone [8–10].

AOPs rely on the formation of reactive species, such as sulfate and hydroxyl radicals, which can be used to degrade and mineralize recalcitrant pollutants [9,10]. Photo-assisted AOPs processes, such as UV/O_3, UV/H_2O_2, UV/$S_2O_8^{2-}$, and UV/TiO_2 have been reported to be efficient for degradation of micropollutants. Sulfate radical ($SO_4^{\cdot-}$) based AOPs offer several advantages compared to hydroxyl radical ($HO^{\cdot}$) based AOPs. The standard reduction potential of $SO_4^{\cdot-}$ ($E° = 2.5$–3.1 V) is almost similar to that of $HO^{\cdot}$ ($E° = 1.9$–2.7 V), so that $SO_4^{\cdot-}$ can act as a powerful and selective oxidant to degrade organic compounds through electron transfer mechanism [11]. In addition, the consumption of $SO_4^{\cdot-}$ by natural organic matter (NOM) is lower than that of $HO^{\cdot}$, so that $SO_4^{\cdot-}$ based AOPs have been reported to be more efficient in natural water matrices [12]. Another advantage of the AOPs based on $SO_4^{\cdot-}$ is that the final product of the oxidation is sulfate ion (SO_4^{2-}), which is practically inert and is not considered to be a pollutant [13]. Persulfate ion (PS, $S_2O_8^{2-}$) is the most common oxidant used for the generation of $SO_4^{\cdot-}$. PS is generally stable under typical water treatment conditions, and its activation can be performed
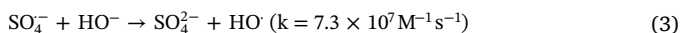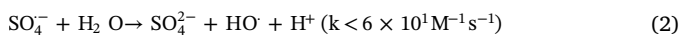
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by various approaches, including heat, transit-metal cations or metal oxides, UV irradiation, and heterogeneous activation by metallic glass [14–17]. Specifically, formation of $SO_4^{\cdot-}$ can be induced via thermal and photochemical activation according to Eq. (1). A 254-nm monochromatic UV irradiation was used in this work for the activation of $S_2O_8^{2-}$, which has been successfully applied in previous investigations [18,19].

$$S_2O_8^{2-} \xrightarrow{\Delta/h\nu} 2SO_4^{-} \qquad (1)$$

Several studies reported that $SO_4^{\cdot-}$ can subsequently produce $HO^{\cdot}$ by means of reactions (2) and (3) [19,20].

$$SO_4^{-} + H_2O \rightarrow SO_4^{2-} + HO^{\cdot} + H^+ \ (k < 6 \times 10^1 M^{-1} s^{-1}) \qquad (2)$$

$$SO_4^{-} + HO^{-} \rightarrow SO_4^{2-} + HO^{\cdot} \ (k = 7.3 \times 10^7 M^{-1} s^{-1}) \qquad (3)$$

Therefore, both reactive oxygen species, $SO_4^{\cdot-}$ and $HO^{\cdot}$, are responsible of the oxidizing action of this AOP. Specifically, at pH below 7, $SO_4^{\cdot-}$ is the dominant free radical, while the fraction of $HO^{\cdot}$ increased gradually from pH 7 to 9, and $HO^{\cdot}$ became the main radical when pH > 9 [21].

The ECs selected as target micropollutants in this work were previously used in other advanced oxidation studies [22,23] and include: (i) 1H-benzotriazole (BZ), an anticorrosive agent used in dishwasher detergents, aircraft deicing and antifreeze fluid of motor vehicles; (ii) N,N-diethyl-m-toluamide or DEET (DT), an active ingredient of most commercial insect repellent products; (iii) chlorophene (CP), a biocide used as cosmetic preservative and for general cleaning and disinfection in hospitals and households; (iv) 3-methylindole (ML), a fragrance widely used in perfumes, herbicides, fungicides, dyes, antihypertensive and anticancer medicines, and (v) the antidepressant nortriptyline hydrochloride (NH). These ECs, with different physico-chemical properties (MW, molecular size, pK_a, log K_{ow}), are frequently found in surface waters and wastewaters [24–26]. According to previous investigations, DT and BZ were found to be recalcitrant to conventional water treatment [26,27]. Although rate constants of these selected ECs with $HO^{\cdot}$ were determined in a previous work [28], rate constants for their reactions with $SO_4^{\cdot-}$ are still unknown. In addition, the degradation of selected ECs by UV/PS has not been reported so far.

With these considerations in mind, the aim of this work was to establish the efficiency of the UV/PS process in the oxidation of the selected ECs. Second order rate constants for the reactions between each EC and $SO_4^{\cdot-}$ were determined by competition kinetics. Also, the influence of the main process parameters (PS dosage, pH) and the effects of natural water constituents, such as carbonate/bicarbonate and NOM, on the oxidation process were also investigated. In addition, some experiments were performed in presence of 2-propanol (IPA) and tert-butyl alcohol (TBA) for determining the role of the main reactive radicals. Finally, ECs degradation efficiency in different real water matrices was examined to evaluate the technical feasibility of UV/PS oxidation technology on the treatment of ECs contaminated water.

2. Materials and methods

2.1. Chemicals and water matrices

The selected ECs and the reference compound (isoproturon, ISOP) were purchased from Sigma-Aldrich (Germany) and were of the highest purity available (> 99%). Sodium persulfate ($Na_2S_2O_8$), IPA, TBA, humic acids (HA) and other chemicals were also purchased from Sigma-Aldrich and used as received without further purification. The solutions used in this study were prepared by dissolving the ECs in deionized (DI) water (from a Milli-Q Water System, Millipore Ibérica, Spain). In addition, three real water matrices were used in order to reproduce realistic water treatment conditions: a surface water collected from the public reservoir "Peña del Aguila" (PA), located in the Extremadura

Table 1
Characterization of the selected real water matrices: public reservoir "Peña del Aguila" (PA), and two secondary effluents from WWTPs located in La Albuera (LA) and Badajoz (BA).

	PA	LA	BA
pH	7.4 ± 0.2	7.9 ± 0.3	8.3 ± 0.3
Conductivity ($\mu S\,cm^{-1}$)	80.2 ± 3.2	570 ± 12	550 ± 15
$A_{254\,nm}$ (cm^{-1})	0.187 ± 0.012	0.041 ± 0.005	0.245 ± 0.020
COD ($mg\,O_2\,L^{-1}$)	24 ± 1.7	12.4 ± 1.1	53 ± 3.2
Alkalinity ($mg\,CaCO_3\,L^{-1}$)	30 ± 3.2	335 ± 11	325 ± 14
DOC ($mg\,L^{-1}$)	6.8 ± 0.8	2.5 ± 0.2	19.2 ± 1.9
Total nitrogen ($mg\,N\,L^{-1}$)	1.51 ± 0.20	21.3 ± 2.7	35.5 ± 3.3
Total phosphorus ($mg\,P\,L^{-1}$)	0.041 ± 0.006	0.156 ± 0.015	1.76 ± 0.20

COD: chemical oxygen demand. DOC: dissolved organic carbon.

Community, south-west of Spain; and two secondary effluents from Badajoz (BA) and La Albuera (LA) wastewater treatment plants (WWTPs), also in the Extremadura Community. These water samples were previously filtered by Whatman filter paper No. 1 in order to remove suspended matter, and stored at 4 °C until use. These waters were analyzed for a variety of general water quality parameters, such as pH, conductivity, absorbance at 254 nm (UV_{254nm}), chemical oxygen demand (COD), alkalinity, dissolved organic carbon (DOC), total nitrogen (TN), and total phosphorus (TP). After replicated analysis, the average values depicted in Table 1 were determined.

2.2. Experimental procedures

The experiments of ECs degradation by UV/PS were performed in a 500 mL jacketed column reactor thermostatized at the selected temperature (20 ± 0.5 °C). A low pressure vapour mercury lamp (TNN 15/32, nominal electrical power 15 W; Heraeus, Madrid, Spain) which emitted monochromatic radiation at 254 nm, was located inside the reactor in axial position and was protected by a quartz sleeve which housed the lamp. UV fluence rates were determined by atrazine actinometry according to Canonica et al. [29]. The average UV fluence rate was determined to be 4.23 mW cm^{-2}. For every experiment conducted, the reactor was filled with 350 mL of solution containing 1 μM of each EC dissolved in DI water at the selected pH in the range 5–9 (2 mM phosphate buffer). The concentration of each EC (1 μM) was higher than typically found in environmental samples in order to facilitate the accurate measurement in reaction samples while providing insight into the process working at lower concentration. Then, the required amount of PS to reach the desired concentration in the solution (10–200 μM) was added to the reactor. Once connected the lamp, the reaction started and samples were periodically withdrawn from the reactor and quenched immediately with 0.1 M sodium thiosulfate to determine the residual concentration of ECs by HPLC analysis. Some of the preliminary experiments carried out to establish the experimental conditions were replicated. The results obtained for each experiment were quite similar and errors obtained were rather low, normally below 3%.

The same procedure was followed to investigate the effects of various parameters on the degradation of ECs. Thus, control experiments were performed either in the absence of PS or in the absence of UV irradiation. The presence of different water constituents such as bicarbonate (1 and 2 mM) and HA (2.5 and 7.5 mg L^{-1}) was also investigated in experiments performed with DI water. Besides, TBA (10 mM) and IPA (10 mM) were used as $HO^{\cdot}$ and $SO_4^{\cdot-}$ scavengers to evaluate the contribution of the reactive oxygen species on the overall degradation of ECs by UV/PS. Finally, some experiments were carried out by dissolving the ECs (1 μM of each) in the real water matrices above mentioned without pH adjustment.

Competition kinetics was used for determining the second order rate constant of the reaction of each EC with $SO_4^{\cdot-}$. These experiments were carried out at pH 7 in DI water, but adding a reference compound