Journal of Photochemistry and Photobiology A: Chemistry 286 (2014) 40–46

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Photochemical degradation of sulfadiazine, sulfamerazine and sulfamethazine: Relevance of concentration and heterocyclic aromatic groups to degradation kinetics

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ARTICLE INFO

Article history:
Received 21 February 2014
Received in revised form 20 April 2014
Accepted 24 April 2014
Available online 2 May 2014

Keywords:
UV-based technologies
Sulfonamides
SPE technique
Photo-Fenton processes

ABSTRACT

Sulfonamides are often not satisfactorily removed in wastewater treatment plants, reaching surface and ground waters at low concentrations. Photo-oxidation treatments appear as a viable alternative for the remediation of water and wastewater containing these pollutants. Moreover, the use of solid phase extraction (SPE) techniques for the quantification of sulfonamides at very low levels during photo-oxidation treatments is not usually discussed.

In this study, three different processes (UV photolysis, UV/H_2O_2 and photo-Fenton) were investigated for the degradation of sulfadiazine (SDZ), sulfamerazine (SMR), and sulfamethazine (SMT) to final concentrations below mg L^{-1}. A tubular photochemical reactor with a concentric low pressure mercury vapor lamp emitting at 254 nm was used. Sulfonamide concentrations were determined using ultra-fast liquid chromatography (UFLC). Hydrogen peroxide consumption was monitored spectrophotometrically. In particular, we optimized the SPE technique for the quantification of the three sulfonamides and determined the most appropriate stationary phase cartridge and pH for sample extraction.

In comparison to UV photolysis and H_2O_2/UV processes, the photo-Fenton reaction was able to degrade sulfonamides to final concentrations of nmol L^{-1} ($\mu g\,L^{-1}$), attaining the method detection limit after 20, 12 and 6 min of irradiation for SMT, SMR and SDZ, respectively. SDZ is more hydrophilic than SMR and SMT, which is related to the presence of methyl groups bonded to the heterocyclic group. The increase in the number of —CH_3 substituents in the heterocyclic group of SMT and the corresponding increased steric hindrance to radical addition, resulted in slower degradation rates in comparison with those observed for SMR and SDZ.

The optimized SPE technique can be used in further studies of sulfonamides degradation by advanced oxidation processes at more realistic concentration levels as those detected in real wastewater and in the environment.

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1. Introduction

Detection of pharmaceuticals in aquatic environment has been reported by many different authors [1–3]. Molecules containing sulfonamide (—SO_2NH—) groups constitute one of the largest classes of antibiotics widely used in humans and especially in animals. Sulfonamides with different heterocyclic aromatic groups are found in effluents from wastewater treatment plants (WTPs) [4–7]. Sulfonamides have been reported to be more resistant to degrade than the recalcitrant pentachlorophenol [8]. The debate on the relevance of destroying antibiotics in water and wastewater matrices is due to the facts that these compounds are designed to elicit biological responses that may have toxic risks for aquatic environments, and also to the potential development of pathogenic organisms more resistant to antibacterial drugs [9]. Since pharmaceuticals are not satisfactorily removed from WTPs and may reach surface and ground waters, alternative processes such as UV-based technologies have been proposed for their degradation [10–13]. For example, significant removals of the pharmaceuticals mefenamic acid, diclofenac, ketoprofen, and of the herbicide diuron within 10 min of irradiation at 254 nm, have been reported [14].

The photolysis of pharmaceutical compounds has been investigated and showed to be an important process for the removal of sulfonamides from surface waters [15,16]. Boreen, Arnold and

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http://dx.doi.org/10.1016/j.jphotochem.2014.04.022
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McNeill [17] have attributed the photodegradation of sulfonamides in natural water samples solely to photolysis. Focusing on advanced oxidation processes (AOPs), previous studies reported the degradation of pharmaceuticals using the photo-Fenton reaction in aqueous solutions [18–23]. Nevertheless, some investigations related to sulfonamide degradation were performed at relatively high initial concentrations ($\geq$0.1 mmol L^{-1}/25 mg L^{-1}), reporting final concentrations of the same order of magnitude [19,20,22].

Sulfonamides have frequently been detected in aqueous medium ranging from ng L^{-1} to μg L^{-1} in river basins [6], in wastewater from livestock farming and surface water around farms [7], in water wells [24] and in effluents from WWTPs [6] as well. Because of low levels of sulfonamide concentration in the environment, a pre-concentration step is required prior to their quantification using liquid chromatography [25,26]. The solid phase extraction (SPE) technique has been developed and optimized for sulfonamides extraction from distilled water, groundwater, surface water and wastewaters, into organic solvents [25–27]. Nevertheless, although previous investigations reported the optimization of SPE techniques for improving the sensitivity of analytical methods, the use of SPE for quantification of sulfonamides in aqueous samples withdrawn during photo-oxidative treatments is a procedure that has not usually been examined in detail in such investigations.

In this study, we evaluate three photo-oxidation processes (UV photolysis, UV/H_2O_2 and photo-Fenton) for the degradation of the sulfonamides sulfadiazine (SDZ), sulfamerazine (SMR), and sulfamethazine (SMT) to final concentrations below mg L^{-1}. In particular, we improved the sensitivity of the analytical method for detecting sulfonamides at low levels by determining the most appropriate stationary phase cartridge and pH for sample extraction before UFLC analysis. The effect of the initial concentration of the target compounds on the degradation kinetics is quantified, and the role of the heterocyclic aromatic group bonded to the sulfonamide molecule on degradation is discussed.

2. Experimental

2.1. Chemicals

All the solutions were prepared using ultrapure water (Millipore Milli-Q®). A 30% (w/w) H_2O_2 solution (Merck) was used. Sulfamethazine (SMT, 278 g mol^{-1}, Sigma–Aldrich > 99%), sulfamerazine (SMR, 264 g mol^{-1}, Sigma–Aldrich > 99%) and sulfadiazine (SDZ, 250 g mol^{-1}, Sigma–Aldrich > 99%), were used as standards in ultra-fast liquid chromatography (UFLC) analysis, solid phase extraction (SPE) and in photochemical experiments. Each sulfonamide standard solution was prepared in methanol and after was diluted up to a maximum of 0.1% methanol in ultrapure water to avoid hydroxyl radicals scavenging. Acetonitrile and methanol (HPLC grade) were purchased from Sigma–Aldrich.

2.2. Photodegradation procedure

Photochemical degradation experiments were performed at room temperature in batch in a tubular photochemical reactor, which consists of a borosilicate glass tube equipped with a concentric low-pressure (LP) mercury vapor lamp (TUV Philips 36 W). The reactor was connected to a circulation tank, from which samples were withdrawn using an automatic pipette. The initial concentrations of the antibiotics were 0.100 or 0.0250 mmol L^{-1}. The initial pH of the solutions was adjusted at the beginning of the experiments but not corrected over time, using either H_2SO_4 or NaOH. All experiments were carried out at an initial pH of 6 except for the photo-Fenton reaction, for which $Fe(NO_3)_3$ was used and the initial pH was set to 3. The solution was recirculated at a flow rate of 80.0 mL min^{-1} through the reactor and the tank by means of a centrifugal pump, which enabled the continuous oxygenation of the reaction medium. The flow rate was adjusted using a needle valve and read with a rotameter. The irradiation time (t_{irrad}) was calculated according to $t_{irrad} = (t_{total} \times V_{reactor})/V_{total}$, where t_{total} represents total time, $V_{reactor}$ is the reactor volume and V_{total} is the total volume of the sulfonamides solution. The total and irradiated volumes of sulfonamides solutions were 5.00 L and 3.93 L, respectively. The monitoring time (t_{total}) started when the reaction vessel was completely filled and the lamp was switched on. In this study, standard deviations were calculated from three replicates of the experiments carried out at each experimental condition.

2.3. Chemical analysis

2.3.1. Chromatographic conditions

Sulfonamide concentrations were determined by ultra-fast liquid chromatographic (UFLC) analysis using Shimadzu equipment (LC 20AD) with a UV-visible detector (SPD 20A) and a C18 column (Phenomenex Synergi Fusion-RP, 250 mm × 4.60 mm, 4 μm). The oven temperature and sample injection volume were 40 °C and 50 μL, respectively. The eluents were (A) H_2O + 0.200% acetic acid and (B) acetonitrile at 80:20 ratio and 1.00 mL min^{-1} flow rate. The detection wavelengths of SDZ, SMR and SMT were 265, 260, and 268 nm, respectively. Under these conditions, the detection limits obtained without using solid phase extraction (SPE) (cf. Section 2.3.2) were 0.170, 0.0540, and 0.0980 mg L^{-1} for SMT, SMR and SDZ, respectively; the corresponding quantification limits were 0.500, 0.170, and 0.300 mg L^{-1}, respectively. Hydrogen peroxide concentration was determined spectrophotometrically measuring the absorbance of the solution at 450 nm after reaction with ammonium metavanadate [28].

2.3.2. SPE conditions

For sulfonamide quantification at μg L^{-1} concentration levels, solid phase extraction (SPE) was carried out at room temperature using a manifold system (Agilent Vac Elut SPS 24). Prior to the addition of 100 mL samples, the stationary phase cartridge had been previously activated by passing through 2.00 mL of methanol followed by 2.00 mL of water. The pH of the solution containing the particular sulfonamide was corrected using either NaOH or H_2SO_4. In preparation for UFLC analysis, the analytes were eluted from the SPE cartridge using 1 mL of acetonitrile + 0.200% acetic acid. In order to optimize the selection of both the stationary phase cartridge and the pH used for sample extraction, three replicates of the SPE procedure for each pH were performed for each sulfonamide. Tukey's multiple comparison significance test (at $p = 0.05$) was applied to assess the existence of significant differences between the results obtained.

2.3.3. UV–visible absorption spectroscopy

The UV–vis absorption spectra were measured with a Varian Cary 50 UV-Vis spectrophotometer using 1 cm path-length quartz cuvette.

3. Results and discussion

Sulfonamide drugs differ in the heterocyclic aromatic group (—R) attached to the amide nitrogen via a carbon atom. A previous study mentions the contribution of the —R group to the reactivity of sulfonamides during photodegradation processes [22]. According to the studies of Vowles and Mantoura [29] and Gawlik et al. [30], the correlation coefficient between the log of the octanol–water partition coefficient (K_{ow}) and the log of the capacity factor (k') is an important parameter describing the hydrophilic behavior of

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