



Research article

Sulfonamides degradation assisted by UV, UV/H₂O₂ and UV/K₂S₂O₈: Efficiency, mechanism and byproducts cytotoxicity



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ABSTRACT

The objective of this study was to analyze the effectiveness of UVC, UVC/H₂O₂ and UVC/K₂S₂O₈ on the degradation of SAs. Rate constant values increased in the order SMZ < SDZ < SML and showed the higher photodegradation of sulfonamides with a penta-heterocycle. Quantum yields were $1.72 \times 10^{-5} \text{ mol E}^{-1}$, $3.02 \times 10^{-5} \text{ mol E}^{-1}$, and $6.32 \times 10^{-5} \text{ mol E}^{-1}$ for SMZ, SDZ and SML, respectively, at 60 min of treatment. R₂₅₄ values show that the dose habitually utilized for water disinfection is inadequate to remove this type of antibiotic. The initial sulfonamide concentration has a major impact on the degradation rate. The degradation rates were higher at pH 12 for SMZ and SML. SMZ and SML photodegradation *k_d* values are higher in tap versus distilled water. The presence of radical promoters generates a greater increase in the degradation rate, UVC/K₂S₂O₈ cost less energy, a mechanism was proposed, and the degradation by-products are less toxic than the original product.

1. Introduction

Ultraviolet radiation (UVC-254nm) is frequently applied to disinfect water intended for human consumption and wastewaters because it is effective to remove organic pollutants due to occupies a small space, and is readily managed and maintained (Lian et al., 2015; Ocampo-Pérez et al., 2010; Prados-Joya et al., 2011). Sulfonamides (SAs) are widely used as antibiotics in human and veterinary medicine due to their strong antimicrobial activity, stable chemical properties, and low cost (Magureanu et al., 2015; Wang and Wang, 2016). SAs have been detected in surface waters at concentrations of 148–2978 ng L⁻¹ (Iglesias et al., 2012). Prolonged exposure to low concentrations of antibiotics that accumulate in waters can be toxic for cells or lead to resistance in bacterial strains, posing a major public health problem (Baran et al., 2006). Previous studies have found that the direct photolysis based in the fluence quantification can be photodegraded only part of SAs during the UVC disinfection of water, SAs with penta-heterocycle are degraded faster (Li et al., 2017; Yang et al., 2017). By UVC-activated hydrogen peroxide (H₂O₂), peroximonosulfate (PMS) and peroxydisulfate (PDS) the SAs oxidation have been studied (Babić et al., 2015; Cui et al., 2016; Zhang et al., 2016b; Zhu et al., 2016). However, these efforts have focused in developed and optimized methods to

determination parameter quantic (direct photolysis) or compare the efficacy of the methods (indirect photolysis). These methods are characterized by generation of oxidizing species such as OH· or SO₄·⁻ radicals, which have a redox potential of 1.8–2.7 V and 2.5–3.1 V, respectively, with the latter being a more selective oxidant (Yang et al., 2017), have been successfully applied to destruct organic micro-pollutants in different water matrices (Souza et al., 2016). The major of studies using the *Vibrio fischeri* bacteria test to determine the toxicity of SAs (Białk-Bielińska et al., 2011; Sági et al., 2018). Knowledge of their byproducts cytotoxicity is still basic and restricted to just a few SAs (Cizmas et al., 2015). HEK 293 cells lack the expression of hormone receptors an important characteristic for studying basal toxicity associated with drugs (Pomati et al., 2006, 2007). The studies that using UV photolysis and its combination with PDS to eliminated sulfonamides still deficient in terms of mechanism, by-products, toxicity and quantification of radicals generated. Therefore, in this study, we evaluate the effectiveness of UVC photolysis, UVC/H₂O₂ and UVC/PDS in the oxidation of three SAs; sulfamethazine (SMZ), sulfadiazine (SDZ) and sulfamethazole (SML). The objectives of our work were to: i) A kinetic study was conducted to determine the quantum yield (Φ_λ) of the UVC photolysis, ii) The influence of different operational variables (initial SAs concentration, oxidant dosage, solution pH, and water matrix) was

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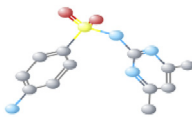
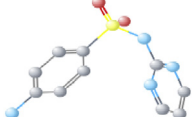
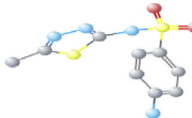
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Table 1
Molecular structure and physicochemical properties of the studied SAs.

Sulfonamide (SA)	Molecular structure	Molecular weight (g mol ⁻¹)	LogK _{ow}	Solubility (mg/L)	pK _a
Sulfamethazine C ₁₂ H ₁₄ N ₄ O ₂ S (SMN)		278.33	0.19	1500 (29 °C)	pK _{a1} : 2.00 pK _{a2} : 6.99
Sulfadiazine C ₁₀ H ₁₀ N ₄ O ₂ S (SDZ)		250.278	-0.09	77 (25 °C)	pK _{a1} : 2.01 pK _{a2} : 6.99
Sulfamethizole C ₉ H ₁₀ N ₄ O ₂ S ₂ (SML)		270.33	0.54	1050 (37 °C)	pK _{a1} : 1.95 pK _{a2} : 6.71

evaluated, iii) The quantification of OH· and SO₄·⁻ radicals generated was determined, iv) Degradation by-products were identified, and v) by-product cytotoxicity in cell HEK-293 was measured.

2. Material and methods

2.1. Chemical substances

All chemical reagents used were high-purity analytical grade reagents supplied by Sigma-Aldrich. All solutions were prepared with ultrapure water obtained using the Milli-Q[®] system (Millipore). Table 1 lists the molecular structures and physicochemical properties of the sulfonamides under study.

2.2. SAs degradation by UVC-254nm

The experimental system for SAs degradation kinetics was in a photoreactor equipped with a low-pressure (254 nm Hg) TNN 15/32 Heraeus Noblelight mercury lamp (nominal power 15 W). Solutions were deposited in six quartz tubes 1 cm in diameter with 35 mL capacity, which were placed in parallel and equidistant to the Hg lamp. The tubes were immersed in recirculating distilled water to maintain a constant temperature of 25 °C, using a Frigiterm ultra-thermostat and magnetic agitation system in each tube. SAs initial concentration was 15 mg L⁻¹, samples were drawn from each solution at regular time intervals for subsequent measurement of the SAs concentration. The influence of experimental parameters such as initial pH (1.5, 6.5 and 12), initial SMZ concentration (5, 10 and 15 mg L⁻¹), oxidant dosage (1.4 × 10⁻⁴ and 4.4 × 10⁻⁴ M) and water matrix (distiller and tap) was investigated.

2.3. Determination of the rate constant of SMZ with OH· and SO₄·⁻ radical

The rate constant of SMZ with OH· and SO₄·⁻ radical was determined in competitive kinetics experiments, using para-chlorobenzoic acid (PCBA) as reference compound for OH· ($k_{OH^*/PCBA} = 5.2 \times 10^9 M^{-1} s^{-1}$) (Kelner et al., 1990) at molar ratio of 1:1 with excess H₂O₂, and using citarabine (CTB) as reference compound for SO₄·⁻ ($k_{OH^*/PCBA} = 5.2 \times 10^9 M^{-1} s^{-1}$) (Ocampo-Pérez et al., 2010) at molar ratio of 1:1 with excess K₂S₂O₈. When $\ln\left(\frac{[SMZ]}{[SMZ]_0}\right)$ is plotted against $\ln\left(\frac{[CTB]_0 + pCBA]}{[CTB]_0 + pCBA]}\right)$, depending on the case, the slope of the graph (k_{ob}) allows the reaction constants of $k_{OH^*/SMZ}$ and $k_{SO_4^{\cdot-}/SMZ}$ radicals to be calculated according to Equations (1) and (2):

$$k_{SO_4^{\cdot-}/CTB} = 1.61 \times 10^9 M^{-1} s^{-1} \quad (1)$$

$$k_{ob} = \frac{k_{SO_4^{\cdot-}/CTB}}{k_{SO_4^{\cdot-}/SMZ}} \quad (2)$$

where k_{ob} is the mean value of the slopes, $k_{ob} = \frac{k_{OH^*/PCBA}}{k_{OH^*/SMZ}}$, are the reaction rate constants, and $k_{SO_4^{\cdot-}/CTB}$ and $k_{OH^*/PCBA}$ are the SMZ reaction rate constants with each radical.

The photodegradation rate constant was determined by applying a pseudo-first-order model and considering 1 h as reaction follow-up time, the quantum yield (Φ_λ) of each SA, the apparent photodegradation rate constant normalized by the lamp energy (k'_E) (constant independent of fluctuations), the molar absorption capacity (ϵ_λ) and R₂₅₄ parameter representing the elimination percentages of SAs in water treatment plants to 400 J m⁻², the radiant energy emitted by the lamp was 8.49 × 10⁻⁴ E m⁻² to 254 nm determined by actinometry (Canonica et al., 1995; Prados-Joya et al., 2011; Sharpless and Linden, 2003).

2.4. Quantification of OH· and SO₄·⁻ radical concentration

The concentration of OH· radical generated was calculated using PCBA. PCBA degradation with OH· radicals were quantified in the UV radiation system, in which radicals are responsible for the oxidation. Total concentrations of OH· radical at different time points were calculated the same way as other authors (Velo-Gala et al., 2017). The concentration of SO₄·⁻ radicals generated were quantified by identifying the reaction by-product, benzoquinone (BQ) (Oh et al., 2017), obtained through oxidation of p-hydroxybenzoic acid (HBA) by the SO₄·⁻ radicals generated in the system under UV radiation. Based on reaction stoichiometry (equation (3)), 1 mol HBA reacts with 1 mol SO₄·⁻ to form hydroquinone, which immediately transforms into a stable by-product, BQ, due to excess PDS. The excess PDS is added outside the UV radiation system.

$$k_{OH^*/SMZ} \text{ and } k_{SO_4^{\cdot-}/SMZ} \quad (3)$$

In general, BQ concentrations are proportional to SO₄·⁻ concentrations. The BQ generated is relatively stable up to pH 9.0, when excess C_{HBA} > C_{BQ}, because HBA inhibits the reaction between BQ and SO₄·⁻, whose constants are $HBA(excess) + SO_4^{\cdot-} \rightarrow hydroquinone + PDS(excess) \rightarrow BQ$.

2.5. Analytical methods

2.5.1. Determination of SAs, PCBA, CTB, and BQ concentration in aqueous solution

Concentration of the SAs was determined by reverse-phase high-performance liquid chromatography (HPLC), using a liquid chromatographer (Thermo-Fisher) equipped with visible UV-detector and

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