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Research article

Degradation of sulfadiazine, sulfachloropyridazine and sulfamethazine in aqueous media

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ABSTRACT

Antibiotics discharged to the environment constitute a main concern for which different treatment alternatives are being studied, some of them based on antibiotics removal or inactivation using by-products with adsorbent capacity, or which can act as catalyst for photo-degradation. But a preliminary step is to determine the general characteristics and magnitude of the degradation process effectively acting on antibiotics. A specific case is that of sulfonamides (SAs), one of the antibiotic groups most widely used in veterinary medicine, and which are considered the most mobile antibiotics, causing that they are frequently detected in both surface- and groundwaters, facilitating their entry in the food chain and causing public health hazards. In this work we investigated abiotic and biotic degradation of three sulfonamides (sulfadiazine –SDZ-, sulfachloropyridazine –SCP-, and sulfamethazine –SMT-) in aqueous media. The results indicated that, in filtered milliQ water and under simulated sunlight, the degradation sequence was: SCP > SDZ ≈ SMT. Furthermore, the rate of degradation clearly increased with the raise of pH: at pH 4.0, half-lives were 1.2, 70.5 and 84.4 h for SCP, SDZ and SMT, respectively, while at pH 7.2 they were 2.3, 9.4 and 13.2 h for SCP, SMT and SDZ. The addition of a culture medium hardly caused any change in degradation rates as compared to experiments performed in milliQ water at the same pH value (7.2), suggesting that in this case sulfonamides degradation rate was not affected by the presence of some chemical elements and compounds, such as sodium, chloride and phosphate. However, the addition of bacterial suspensions extracted from a soil and from poultry manure increased the rate of degradation of these antibiotics. This increase in degradation cannot be attributed to biodegradation, since there was no degradation in the dark during the time of the experiment (72 h). This indicates that photo-degradation constitutes the main removal mechanism for SAs in aqueous media, a mechanism that in this case was favored by humic acids supplied with the extracts from soil and manure. The overall results could contribute to the understanding of the environmental fate of the three sulfonamides studied, aiding to program actions that could favor their inactivation, which is especially relevant since its dissemination can involve serious environmental and public health risks.

1. Introduction

Antibiotics are (and have been for decades) a main and essential resource for the treatment of multiple types of infectious diseases, both in humans and animals (Kumar et al., 2005). However, in recent years its widespread use in intensive livestock, both to treat diseases and to promote growth and improve the efficiency of food has generated serious concerns (Carvalho and Santos, 2016; Sarmah et al., 2006), mainly due to the increase in the diversity and dispersion of organisms resistant to these compounds (Kumar et al., 2005; Pikkemaat et al., 2016). Maron et al. (2013) pointed out that the amount of antibiotics sold in USA for animals destined to food is approximately four times greater than for human use, whereas Van Boeckel et al. (2015) calculated that the world consumption of veterinary antibiotics in livestock in 2010 was approximately 63151 ± 1560 tons, and estimated an increase of 67% for the year 2030, to reach 105596 ± 3605 tons.

Among antibiotics, sulfonamides are one of the most widely used in veterinary medicine (Thiele-Bruhn, 2003). In 2014, sulfonamides were the third group of veterinary antibiotics most used in Europe, reaching 11% of the total sale of antibiotics for veterinary (European Medicines Agency, 2016). Its extensive use is due to their broad spectrum against most Gram-positive organisms and many Gram-negative organisms

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(Baran et al., 2011). Once administered to animals, sulfonamides are poorly absorbed, excreting up to 90% (Sarmah et al., 2006). These excreted antibiotics reach the soil mainly through the spreading of organic amendments or directly through excreta when animals are grazing (Tasho and Cho, 2016). In fact, these antibiotics have been detected both in manures, at concentrations of up to 91 mg kg^{-1} (Martínez-Carballo et al., 2007), and in soils, at concentrations up to 0.18 mg kg^{-1} (Conde-Cid et al., 2018a; Hou et al., 2015).

The massive use of byproducts such as organic fertilizers and slurry derived from animal excreta in agricultural soils can be considered very positive to favor productive and sustainable recycling for such materials, but it has generated concern due to the presence of high levels of various chemical substances and microorganisms (López-Periago et al., 2000, 2002; Núñez-Delgado et al., 1997, 2002), and this concern has reached antibiotics in recent years. In the specific case of sulfonamides, they are considered the most mobile antibiotics, weakly adsorbed on soils, with distribution coefficients (K_d) between 0.6 and 4.6 L kg^{-1} (Sarmah et al., 2006), easily transported to water bodies and absorbed by plants, entering the food chain. In fact, these compounds are frequently detected in surface waters (Binh et al., 2018; Carvalho and Santos, 2016; Kümmerer, 2009; Iglesias et al., 2014; Wei et al., 2011; Yao et al., 2015; Zhang et al., 2011), groundwater (Carvalho and Santos, 2016; Holm et al., 1995; Kümmerer, 2009; Yao et al., 2015) and in different types of crops (Dolliver et al., 2007; Du and Liu, 2012; Hu et al., 2010).

Therefore, the study of the degradation of sulfonamides, both chemical and biological, is crucial to establish the environmental impact of these compounds (Sukul and Spiteller, 2006). Among the different mechanisms of degradation, photo-degradation is considered one of the most important to control the persistence of these compounds in the environment (Batchu et al., 2014a). In this way, Liu et al. (2017, 2018) found that both electro-Fenton and photo-Fenton processes can be appropriate and efficient techniques to achieve high removal rates for antibiotics. In addition, the composition of the aqueous medium can influence the speed of that process, favoring it by catalysis, or inhibiting it. Another important route of chemical degradation for antibiotics in the environment is hydrolysis, which has been highlighted as important for tetracyclines (Kümmerer, 2009; Xuan et al., 2010), but it is not considered as a main degradation mechanism for sulfonamides and macrolides (Kümmerer, 2009).

Regarding microbial degradation, results from different studies are contradictory. Specifically, several authors concluded that sulfonamides are not easily biodegradable (Biošić et al., 2017; Ingerslev and Sørensen, 2000; Lai and Hou, 2008), while other authors have observed biodegradation (Adamek et al., 2016; Li and Zhang, 2010; Zhang et al., 2017). Biošić et al. (2017) studied SDZ degradation in wastewater, finding less than 4% degradation after 20 days. However, Adamek et al. (2016) found > 90% SDZ degradation in a river water sample after 28 days. These divergences can be attributed to differences in the microbial activity of the matrix, to the inoculum, or to differences in the methods used to evaluate biodegradation (Baran et al., 2011).

Taking all that into account, the objective of this work is to study the degradation (both chemical and biological) in aqueous media of three sulfonamides: sulfadiazine (SDZ), sulfachlorpyridazine (SCP) and sulfamethazine (SMT). To achieve this goal, three different types of experiments were carried out (all of them under simulated sunlight and in the dark): (a) using filtered milliQ water at different pH values, aimed to study photo-degradation (under simulated sunlight) and hydrolysis (in the dark), (b) in the presence of a culture medium, in order to determine the influence of different chemical elements present in that medium on the photo-degradation process, and (c) in the presence of soil and poultry manure extracts (bacterial suspensions), to study biodegradation of the three sulfonamides. The methodology used was equivalent to that previously described by Conde-Cid et al. (2018b), performed to study the degradation of three tetracyclines. However, as far as we know, no similar studies have been carried out regarding the degradation of sulfonamides in the substrates and conditions used in the present work.

2. Materials and methods

2.1. Chemicals

All solutions were prepared using milliQ water obtained by means of Millipore equipment (Millipore, Spain). Acetonitrile (HPLC grade) was from Fisher Scientific (Madrid, Spain). The rest of the chemical products used were of high purity analytical grade and were from Panreac (Barcelona, Spain). Sulfadiazine (99.7% purity), sulfachloropyridazine (99.7% purity) and sulfamethazine (99.6% purity) were from Sigma-Aldrich (Madrid, Spain). Table S1 (Supplementary Material) shows the main properties of the three antibiotics used.

2.2. Soil, poultry manure and bacterial suspensions

To study the microbial degradation of the three sulfonamides, two bacterial suspensions were used, one extracted from a soil and the other from a waste material (poultry manure). Both soil and poultry manure were previously used and described by Conde-Cid et al. (2018b) and were characterized with methodologies that are presented in Supplementary Material.

The soil had an acidic pH (4.7 in water and 4.5 in KCl), loam texture (23.1% clay, 32.0 silt and 44.9% sand), 5.3% C and 0.51% N, and an effective cation exchange capacity (eCEC) of 11.65 $cmol_{(+)}kg^{-1}$ (Table S2, Supplementary Material). On the other hand, the poultry manure had a pH in water of 7.8, 31.8% C and 2.93% N.

Bacterial extractions from soil and poultry manure were performed as indicated in Conde-Cid et al. (2018b). More details, as well as methods used to characterize chemical parameters in these suspensions are presented in Supplementary Material.

2.3. Quantification of sulfonamides

The quantification of sulfonamides in the solutions was carried out using a HPLC liquid chromatograph (Dionex Corporation, Sunnyvale, USA) equipped with a P680 quaternary pump, an ASI-100 auto-sampler, a TCC-100 thermostatized column compartment and a UVD170U detector. Chromatographic separations were performed in a Luna C18 column (150 mm long; 4.6 mm internal diameter; 5 µm particle size) obtained from Phenomenex (Madrid, Spain) and a guard column (4 mm long; 2 mm i.d.; 5 µm particle size), packed with the same material as the column. The injection volume was 50 µL and the flow rate 1.5 mL min^{-1}. The mobile phase consisted of acetonitrile (phase A) and 0.01 mol L^{-1} phosphoric acid (phase B). A linear gradient elution program was run from 5 to 32% of phase A (and 95 to 68% of phase B) within 10.5 min. The initial conditions were re-established in 2 min and held for 2.5 min. The total analysis time was 15 min, with a retention time of 5.3 for SDZ, 7.0 for SMT and 9.6 for SCP, and the wavelength used for detection was 270 nm. Some chromatograms are included as example in Supplementary Material (Fig. S1).

2.4. Experiments to study degradation of sulfonamides

As previously made by Conde-Cid et al. (2018b), for tetracyclines, we performed three different kinds of experiments to study kinetics corresponding to sulfonamides degradation in various aqueous media:

i) Experiments with filtered milliQ water. Individual solutions of each of the three sulfonamides (SDZ, SCP and SMT) were prepared at concentrations of 50 µmol L^{-1}. Three individual samples were prepared in vials for each antibiotic and for each period of time used to simulate sunlight exposition (0.5, 1, 2, 4, 8, 12, 24, 48 and 72 h, i.e. between 30 and 4320 min). Then, the vials were

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