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Municipal wastewater spiramycin removal by conventional treatments and heterogeneous photocatalysis

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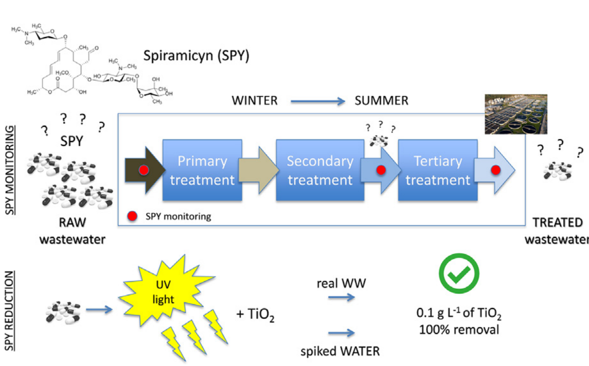
HIGHLIGHTS

- SPY in WWTP before and after wastewater treatment was up to 35 μg L^{-1}.
- SPY reduction was more effective in summer than winter by AS treatment.
- Photocatalysis (winter samples) (0.1 g TiO_2 L^{-1}, 80 min) reduced SPY up to 91%.
- After treatment, ecotoxicity was 7–18% due to residual oxidation by-products.

GRAPHICAL ABSTRACT



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ABSTRACT

This study assessed the effects and removal options of the macrolide spiramycin, currently used for both in human and veterinary medicine- with a special focus on advanced oxidation processes based on heterogeneous TiO_2-assisted photocatalysis. Spiramycin real concentrations were investigated on a seasonal basis in a municipal wastewater treatment plant (up to 35 μg L^{-1}), while its removal kinetics were studied considering both aqueous solutions and real wastewater samples, including by-products toxicity assessment. High variability of spiramycin removal by activated sludge treatments (from 9% (wintertime) to >99.9% (summertime)) was observed on a seasonal basis. Preliminary results showed that a total spiramycin removal (>99.9%) is achieved with 0.1 g L^{-1} of TiO_2 in aqueous solution after 80 min. Integrated toxicity showed residual slight acute effects in the photocatalytic treated solutions, independently from the amount of TiO_2 used, and could be linked to the presence of intermediate compounds. Photolysis of wastewater samples collected after activated sludge treatment during summer season (SPY 5 μg L^{-1}) allowed a full SPY removal after 80 min. When photocatalysis with 0.1 g L^{-1} of TiO_2 was carried out in wastewater samples collected in winter season (SPY 30 μg L^{-1}) after AS treatment, SPY removal was up to 91% after 80 min.

1. Introduction

Antibiotics released into the environment through the wastewater cycle are considered contaminants of emerging concern belonging to

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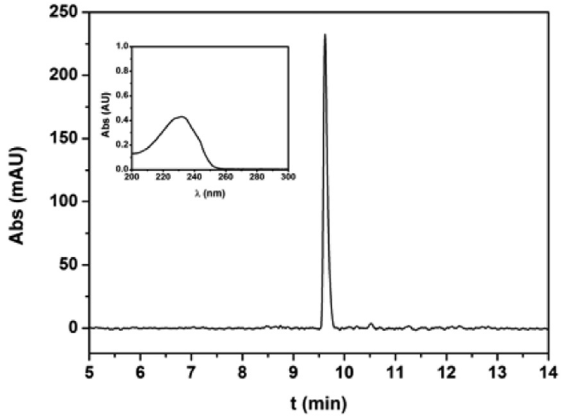

Fig. 1. HPLC chromatogram of SPY; (inlet) UV spectra of SPY.

the class of micro- and nano-pollutants similarly to engineered nanomaterials (Minetto et al., 2016), textile dyes and other textile by-products and personal care residues (Lofrano et al., 2016a; Libralato et al., 2011).

In the European Union between 2010 and 2014, the overall human antibiotic consumption showed a significant increasing trend with a large inter-country dissimilarity (i.e. from 1.1 packages/1000 inhabitants per day in Sweden up to 3.8 packages/1000 inhabitants per day in Italy) (ECDC, 2014). Sarmah et al. (2006) stated that veterinary antibiotics might play a leading role in wastewater contamination largely contributing to the final load of drugs discharged into the environment on a specific geographical basis (e.g. presence of intensive livestock breeding). According to Wang and Tang (2010), the total worldwide amount of used antibiotics (medical and veterinary) reached up to 2 10^5 ton/y. The consumption of antimicrobials by livestock is expected to increase from 63,151 ± 1,560 ton in 2010 to 105,596 ± 3,605 ton in 2030 (Van Boeckel et al., 2015). As antibiotics are poorly adsorbed in animal guts, a great part of them is excreted into faeces and urine, and, frequently, in a form that is not metabolized. When zootechnical wastewater is discharged into sewage (i.e. with or without in situ pre-treatment) and subsequent into municipal wastewater treatment plants (WWTPs), a significant increase in the antibiotic load is expected at the influent (Sarmah et al., 2006). Indeed, several studies showed that conventional WWTPs could not completely remove antibiotics, thus, they can finally enter the aquatic and terrestrial environment via conventional effluent and sewage sludge disposal (Watkinson et al., 2007; Batt et al., 2007; Zuccato et al., 2010; Gracia-Lor et al., 2012; Michael et al., 2013; Birošová et al., 2014). According to Zuccato et al. (2010), wastewater samples from northern Italy WWTPs (Milan, Como and Varese) presented an amount of antibiotics ranging within 115–237 g per 1000 inhabitants per year in both influent and effluent and, thus, being potentially released into the receiving water bodies. Macrolides, particularly clarithromycin, spiramycin, and quinolones are the most abundant antibiotics in untreated wastewater. After penicillin and quinolones, ECDC (2014) estimated that macrolides are the third class of antibiotics consumed in Italy.

Antibiotics both taken singly and as mixtures showed to influence both the structure and function of algal communities (Wilson et al., 2003). They showed to influence the development, transfer, or spread of antibiotics resistant bacteria and/or antibiotics resistant genes in a long-term perspective (Ferro et al., 2015). They can impair human embryonic cells and affect zebrafish liver cells proliferation (Pomati et al., 2006, 2007), but data are still scarce for (environmental) risk assessment.

The environmental concern associated to the release of antibiotics in the aquatic ecosystems is expected to increase over time especially when considering the reuse of conventionally treated wastewater (e.g. industry, hospital and household) increasing the risk of drinking water contamination and, thus, non-voluntary human exposure (Kim and Aga, 2007; Benotti et al., 2008). Consequently, the European Commission updated the (Watch List, 2015) of substances for Union-wide monitoring (Commission Implementing Decision 2015/495) including erythromycin, clarithromycin, and azithromycin.

To face up the antibiotic removal, the performance of traditional activated sludge (AS) WWTP should be improved including further treatments like advanced oxidation processes (AOPs) such as ozonation, Fenton, photo-Fenton oxidation, and heterogeneous photocatalysis that are gaining growing interest as complementary treatments (De Luca et al., 2013; Carotenuto et al., 2014; Lofrano et al., 2016b; Lofrano et al., 2017; Rasheed et al., 2017a, 2017b). Among AOPs, TiO_2-assisted photocatalysis is being considered as an effective and sustainable technology for the degradation and detoxification of complex organic chemicals (Vaiano et al., 2015). The photocatalytic process consists in utilizing the ultra-violet (UV) irradiation ($\lambda < 380$ nm) to photoexcite a semiconductor catalyst in presence of oxygen. Within this scenario, oxidizing species (i.e. bound hydroxyl radical (•OH) or free holes) attack oxidable substances producing a progressive breaking down of macromolecules yielding to CO_2, H_2O and diluted inorganic acids. The most commonly used catalyst is the semiconductor TiO_2, mainly because it is an abundant, non-expensive, and relatively low toxic product (Malato et al., 2002).

Nevertheless the huge amount of papers about AOPs, gaps into the knowledge about the proper management of antibiotics in wastewater treatment is still present mainly due to the absence of toxicity identification evaluation of treated effluents that only rarely consider a complete battery of toxicity tests and final toxicity data integration. Scarce information exists about spiramycin (SPY) behaviour in wastewater. SPY is a macrolide antibiotic widely used to treat human (e.g. oropharynx, respiratory system, and genito-urinary tract) and veterinary infections (e.g. cryptosporidiosis and toxoplasmosis). This research investigated on a seasonal basis SPY presence in wastewater samples collected before and after treatment in a municipal AS WWTP (Campania Region, Italy) to monitor the state-of-the-art and assess the potentiality for its reduction/removal at real scale via AOPs. The photocatalytic degradation of SPY was evaluated by using a range of TiO_2 concentrations both in biologically treated wastewater samples and aqueous solutions. Photodegradation by-products were investigated, and toxicity of samples using a full battery of bioassays was provided to complete the characterization of the performance of the treatment process.

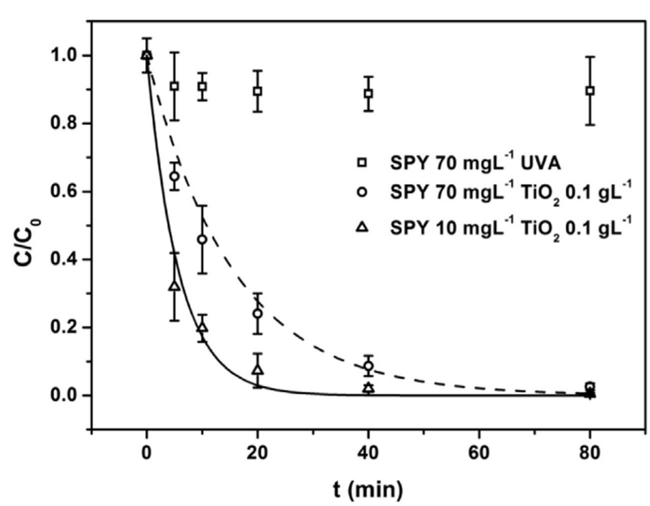

Fig. 2. Photocatalytic kinetic curves of SPY (10 and 70 mg L^{-1}) after 5, 20, 40, 80 min at 0.1 g L^{-1} of TiO_2 at pH 5.5; error bars represent standard error (n = 3).