Chemosphere 180 (2017) 523–530

Contents lists available at ScienceDirect

Chemosphere

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

Sulfonamides photoassisted oxidation treatments catalyzed by ilmenite

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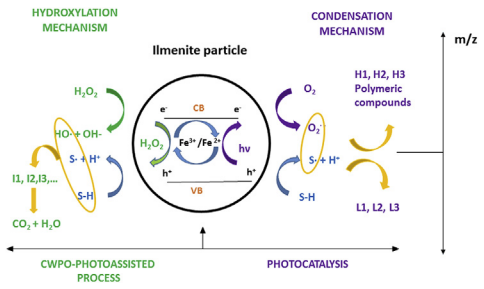
HIGHLIGHTS

- Two AOPs with ilmenite as catalyst were employed for sulfonamides degradation.
- Total conversion of sulfonamides were reached within 30 min reaction time.
- Huge differences in TOC conversion were observed for each process.
- In CWPO-Photoassisted process prevailed an hydroxylation mechanism.
- In photocatalysis prevailed a condensation mechanism.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 December 2016
Received in revised form
24 March 2017
Accepted 11 April 2017
Available online 18 April 2017

Handling Editor: Jun Huang

Keywords:
Raw ilmenite
CWPO-Photoassisted
Photocatalysis
Radical organic condensation
Advanced oxidation processes
Hydroxyl radical

ABSTRACT

This work assesses the feasibility of several advanced oxidation processes (CWPO *Catalytic Wet Peroxide Oxidation*), Photocatalysis and their combination (CWPO-Photoassisted process) for sulfonamide antibiotic degradation. Raw ilmenite was used as catalyst in both processes, because of the presence of iron and titanium in its structure.

Despite both treatments allowed reaching a total starting antibiotic depletion working at $pH_0 = 3$ and $T_0 = 30\ ^{\circ}C$ within 30 min reaction time, significant differences were observed in terms of mineralization. Thus, whereas photocatalytic process just reduced 35% of initial TOC after 120 min, a 85% of mineralization was reached in the presence of H_2O_2 (CWPO-Photoassisted process) which was related to the oxidation pathway. Only a 35% of mineralization was reached in case of CWPO. In this sense, the degradation route under CWPO-Photoassisted process displayed a mechanism based on the hydroxylation that led to lower molecular weight intermediates. On the contrary, under photocatalysis conditions, the appearance of higher molecular weight intermediates due to organic radical recombination indicates the prevailing of a condensation mechanism.

1. Introduction

Water is a valuable resource for living organisms and also for human domestic, agricultural or industrial activities. In the last decades, the European Union (EU) has made several efforts to improve and protect the quality of water resources through different legislations. The European Water Framework *Directive 2000/60/CE* established a list of priority substances that must receive special attention to be removed from wastewater (including selected existing chemicals, herbicides, biocides, metals, groups

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http://dx.doi.org/10.1016/j.chemosphere.2017.04.047
0045-6535/

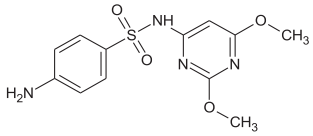
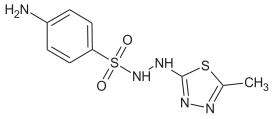
like polyaromatic hydrocarbons (PAHs) and poly-brominatedbiphenylethers (PBDEs), …).

However, there is still a lack of legislation about the so-called emerging contaminants (ECs) whose presence in wastewater is raising due to the population growth, a widespread use and the poor elimination in the current wastewater treatment plants (WWTPs) since these facilities are not designed for the specific degradation of these compounds (Tijani et al., 2013). This provokes their detection in surface water, ground water and even in drinking water at concentrations between $ng \cdot L^{-1}$ and $\mu g \cdot L^{-1}$ (Verlicchi et al., 2012a,b). Among these pollutants, components of personal care products and pharmaceutical formulations are found. Recently, EU reported the first watch list of substances to be monitored in its Decision *2015/498/EU* (Barbosa et al., 2016).

Among ECs, antibiotics deserve a special attention. This group begins to be legislated (Barbosa et al., 2016) because of their negative effects on microorganisms and aquatic species and their toxicity, which can produce risks to human health through drinking water and food chain. For instance the median EC_{50} value obtained for different toxicity tests (including *Vibrio fischeri*) of sulfonamide is between 1 and 100 mg L^{-1} (Petrie et al., 2015). Despite this, Bialk-Bielinska (Bialk-Bielinska et al., 2011) also studied the EC_{50} of different sulfonamides. In case of *Lemna minor* (a kind of plant), the EC_{50} was less than 1 mg L^{-1}. EC_{50} obtained with *Vibrio fischeri* test showed a value of >50 mg L^{-1}, similar to other authors. In this sense, sulfonamides could not be considered toxic compounds. Nevertheless, these compounds can have toxicity associated to the accumulation. Zhao (Zhao et al., 2015) studied such bio-accumulation in liver and muscles of fishes, concretely in carps (*Cyprinus carpio*). Their results proved that such bioaccumulation increased with low-dose exposition. Otherwise, the overall eco-toxicity of a complex mixture of these antibiotics in water could be higher than the presence of a single component.

The presence of sulfonamides in the WWTP effluents constitute the main source of these contaminants into the environmental. These compounds, persistent over time, could suffer biological, chemical and physical changes and could be the result of natural photochemical reactions of such sulfonamides in surface water. In this sense, these pharmaceutical compounds and their degradation products have been frequently detected (around 4 mg L^{-1}) in rivers

Table 1
Chemical structure of Sulfonamides.

Pharmaceutical compound	Sulfadimethoxine (SFX)	Sulfamethizole (SFZ)
Molecular formula	$C_{12}H_{14}N_4O_4S$	$C_9H_{10}N_4O_2S_2$
Structure		
Molecular weight	310 g mol^{-1}	270 g mol^{-1}

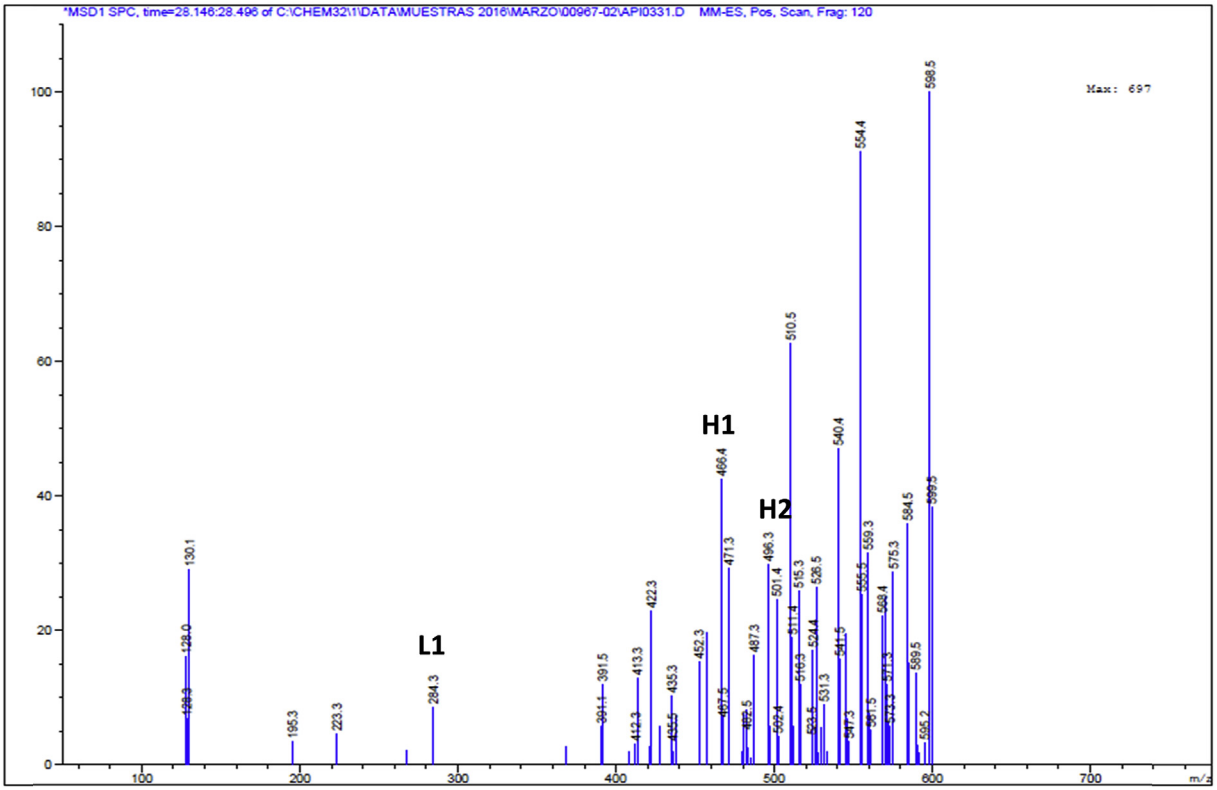


Fig. 1. SFZ spectrum during photocatalytic process.