



# Mineralization of synthetic and industrial pharmaceutical effluent containing trimethoprim by combining electro-Fenton and activated sludge treatment



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## ABSTRACT

A combined process coupling of an electro-Fenton and a biological degradation was investigated in order to mineralize synthetic and industrial pharmaceutical effluent containing trimethoprim, a bacteriostatic antibiotic. Electro-Fenton degradation of trimethoprim was optimized by means of a Doehlert experimental design, showing that 0.69 mM Fe<sup>2+</sup>, 466 mA and 30 min electrolysis time were optimal, leading to total trimethoprim removal, while mineralization remained limited, 12% for 30 min electrolysis times. The aromatic and aliphatic by-products were identified and a plausible degradation pathway was proposed. Biodegradability was improved, since the BOD<sub>5</sub>/COD ratio increased from 0.11 initially to 0.32 and 0.52 after 30 and 60 min electrolysis times respectively, confirmed by activated sludge culture, 47 and 59% mineralization of the byproducts from electrolysis.

The relevance of the proposed combined process was then confirmed on an industrial pharmaceutical effluent. Its electrolysis under the above conditions showed an almost total removal of trimethoprim after 180 min of electrolysis, while TOC removal remained low, 14 and 16% for 180 and 300 min reaction times, respectively. Overall removal yields of the industrial effluent during the combined process were therefore 80 and 89% for 180 and 300 min of effluent pretreatment followed by 15 days activated sludge culture, respectively.

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## 1. Introduction

In the last years, antibiotics were considered to be an emerging environmental problem due to their continuous entry and persistence in the aquatic ecosystem [1]. The pollution proceeds from human excretion after drug administration and passes through wastewater treatment plants (WWTPs). Comparatively, veterinary antibiotics do not undergo WWTPs treatment and may directly enter surface water. Animal manure, dispersed in the fields as fertilizer, can contaminate soil and consequently surface and groundwater [2]. Moreover, waste effluents from manufacture can also be considered as significant points of contamination [3].

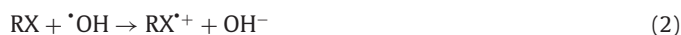
Most conventional treatments applied in WWTPs were unsuccessful in the removal of antibiotics [4–6]. Consequently, the accumulation and persistence of these compounds in the environment can threaten aquatic and terrestrial ecosystems [1]. Moreover, antibiotics residues in water are also suspected to be responsible for the production of resistant microorganisms, causing serious problems of public health, namely difficulties in treating pathologies and imbalance of microbial ecosystems [7]. Therefore, efficient and economical methods must be developed as an urgent need to remove these pollutants.

Advanced oxidation processes (AOPs) are potentially powerful methods; they are based on the generation of hydroxyl radicals (<sup>•</sup>OH) which are very reactive and non-selective oxidizing agents, leading to the degradation of organic pollutants by hydrogen atom abstraction reaction (Eq. (1)), electron transfer (Eq. (2)), or electrophilic addition to  $\pi$  systems (Eq. (3)) [8–12]. These processes involve chemical, photochemical or electro-chemical techniques such as Fenton,

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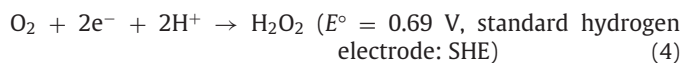
UV/ or H<sub>2</sub>O<sub>2</sub>/ozonation, photo-Fenton, heterogeneous photocatalysis and electro-Fenton [11–15].



Nevertheless, AOP used for complete mineralization can be expensive, and hence its combination with a biological treatment can significantly reduce operating costs [16]. This combination is especially suitable when microorganisms present in activated sludge are not able to metabolize the parent compound; the AOP, applied as a pre-treatment step, may enhance the overall biodegradability by transforming this parent compound into easily biodegradable and less toxic intermediates, preventing cellular lysis [1,17,18].

The present work intends to perform three objectives. The first one is the use of Doehlert methodology design to optimize the electro-Fenton operating conditions for the removal of trimethoprim (TMP) *i.e.* its degradation into organic by-products; the second aim is to combine electro-Fenton process and biological treatment for the mineralization of TMP *i.e.* its transformation into water, carbon dioxide and inorganic ions; and the last one is the validation of the combined process through the remediation of an industrial pharmaceutical effluent.

Electro-Fenton is an electrochemical advanced oxidation process based on the continuous generation of H<sub>2</sub>O<sub>2</sub> in an acidic medium through the electrochemical reduction of O<sub>2</sub> at the cathode (Eq. (4)). The generated H<sub>2</sub>O<sub>2</sub> reacts with the added Fe<sup>2+</sup> ions to produce hydroxyl radicals ( $\cdot\text{OH}$ ) and Fe<sup>3+</sup> ions via the Fenton's reaction (Eq. (5)), which is favored by the catalytic action of the Fe<sup>3+</sup>/Fe<sup>2+</sup> system, mainly from the regeneration of Fe<sup>2+</sup> by the cathodic reduction of Fe<sup>3+</sup> (Eq. (6)) [8,11,13,19]. At the anode, oxygen is formed by the oxidation of water (Eq. (7)). Moreover, the method and the involved reactor are easy to handle and to use.



As mentioned above, the chosen target compound is trimethoprim (C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>, 290.32 g/mol, CAS 738-70-5), a bacteriostatic antibiotic commonly prescribed in combination with sulfamethoxazole for the treatment of infectious diseases in humans. It is also widely used in veterinary medicine, for prevention and treatment of infections and as a growth promoter. The removal of TMP in wastewater treatment plants has been reported to be less than 10% [20]. Therefore, the TMP (water solubility of 400 mg/L at 25 °C) has been detected in many environmental monitoring studies in the concentration range of μg/L (0.1–5 μg/L) in WWTP effluents [21].

## 2. Materials and methods

### 2.1. Chemicals

Trimethoprim (98%) was purchased from Sigma Aldrich (Saint Quentin Fallavier, France). FeSO<sub>4</sub>·7H<sub>2</sub>O (purity 99%) and Na<sub>2</sub>SO<sub>4</sub> (purity 99%), used as a catalyst source and inert supporting electrolyte respectively, were provided from Acros Organics (Thermo Fisher Scientific, Illkirch, France). Acetonitrile (purity 99.9%) (HPLC grade) was

also obtained from Sigma Aldrich. The initial pH of the solutions was adjusted using analytical grade sulfuric acid from Acros. All solutions were prepared in ultra-pure water and all the other chemicals used for analysis were purchased from Acros Organics and Sigma Aldrich.

### 2.2. Characterization of the pharmaceutical effluent

The effluent used in this study was supplied by a pharmaceutical industry located in north Tunisia, collected in a container, closed and stored in obscurity at 4 °C. This effluent contained a high TMP concentration of 3.56 g/L and was characterized by a conductivity of 4.36 mS/cm, a COD of 438.50 g/L and a TOC of 125.40 g/L. Before treatment, the effluent was diluted to obtain an initial TMP concentration of 0.2 mM, in order to conduct the treatment in the same conditions as the synthetic solution.

### 2.3. Analytical determinations

#### 2.3.1. High performance liquid chromatography (HPLC)

The evolution of trimethoprim concentrations was monitored by HPLC using a Waters 996 system equipped with Waters 996 PDA (Photodiode Array Detector) and Waters 600LCD Pump. The separation was achieved on a Waters C<sub>18</sub> (5 μm; 4.6 mm × 250 mm) reversed-phase column. The eluent consisted of a mixture of acetonitrile/ultra-pure water (20/80, v/v) buffered at pH 3 with phosphoric acid and 0.01M Na<sub>2</sub>HPO<sub>4</sub>, delivered at a flow rate of 1 mL/min. Detection of trimethoprim was carried out at 204 nm.

#### 2.3.2. Chemical oxygen demand (COD) measurements

Chemical oxygen demand (COD) was measured by means of Nanocolor<sup>®</sup> tests CSB 160 and 1500 from Macherey-Nagel (Düren, Germany). The amount of oxygen required for the oxidation of the organic and mineral matter at 148 °C for 2 h was quantified after oxidation with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at acidic pH [22].

#### 2.3.3. Total organic carbon (TOC) measurements

The solutions were filtered on Sartorius Stedim Minisart 0.40 μm GF prefilters (Goettingen, Germany). TOC was measured by means of a TOC-V<sub>CPH/CPN</sub> Total Organic Analyzer Shimadzu. Organic carbon compounds were combusted and converted to CO<sub>2</sub>, which was detected and measured by a non-dispersive infrared detector (NDIR). Reproducible TOC values were always obtained using the standard NPOC (non purgeable organic carbon) method. For each sample, each measurement was triplicated [16].

#### 2.3.4. Activated sludge preparation

Activated sludge used in this study was collected from a local wastewater treatment plant (Rennes Beaurade, Bretagne, France). It was washed several times by successions of centrifugation, supernatant withdrawing and resuspension of pellet in water, in order to remove any residual carbon or mineral nutrients.

#### 2.3.5. Biological oxygen demand (BOD<sub>5</sub>) measurements

BOD<sub>5</sub> measurements were carried out in Oxitop IS6 (WTW, Alès, France). The following mineral basis was used for all experiments (g/L): MgSO<sub>4</sub>·7H<sub>2</sub>O, 22.50; CaCl<sub>2</sub>, 27.50; FeCl<sub>3</sub>, 0.15; NH<sub>4</sub>Cl, 2.00; Na<sub>2</sub>HPO<sub>4</sub>, 6.80; KH<sub>2</sub>PO<sub>4</sub>, 2.80. Washed activated sludge was added in order to have 0.05 g/L initial concentration of dry matter. The BOD<sub>5</sub> value was initially estimated based on the COD value experimentally measured, BOD<sub>5</sub> = COD/1.46. The range of expected BOD<sub>5</sub> measurement was then deduced and hence led to the volumes of sample of activated sludge solution and nitrification inhibitor (10 mg/L solution of N-allylthiourea) which have to be added to the shake flask of the Oxitop apparatus. Similar protocol was applied for the control sample except that it was replaced by a solution of easily biodegradable compounds, namely glutamic acid (150 mg/L) and glucose (150 mg/L).

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