



Kinetics of oxidative degradation/mineralization pathways of the antibiotic tetracycline by the novel heterogeneous electro-Fenton process with solid catalyst chalcopyrite

Natija Barhoumi^{a,b}, Hugo Olvera-Vargas^b, Nihal Oturan^b, David Huguenot^{a,b,c,d}, Abdellatif Gadri^e, Salah Ammar^e, Enric Brillas^d, Mehmet A. Oturan^{b,*}

^a Département de chimie Faculté des Sciences de Gabès, Cité Erriadh, Université de Gabès, 6027 Gabès, Tunisia

^b Université Paris-Est, Laboratoire Géomatériaux et Environnement, EA 4508, UPEM, 5 Bd Descartes, 77454 Marne-la-Vallée, Cedex 2, France

^c Département de chimie Faculté des Sciences de Bizerte, Cité Zarzouna, Université de Carthage, Tunisia

^d Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

^e Unité de recherche Electrochimie, Matériaux et Environnement UREME (UR17ES45), Faculté des Sciences de Gabès, Université de Gabès, Cité Erriadh, 6072 Gabès, Tunisia

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ABSTRACT

The degradation of solutions of the antibiotic tetracycline (TC) has been studied by a novel electrochemical advanced oxidation process, consisting in electro-Fenton (EF) process using chalcopyrite as heterogeneous catalyst. In fact, chalcopyrite powder was the source of Fe^{2+} and Cu^{2+} ions instead of a soluble catalyst salt used in conventional EF. Experiments were performed in an undivided cell equipped with a Pt or boron-doped diamond (BDD) anode and a carbon felt cathode, where TC and its oxidation intermediate products were destroyed by hydroxyl radicals ($\cdot\text{OH}$) formed both, in the bulk solution from electrochemically induced Fenton's reaction (Fe^{2+} and H_2O_2) and Fenton's-like reaction (Cu^+ and H_2O_2), and at the anode surface from water oxidation. The effects of operating parameters such as applied current, chalcopyrite concentration and anode material were investigated. TC decay followed pseudo-first-order reaction kinetics. The absolute rate constant for TC oxidation by $\cdot\text{OH}$ was found to be $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, as determined by the competition kinetic method. EF process using chalcopyrite as heterogeneous catalyst showed to be more efficient than conventional EF, achieving almost total mineralization of the TC solution (98% of total organic carbon removal) after 360 min under optimum operating conditions. A plausible mineralization pathway for mineralization of TC aqueous solution by $\cdot\text{OH}$ was proposed based on the identification of different oxidation by-products. Moreover, toxicity tests pointed out that this heterogeneous EF process was able to detoxify the TC solutions.

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1. Introduction

The presence of pharmaceuticals in the aquatic environment is now well recognized as an important issue, causing long-term adverse impacts on the ecosystems and human health [1,2]. Pharmaceutical industries, hospitals and urban wastewater effluents are important points of drug discharge into the environment, leading to a significant effect on the physical, chemical and biological composition of water bodies [3]. Among drugs, antibiotics are

widely used in human and veterinary medicine to treat diseases. The presence of low levels of antibiotics and their transformation products in the environment could have adverse effects, such as bacterial resistance and disruption of key cycles critical to aquatic ecology or crop and animal production [4,5]. Because of their recalcitrant character, antibiotics, and drugs in general, are ineffectively removed in conventional wastewater treatment plants [2,5,6]. Nevertheless, advanced oxidation processes (AOPs) have proved to be a suitable alternative for rapid degradation of recalcitrant and non-biodegradable compounds in water [7,8]. Among them, electrochemical advanced oxidation processes (EAOPs) have received great attention over the last decade as an effective and suitable technology for the remediation of wastewater contaminated with toxic and persistent organic pollutants [9–11].

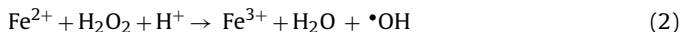
* Corresponding author.

E-mail addresses: mehmet.oturan@univ-paris-est.fr, mehmet.oturan@u-pem.fr (M.A. Oturan).

One of the most attractive EAOPs is the electro-Fenton process (EF), in which H_2O_2 is formed by the two-electron reduction of dissolved O_2 (Eq. (1)) at a suitable carbonaceous cathode, such as graphite, carbon felt, reticulated vitreous carbon, gas diffusion electrodes (GDE), boron-doped diamond (BDD), carbon nanotubes, activated carbon fiber, and so on [12–18].



In acidic medium, the oxidizing power of H_2O_2 is strongly enhanced by the addition of a catalytic amount of Fe^{2+} (or Fe^{3+}) ions, which promotes the generation of homogeneous $\bullet\text{OH}$ via Fenton's reaction (Eq. (2)). Furthermore, Fe^{2+} ions are rapidly regenerated from reduction of Fe^{3+} ion at the cathode according to Reaction (3) [12].

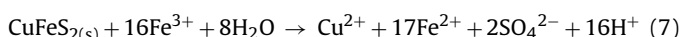
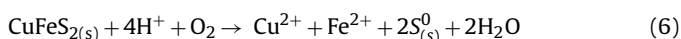
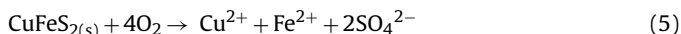


When a non-active anode material (M) with a high O_2 evolution overpotential such as BDD is used in EF process, heterogeneous $\text{M}(\bullet\text{OH})$ radicals are also formed at the anode surface by water oxidation (Eq. (4)), whence enhancing the efficiency of the process [19,20]. BDD electrodes are currently the most powerful and preferred anodes for electrochemical oxidation [10,21,22].



EF process is typically performed using soluble ferric salts as catalyst (Fe^{2+}) source. However, other transition metals have also been used to promote Fenton like reaction, such as Cu^{2+} ions, showing good results [23,24]. On the other hand, the use of alternative heterogeneous catalyst has been proposed aiming to enhance the effectiveness of Fenton's-based processes with parallel sustainability purposes. These "green" catalysts containing Fe and/or Cu solids include pyrite (FeS_2), chalcocite (Cu_2S), bornite (Cu_5FeS_4), magnetite (Fe_2O_3) or wustite (FeO) [25–28].

On the other hand, the chalcopyrite is one of the most important copper sulfide minerals in the world [29,30]. It can release Cu^{2+} and Fe^{2+} ions in aqueous solution according to Reactions (5)–(7) [30]. In the present work, we explore the novel possibility of using this mineral for catalyzing the EF process (EF/Chalcopyrite) during the degradation of synthetic aqueous solutions of antibiotic tetracycline (TC).



In addition of self-regulation of catalyst, chalcopyrite allows also the self-regulation of solution pH. Taking into account that pH values around 3 constitute the optimum values for Fenton's reaction, reaction (Eq. (7)) becomes highly important being as the release of H^+ contributes to the acidification of the solution, thus the use of mineral acids for pH adjustment becomes unnecessary.

TC is an antibiotic extensively used for disease control due to their great therapeutic values. It is also widely used in livestock feed to prevent illness and promote growth. Its detection in aquatic systems and soils has raised concern about its biological impacts and potential risks to the environment, as well as to public health [31]. Due to its large global consumption, it was chosen

as a model molecule for assessing the efficiency of the innovative EF/Chalcopyrite heterogeneous process.

Interestingly, in a recent study, synthesized chalcopyrite nanocrystals supported on sawdust were applied for the degradation of organic dyes in a filtration column in which H_2O_2 was externally supplied [32]. Although high efficiency was obtained for the discoloration of dye solutions (via Fenton's reaction), any data on mineralization of the dyes to CO_2 , H_2O and inorganic ions was not reported. However, these results highlighted the potential of chalcopyrite as catalyst for Fenton-based processes, among which EF presents several advantages as discussed above.

This work hence presents a thorough assessment of the performance of the EF/Chalcopyrite process through examination of the main operating parameters affecting degradation and mineralization efficiencies, such as catalyst concentration, applied current, and the effect of the anode material. Additionally, a comparative study with homogeneous EF using Fe^{2+} and Cu^{2+} ions as catalyst is presented. The identification of aromatic intermediates, as well as short-chain carboxylic acids and inorganic ions formed during EF/Chalcopyrite treatment of TC, allowed the proposal of a mineralization pathway of the drug with $\bullet\text{OH}$. Moreover, toxicity evaluation throughout electrolysis by means of the Microtox method is presented.

2. Materials and methods

2.1. Chemicals

Analytical grade TC ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$) with purity >98%, was purchased from Fluka and was used in the electrolytic experiments without further purification. Anhydrous sodium sulphate, used as background electrolyte, as well as H_2SO_4 and NaOH were provided from Acros Organics. Heptahydrated iron (II) sulphate and copper (II) sulphate pentahydrate used as catalysts in conventional EF were of analytical grade from Acros Organics. All solutions were prepared with ultrapure water from a Millipore Milli-Q system (Molsheim, France) with resistivity >18 $\text{M}\Omega\text{ cm}^{-1}$. Carboxylic acids were of reagent grade supplied by Sigma-Aldrich and Merck.

The sonication was made in a BRANSON 2510 equipment with 40 kHz frequency and 237 W energy intensity.

2.2. Characterization of chalcopyrite powder

Chalcopyrite (CuFeS_2) used in this work was mined from Tunisia. It was milled with a ceramic mortar and sieved (<80 μm). To remove surface impurities, the resulting powder was ultrasonicated in 95% ethanol for 5 min (using a BRANSON 2510 equipment with 40 KHz frequency and 237 W energy intensity) and then washed with 1 M HNO_3 , rinsed with deionized water, further with 95% ethanol and finally dried at 30 °C. Table 1 collects the composition found by inductively coupled plasma spectrometry (ICP) analysis of the powder dissolved in 16 M HNO_3 . The great purity of the sample prepared with 1 g L^{-1} in mass of CuFeS_2 , corresponding to 27% in mass of iron and 21% in mass of copper, is worth noting. The crystal structure of chalcopyrite powder was characterized by X-ray diffraction (XRD) using a SIEMENS D5000 diffractometer with secondary graphite monochromator and $\text{CuK}\alpha$ radiation. XRD spectrum depicted in Fig. 1, shows a series of peaks, which are in

Table 1
Chemical composition of the chalcopyrite powder used in this study.

Element	Fe	Cu	S	Zn	Pb	Al	Cd	Cr	Ni	Co	Mn	Ca	Mg
Mass (%)	27.03	21.0	47.72	0.25	0.49	0.52	0.31	0.25	0.26	0.25	0.45	0.97	0.49

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