



Electrochemical removal of pharmaceuticals from water streams: Reactivity elucidation by mass spectrometry



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ABSTRACT

Electrochemical technology has attracted increasing interest in recent years as an environment-friendly solution to many industrial problems and challenges. First, we give an overview on the fundamentals of electrochemical processes for the removal of pharmaceuticals from water, particularly electrochemical oxidation and Fenton-based processes, such as electro-Fenton and ultraviolet (UV) and solar photoelectro-Fenton, that have improved performance. We also mention other less studied methods, although the main focus is on reactivity elucidation by chromatography with UV or conductivity detection, especially by mass spectrometry techniques (e.g. coupled to gas chromatography or liquid chromatography), in order to discuss the degradation pathways of pharmaceuticals on the basis of the reactive species electrogenerated in each technology. In some cases, simultaneous assessment of toxicity adds crucial information for the future integration of these technologies in water-treatment facilities where pharmaceuticals and their byproducts can occur.

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1. Introduction

Over the past 20 years, the role of pharmaceuticals as potential bioactive chemicals in the environment has received increasing attention [1]. Thousands of tons of these compounds are yearly produced worldwide for usage in human and veterinary medicines, and agricultural and consumer products. Consequently, their occurrence in the aquatic environment may arise from direct

disposal, excretion and treatments in animal-feeding operations, such as aquaculture [2]. The inefficient removal of these pharmaceuticals by conventional processes used in wastewater-treatment facilities (WWTFs) causes the presence of a large plethora of drugs and metabolites in surface, ground and drinking waters at contents from nanograms to micrograms per liter (ng/L to µg/L) [1,2]. These pollutants affect the quality of water and are considered emerging pollutants, since they are unregulated, thus becoming potentially toxic for ecosystems and living beings. Even low drug contents can favor the development of multi-resistant strains of microorganisms, may affect the endocrine system of fishes and can exert toxic effects on algae and invertebrates [2,3]. Furthermore, the toxicity of complex drug cocktails, such as those routinely detected,

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has seldom been predicted [1]. Many research efforts are being devoted to develop efficient techniques for total removal of pharmaceuticals and their products from water.

Recent reviews described effective methods, such as advanced oxidation processes (AOPs), for the remediation of water containing pharmaceuticals [1,3–7]. AOPs are considered environmentally-friendly technologies because no hazardous additives or only small amounts of non-toxic substances are added to the solution. They are chemical, photochemical or electrochemical methods that allow the *in-situ* generation of the hydroxyl radical ($\cdot\text{OH}$), which is the second strongest oxidizing agent known (after fluorine). Due to its high standard redox potential [$E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$], it is able to react non-selectively with most organics via dehydrogenation or hydroxylation steps until their total mineralization to CO_2 , H_2O and inorganic ions [1,3]. Recently, several electrochemical AOPs (i.e. EAOPs) were developed and applied to the treatment of pharmaceuticals in water [3]. The most promising EAOPs are electrochemical oxidation (EO) and indirect methods [e.g. electro-Fenton (EF), photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF)], because they show great ability to mineralize drugs and their metabolites from wastewater. Simpler electrochemical separation technologies, such as electrodialysis and electrocoagulation, already available at industrial scale, transfer only the pollutants out of the contaminated water.

Fig. 1 presents the main analytical methods used to check the viability of electrochemical destruction technologies, such as the

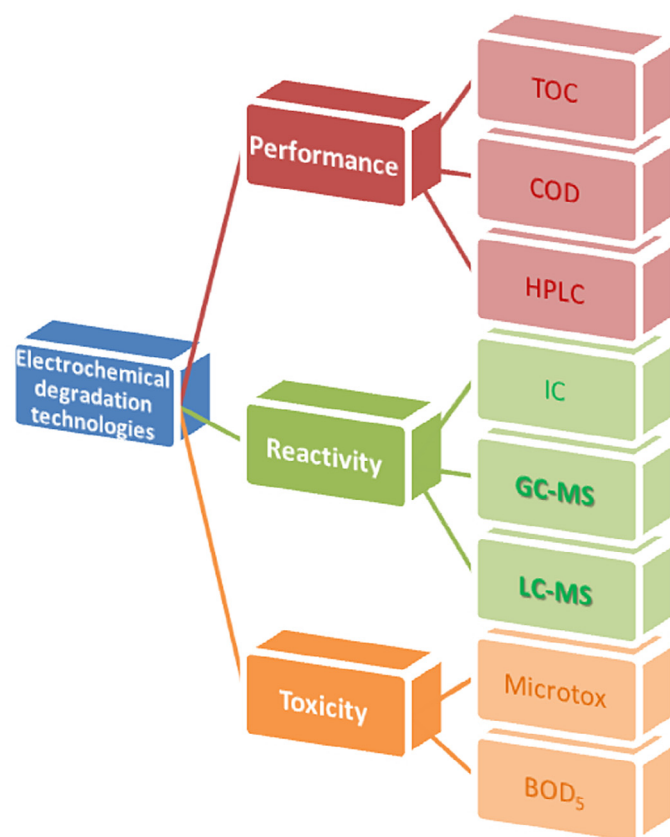


Fig. 1. Analytical techniques to test the viability of new devices aimed at applying electrochemical degradation technologies. Performance assessment: TOC, Total organic carbon; COD, Chemical oxygen demand; HPLC, High-performance liquid chromatography. Reactivity assessment: IC, Ion chromatography; GC-MS, Gas chromatography-mass spectrometry; LC-MS, Liquid chromatography-mass spectrometry. Toxicity assessment: Microtox method, based on determining the bioluminescence inhibition of the marine bacteria *Vibrio fischeri*; BOD_5 , Biological oxygen demand after 5-day incubation.

EAOPs for water remediation. First, their performance may be assessed in terms of:

- 1 organics mineralization from the decay in total organic carbon (TOC) of the solution;
- 2 organics oxidation from the abatement of chemical oxygen demand (COD); and,
- 3 decay kinetics of initial pollutant, determined from reversed-phase high-performance liquid chromatography (RP-HPLC).

Note that GC can be used instead of HPLC whenever the nature of the pharmaceutical and/or its matrix allows simpler analysis. These results should comply with economic criteria, which are intimately related to the electrolysis time factor, since the electrical costs may determine the viability, so they are usually accompanied by estimated figures of merit [e.g. mineralization current efficiency (MCE) and energy consumption]. In this regard, the recent use of photovoltaic systems as a source of power for the electrochemical reactors opens the door to cut energy costs [8].

A second, crucial task concerns reactivity assessment, which is aimed at elucidating the reaction sequence undergone by the drugs, involving the detection of cyclic/aromatic products and short-chain aliphatic carboxylic acids using GC-mass spectrometry (MS) and LC-MS, as well as inorganic ions released by ion chromatography (IC). These analyses are related to technological criteria because knowledge of the gradual transformation of initial pollutants can optimize the integration of novel electrochemical methods on current WWTFs through their smart coupling with pre-existing technologies. Thus, the use of GC-MS and LC-MS becomes mandatory for this purpose.

A third kind of study to evaluate the viability of an electrochemical treatment correctly is related to environmental criteria, and may be performed on the basis of the evolution of solution toxicity with time, which usually arises from the standard Microtox test or determination of biological oxygen demand after 5-day incubation (BOD_5). This is particularly useful for effluents with chloride ions and real wastewater with a complex matrix, which can give rise to toxic residues. Some studies have also evaluated the time course of cytotoxicity and mutagenicity, as in the case of antineoplastics contained in clinical wastewater [9].

This article looks into the reactivity of single drugs in synthetic and real solutions, and mixtures of pharmaceuticals in effluents upon treatment by electrochemical methods to show the large potential of GC-MS and LC-MS to identify the resulting products. We also examine complementary information from HPLC and IC analyses. First, we present an overview of the fundamentals and the performance of the most important electrochemical methods used to degrade drugs to improve understanding of the recent expansion of this research field.

2. Electrochemical technologies for removing pharmaceuticals from water streams

Over the past decade, EAOPs, such as EO, EF, PEF and SPEF, have shown high effectiveness for pharmaceuticals mineralization, as discussed below. We also comment on other electrochemical methods [e.g. photoelectrocatalysis (PEC), and emerging microbial fuel cells (MFCs)], along with coupled methods. Note that the interest in classical electrochemical treatment, such as electrocoagulation, is significantly lower due to its poor oxidation ability, which leads to the accumulation of most removed organics in the final sludge [1,10].

2.1. Electrochemical oxidation

EO, also called anodic oxidation when non-chloride solutions are treated, is the most widespread EAOP for water remediation. It

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