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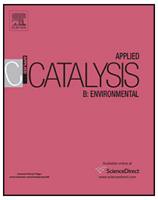

Degradation of trimethoprim antibiotic by UVA photoelectro-Fenton process mediated by Fe(III)–carboxylate complexes

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ABSTRACT

A UVA photoelectro-Fenton (PEF) process mediated by Fe(III)–carboxylate complexes was applied to the removal of trimethoprim (TMP) antibiotic from water using a 2.2 L lab-scale flow plant equipped with a double compound parabolic collector (CPC) and an electrochemical cell composed of a boron-doped diamond (BDD) anode and a carbon–PTFE air-diffusion cathode. The presence of Fe(III)–carboxylate complexes enhances the regeneration of Fe^{3+} to Fe^{2+}, allows to maintain iron in solution at higher pH values and can decrease the formation of Fe(III)–sulfate, Fe(III)–chloride and some Fe(III)–pollutants complexes. First, the efficiency of different carboxylate ligands like oxalate, citrate, tartrate and malate was assessed, followed by the application of various initial Fe(III)-to-carboxylate molar ratios and pH values. The PEF process with Fe(III)–oxalate, Fe(III)–citrate and Fe(III)–tartrate complexes revealed similar ability to degrade the antibiotic solution with the employment of 1:3, 1:1 and 1:1 Fe(III)-to-carboxylate molar ratios, respectively, and using pH of 4.5, Fe^{3+} concentration of 2.0 mg L^{-1} (total iron emission limit for the discharge of treated effluents according to the Portuguese legislation), current density of 5 mA cm^{-2} and 20 °C. The PEF process mediated by Fe(III)–malate complexes was much less effective. 1:6 and 1:9 Fe(III)-to-oxalate molar ratios were required to yield similar TMP removal kinetics at pH 5.0 and 5.5 compared to pH 4.5, respectively. Additionally, the influence of initial TMP content and solution temperature on the PEF process with Fe(III)–carboxylate complexes was assessed and the role of the different reactive oxidizing species was clarified by the addition of scavenging agents. Generated low-molecular-weight carboxylic acids were monitored by ion-exclusion HPLC.

1. Introduction

Recently, several electrochemical advanced oxidation processes (EAOPs) have been applied to the removal of non-biodegradable organic compounds such as synthetic dyes [1,2], pesticides [3,4] and pharmaceuticals [5–7]. These techniques are based on the in situ generation of hydroxyl radicals ($^{\bullet}OH$), which are strong oxidants that can non-selectively react with organic compounds leading to their mineralization to CO_2, water and inorganic ions [8]. The most potent EAOPs use $^{\bullet}OH$ both in heterogeneous and homogeneous phases, i.e. adsorbed at the anode M surface ($M(^{\bullet}OH)$) and in the solution bulk, respectively. $M(^{\bullet}OH)$ is generated as intermediate from O_2 evolution from water oxidation at the anode surface via the following equation [9]:

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \tag{1}$$

The production of $^{\bullet}OH$ in the solution bulk is achieved through the addition of low amounts of Fe^{2+} to the solution to react with H_2O_2 according to Fenton's reaction (2) [10]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{2}$$

The H_2O_2 employed in Eq. (2) can be obtained by direct electro generation at the cathode from the two-electron cathodic reduction of injected O_2 via Eq. (3) [11]:

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{3}$$

Good efficiencies for H_2O_2 generation from Eq. (3) have been reported for various carbonaceous cathodes, with emphasis on carbon-felts [12–14] and carbon–PTFE gas (O_2 or air) diffusion electrodes [6,15,16]. Moreover, Fe^{2+} is continuously regenerated by

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the cathodic reduction of Fe^{3+} to Fe^{2+} from Eq. (4), with further improvement of Fenton's reaction (2) [17].

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (4)$$

Among EAOPs based on Fenton's reaction, UVA photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF) methods acquired especial relevance as they count on the use of UVA artificial light and sunlight, respectively, which yield higher degradation rates since: (i) the photo reduction of photoactive Fe(III)–hydroxy complexes as $FeOH^{2+}$ from Eq. (5) provides Fe^{3+} regeneration to Fe^{2+} and production of more $^{\bullet}OH$ [18]; and (ii) complexes formed between Fe^{3+} and some organic intermediates, especially Fe(III)–carboxylate complexes, are able to absorb in the UV–vis region and therefore can be photodecarboxylated through a ligand-to-metal charge transfer (LMCT) according to the general Eq. (6), providing a quicker pathway for Fe^{3+} regeneration to Fe^{2+} with formation of weak oxidizing species such as $O_2^{\bullet-}$, $CO_2^{\bullet-}$ and H_2O_2 [19–22].

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (5)$$

$$[Fe^{3+}(RCO_2)]^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \quad (6)$$

Some of the main drawbacks for the real application of PEF and SPEF processes are: (i) their optimal operation at acid pH with consequent need for initial acidification and final neutralization steps—pH 2.8 is frequently postulated as optimal since at this pH in most systems precipitation does not take place yet and the dominant iron species in solution is $FeOH^{2+}$, the most photoactive Fe(III)–hydroxy complex [23,24]; (ii) the requirement of excess iron removal at the end of the reaction in order to comply with the discharge limits; (iii) the formation of strong and stable complexes between Fe^{3+} and some pollutants, limiting the photoreduction of Fe^{3+} and then the overall efficiency of the process [25]; and (iv) the adverse influence of the presence of inorganic anions as sulfate and chloride mainly due to the formation of Fe(III) complexes such as $FeSO_4^{+}$ and $Fe(SO_4)_2^{-}$, $FeCl^{+}$, $FeCl^{2+}$ and $FeCl_2^{+}$, which are much less photoactive than $FeOH^{2+}$ [26], and also in virtue of $^{\bullet}OH$ scavenging along with the formation of less reactive species as $SO_4^{\bullet-}$, $Cl^{\bullet}$ and $Cl_2^{\bullet-}$ when compared with $^{\bullet}OH$ [27–29].

Regarding the potentialities of Fe(III)–carboxylate complexes, the efficiency of PEF and SPEF systems may be improved by an initial input of some carboxylic acids along with Fe^{3+} addition to form these complexes, which conveys in a quicker Fe^{3+} regeneration to Fe^{2+} by Eq. (6) from the very first times of reaction. The quantum yield for Fe^{2+} formation in Eq. (6) depends on various parameters including the nature of the carboxylate ligand, Fe(III)-to-ligand ratio, wavelength of the light source and pH [30]. Fe(III)–oxalate, Fe(III)–citrate, Fe(III)–tartrate and Fe(III)–malate complexes have been pointed out as some of the main Fe(III)–carboxylate complexes with the highest quantum yields for Fe^{2+} generation, exhibiting much higher quantum yields for Fe^{2+} formation than $FeOH^{2+}$ complex [22,30,31]. Furthermore, it could be expected that the use of Fe(III)–carboxylate complexes may solve two of the main limitations of PEF and SPEF since: (i) their presence permits iron in solution at higher pH, thus extending the reaction optimal pH range from acid to neutral values and enabling the treatment of real waters and wastewaters without acidification and neutralization steps with the consequent minimization of costs [32]; and (ii) Fe(III)–sulfate and Fe(III)–chloride complexes [33] and some Fe(III)–pollutants complexes [25,33–35] exhibit lower formation constants than Fe(III)–carboxylate complexes, and then the formation of these undesirable species can be avoided with simultaneous increase of Fe^{3+} regeneration to Fe^{2+}.

Trimethoprim (TMP, 2,4-diamino-5-(3,4,5-trimethoxybenzyl)pyrimidine) is an antibiotic commonly prescribed alone or in combination with a sulfonamide (e.g. sulfamethoxazole, sulfadiazine or sulfamoxole) for the treatment of specific bacterial infection, including gastro, respiratory and urinary infections [36]. This antibiotic has been detected in surface waters, wastewater treatment plants (WWTPs) influents and effluents and hospital effluents at the level of ng L^{-1} to μg L^{-1} (0.003–4.30 μg L^{-1}) [37,38]. Since TMP cannot be degraded by conventional treatments, EAOPs can be a useful solution for its removal from waters.

This paper presents a study on the degradation of 68.9 μM (20.0 mg L^{-1}) TMP solutions in 50 mM Na_2SO_4, in terms of antibiotic concentration and dissolved organic carbon (DOC) decays, using a PEF process mediated by Fe(III)–carboxylate complexes. The experiments were performed in a 2.2 L lab-scale flow plant equipped with a double compound parabolic collector (CPC) and an electrochemical reactor containing a boron-doped diamond (BDD) anode and a carbon–PTFE air-diffusion cathode. The aim was to check the feasibility of operating at circumneutral pH (5.5–7.4) with the employment of low amounts of carboxylate ligand and iron. To the best of our knowledge, this is the first time that a PEF process mediated by Fe(III)–carboxylate complexes is studied and its efficiency assessed considering the different iron complexes present in solution and the photoactivity of each ferric species. Carboxylate ligands like oxalate, citrate, tartrate and malate were investigated and the influence of Fe(III)-to-carboxylate molar ratio and pH was also assessed. In addition, the effect of initial TMP concentration and temperature was considered and the role of the different reactive oxidizing species on the degradation processes was clarified by adding scavenging agents. Generated carboxylic acids were followed throughout reactions by ion-exclusion HPLC.

2. Experimental

2.1. Chemicals

Trimethoprim ($C_{14}H_{18}N_4O_3$, ≥99.0%) was of HPLC grade purchased from Sigma-Aldrich. Sodium sulfate anhydrous, used as background electrolyte, and iron(III) chloride hexahydrate, used as catalyst, were of analytical grade purchased from Merck. Oxalic acid dihydrate, citric acid monohydrate, tartaric acid and L(−)-malic acid, used as ligands, were of analytical grade supplied by VWR-Prolabo (the first two), Sigma-Aldrich and Acros Organics, respectively. Concentrated sulfuric acid and sodium hydroxide, both of analytical grade and used for pH adjustment, were supplied by Pronalab and Merck, respectively. D-Mannitol (ACS reagent) and sodium azide (analytical grade), used as scavenging agents, were purchased from Sigma-Aldrich and Panreac, respectively. All the other chemicals were either of HPLC grade or analytical grade supplied by VWR-Prolabo, Sigma-Aldrich, Panreac, Merck, Fisher Chemical and Pronalab. All the solutions were prepared with ultra-pure water produced by a Millipore® Direct-Q system (18.2 MΩ cm resistivity at 25 °C).

2.2. Experimental system

Electrochemical experiments were performed in a 2.2 L lab-scale flow plant composed of: (i) a thermostatically controlled 1.5 L capacity cylindrical glass vessel, (ii) a photo reactor with a double CPC of 694 mL irradiated volume and (iii) an electrochemical filter-press MicroFlowCell reactor with a 10 cm^2 BDD anode and a 10 cm^2 carbon-PTFE air-diffusion cathode. A detailed description of the characteristics of these components has been previously provided in Moreira et al. [39].

2.3. Experimental procedure

The temperature controller was switched on at a temperature set-point that permitted to preserve the solution at 10, 20 or 40 °C.