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Efficient cephalexin degradation using active chlorine produced on ruthenium and iridium oxide anodes: Role of bath composition, analysis of degradation pathways and degradation extent

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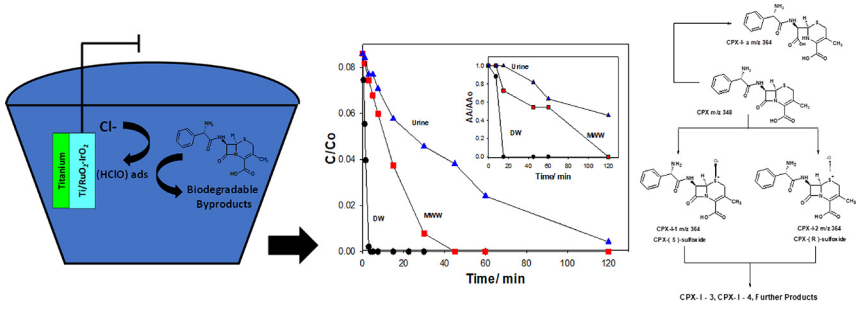
HIGHLIGHTS

- XRD and profile refinement indicate that Ti/RuO_2-IrO_2 forms a solid solution.
- Ti/RuO_2-IrO_2 anode experienced a higher active chlorine production.
- Cephalexin degradation on Ti/RuO_2-IrO_2 was carried out in urine and MWW.
- Initial organic byproducts were identified, and pH and j evaluated.
- Antimicrobial activity was removed and biodegradable byproducts were obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

The elimination of cephalexin (CPX) using electro-generated Cl_2-active on Ti/RuO_2-IrO_2 anode was assessed in different effluents: deionized water (DW), municipal wastewater (MWW) and urine. Single Ti/RuO_2 and Ti/IrO_2 catalysts were prepared to compare their morphologies and electrochemical behavior against the binary DSA. XRD and profile refinement suggest that Ti/RuO_2-IrO_2 forms a solid solution, where RuO_2 and IrO_2 growths are oriented by the TiO_2 substrate through substitution of Ir by Ru atoms within its rutile-type structure. SEM reveals mud-cracked structures with flat areas for all catalysts, while EDS analysis indicates atomic ratios in the range of the oxide stoichiometries in the nominal concentrations used during synthesis. A considerably higher CPX degradation is achieved in the presence of NaCl than in Na_2SO_4 or Na_3PO_4 media due to the active chlorine generation. A faster CPX degradation is reached when the current density is increased or the pH value is lowered. This last behavior may be ascribed to an acid-catalyzed reaction between HClO and CPX. Degradation rates of 22.5, 3.96, and 0.576 μmol L^{-1} min^{-1} were observed for DW, MWW and urine, respectively. The lower efficiency measured in these last two effluents was related to the presence of organic matter and urea in the matrix. A degradation pathway is proposed based on HPLC-DAD and HPLC-MS analysis, indicating the fast formation (5 min) of CPX-(*S*)-sulfoxide and CPX-(*R*)-sulfoxide, generated due the Cl_2-active attack at the CPX thioether. Furthermore, antimicrobial activity elimination of the treated solution is reached once CPX, and the initial by-products are considerably eliminated. Finally, even if only 16% of initial TOC is removed, BOD_5 tests prove the ability of electro-

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generated Cl_2-active to transform the antibiotic into biodegradable compounds. A similar strategy can be used for the abatement of other recalcitrant compounds contained in real water matrices such as urine and municipal wastewaters.

1. Introduction

Cephalexin (CPX) belongs to the cephalosporins family, the second group of antibiotics most consumed worldwide which are characterized by a β-lactam ring within their structures and high-water solubility (Homem and Santos, 2011; Watkinson et al., 2009). This pharmaceutical compound is widely used to treat infectious diseases caused by bacteria on skin, throat, tonsils, and urinary tract, and undergoes a biotransformation rate of only 10%, excreting the remaining 90% via urine (Kümmerer, 2009a; Mirzaei et al., 2018). Consequently, its presence is becoming a serious human risk in aquatic environments, since it is mainly associated with the proliferation of organisms resistant to antibiotics and it can generate toxic effects even at low concentrations (Kümmerer, 2009b). These effects are more severe considering that a maximum residue limit has not been established for this compound by any international health organization (i.e. WHO), whence its use is not regulated. Due to its chemical structure and antimicrobial nature, conventional methods for wastewater treatment (physical, chemical and biological) are ineffective to eliminate this compound; thus, CPX, as antibiotics in general, is considered a pseudo-persistent emergent contaminant (Ma and Zhai, 2014).

In recent years, indirect electrochemical oxidation by active chlorine (Cl_2-active) species (Cl_2/Cl^- E_{red} = 1.36 V vs SHE, $HClO/Cl^-$ E_{red} = 1.49 V vs SHE and ClO^-/Cl^- E_{red} = 0.89 V vs SHE) has emerged as a novel alternative system to degrade organic pollutants in the existence of chloride ions (Palma-Goyes et al., 2015; Palma-Goyes et al., 2016a, 2016b; Serna-Galvis et al., 2017c). Under this context, these ions are used as reagent by the application of an electric current. One advantage is that the activity of electro-generated Cl_2-active occurs at less positive potentials compared to the formation of other oxidants, thus, decreasing the energy consumption and enabling the selective oxidation towards pollutants contained in wastewater with natural organic matter (Deborde and von Gunten, 2008). In electrochemical oxidation with Cl_2-active, the composition of anode materials plays a dominant role, and substantially influences both the selectivity and the efficiency of the process (de Menezes et al., 2017; Palma-Goyes et al., 2016a, 2016b; Steter et al., 2016). These species are efficiently generated using dimensionally stable anodes (DSAs) which are distinguished by their high catalytic activity towards H_2O oxidation, poor corrosion, low energy consumption, and typically based on RuO_2 (Chen et al., 2013). A mixture of RuO_2 and IrO_2 (Ti/Ru-Ir) has been proposed as electrocatalyst since pure RuO_2 despite displaying the highest activity for O_2 evolution becomes inactive over usage, while IrO_2 exhibits adequate corrosion resistance, and promotes the formation of Cl_2-active species (Cheng et al., 2009; Kötz et al., 1984; Lyons and Floquet, 2011; Trasatti, 2000).

Recent studies have described the indirect oxidation of β-lactam antibiotic type-compounds by electrogenerated active chlorine using Ti/IrO_2 anodes (Ti/Ir) (Serna-Galvis et al., 2017b; Serna-Galvis et al., 2016a, 2016b). However, Ti/Ru–Ir anode possesses superior activity compared to Ti/Ir towards the active chlorine production, since it synergistically combines the properties of two catalysts, whence it turns out to be essential to test its degradation capacities towards cephalexin, which to our current state of knowledge has not been conducted. In addition, the influence of matrix effects (i.e. "apparent inactive" components in the wastewater) on the removal efficiency is nowadays of special interest (Paredes-Laverde et al., 2018; Serna-Galvis et al., 2017b; Serna-Galvis et al., 2017a), as well as the elimination of antimicrobial activity, biodegradability and mineralization extent of electro-treated effluent. Thus, the present work is intended to assess for the first time the elimination of CPX and its antibiotic activity from municipal wastewater (MWW) and urine effluents by electro-generated Cl_2-active on a Ti/Ru-Ir anode. Energy dispersive X-ray spectroscopy for scanning electron microscopy (SEM-EDS), and X-ray diffraction (XRD) are employed to account for the chemical structure and morphology of the electrode material, while electrochemical techniques are used to describe the electro-catalytic behavior of the system. The effects of current density, effluent composition and pH are also evaluated, the degradation pathway is elucidated and biodegradability and mineralization extent is analyzed.

2. Experimental

2.1. Chemicals and preparation of effluents

The following analytical reagents were purchased from Merck and used as received: sodium chloride (NaCl), potassium dihydrogenphosphate (KH_2PO_4), monoacid potassium phosphate (K_2HPO_4), acetonitrile (C_2H_3N), sulfuric acid (Na_2SO_4), potassium iodide (KI), sodium hydroxide (NaOH), magnesium sulfate (Mg_2SO_4), sodium hydroxide (NaOH), potassium chloride (KCl), and magnesium chloride ($MgCl_2$), oxalic acid, ethyleneglycol (EG) and citric acid (CA). Ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) was obtained from Pro analysis. Analytic grade reagents of $RuCl_3$, $IrCl_3$ and perchloric acid ($HClO_4$) were obtained from Sigma-Aldrich. Cephalexin (CPX) was provided by Syntopharma laboratories (Bogota, Colombia).

Urine solutions were synthetically prepared according to Udert et al. (2003), while MWW was made according to the ASTM standard D5905-98 (ASTM D5905-98(2013), Standard Practice for the Preparation of Substitute Wastewater, ASTM International, West Conshohocken, PA, 2013) (Table 1).

2.2. Synthesis of anode materials

DSAs films were impregnated on titanium plates using the Pechini method according to Palma-Goyes et al. (2016a, 2016b). Analytic grade reagents of $RuCl_3$ and $IrCl_3$ were utilized as metallic precursors in a polymeric mixture prepared with a molar ratio of Ru/Ir = 1 with 2.4 mol L^{-1} CA as chelating agent, and 18 mol L^{-1} EG as reaction solvent. The polymeric mixture was kept stirred for 30 min at 80 °C and subsequently deposited on Ti plates (2 × 2 cm), which were previously treated in oxalic acid at 75 °C for 30 min. These plates were dried at 180

Table 1
Chemical composition of municipal wastewater and fresh urine used for the electrochemical treatment.

Fresh urine		Municipal wastewater		Distilled water	
pH 6		pH 8		pH 6	
Concentration mg L^{-1}					
Cl^-	6254	Cl^-	18	Cl^-	2900
Urea	16,000	Peptone	160		
NaAc[a]	10,250	Meat extract	110		
Na_2SO_4	2300	Urea	30		
NaH_2PO_4	2900	K_2HPO_4	28		
NaOH	120	$MgSO_4\cdot 7H_2O$	4		

[a] NaAc: sodium acetate.