Unraveling the underlying chemistry enhancing the HOCl and •OH yields on Ru-based anodes in electrochemically assisted photolysis.

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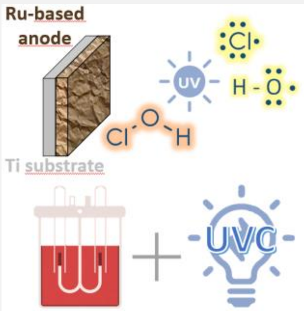

In this work, the addition of Bi, Co and Mn into a Ru-based dimensionally stable anodes (DSAs) is envisaged to produce the chlorine evolution reaction (ClER). ECSA and iodometry measurements are conducted, revealing the highest activity of RuO_2-Mn. An electrochemically assisted photolysis (EAP) is performed at 20 mA cm^{-2}, 0.05M NaCl, pH 5.8, in the presence of a Hg UVC lamp (λ=254 nm), to form •OH and •Cl from active chlorine homolysis, leading the degradation of a wastewater fortified with 20 ppm of carbamazepine (CBZ), cefadroxil (CFX), ciprofloxacin (CIP) and sulfamethoxazole (SMX). HPLC measurements indicated the degradation of all 4 compounds within the first hour, whilst mineralization levels obtained after 2 hours of reaction reached surpassed 97%.

Introduction

Recalcitrant organic pollutants (ROPs) refer to compounds with high stability discharged into wastewater due to human activities which, after being processed by conventional wastewater treatment plants (WWTPs), not only are partially removed, but also a negative potential impact is associated when released into the environment. ROPs includes pharmaceuticals, where CBZ, CIP, CFX and SMX have been widely reported in wastewater, besides groundwater [1]. However, WWTPs are inefficient to remove these pharmaceutical compounds, mainly due to their stability and refractory character.

Electrochemical advanced oxidation processes (EAOPs) have been useful for ROPs abatement, based on •OH production and other oxidants (e.g., HOCl), adopting electrons as clean reagent. Likewise, they have great capacity to reduce organic compounds in water, cost-effective operation, easy adaptation, and scale-up [2]. It has been emphasized that two or even more AOPs could favor efficiency in accordance with a large quantity of oxidant species produced with higher oxidation capacity [3].

Both systems UVC and EAOPs (EAP) have already been used to produce •Cl (2.41V vs SHE), comparable with •OH and •$SO4^-$. Consequently, degradation rates and mineralization have been considerably increased [4]. However, chlorine reactions take place on Ru-based materials, also known as DSAs. It has been highlighted that activity and selectivity over RuO_2-TiO_2 relies on the activation of Ti surface sites by nearby Ru dopants, towards the oxygen evolution reaction (OER) and ClER. Ru is an expensive non-abundant metal from Pt group yet, studies suggest that OER and ClER can be reached by the insertion of Bi, Co, Mn with optimal activity and selectivity [5].

Accordingly, this work aims to investigate Ru-based catalyst with Bi, Co and Mn as precursors, to bring down Ru loads, while using sustainable materials. XRD, SEM-EDS, electrochemical active surface area (ECSA) and iodometry measurements are conducted with the materials. Resulting oxidant species (e.g. HOCl, •OH) were formed by EAP to eliminate CBZ, CFX, CIP and SMX remotion in a synthetic solution. Degradation was followed by high performance liquid chromatography (HPLC) whilst mineralization is evaluated through total organic carbon (TOC).

Material and Methods

The following analytical reagents were purchased and used as received: NaCl (Meyer), CBZ (Merck), CFX (Merck), CIP (Merck) and SMX (Merck).

DSA films were impregnated on titanium plates using Pechini method according to Yañez et al., employing $Bi(NO_3)_3{\cdot}5H_2O$ (Meyer), $CoCl_2{\cdot}6H_2O$ (Merck) and $MnCl_2{\cdot}4H_2O$ (Merck) [4].

All systems were carried out at a conventional three-electrode cell with RuO_2-Mn as working electrode, stainless steel as counter electrode and Ag/AgCl (3M NaCl) as reference electrode, under stirring, 20 mA cm^{-2}, pH 5.8 at 0.05M NaCl, and 254 nm. EAP was conducted using a Hg UVC lamp (3300 μW cm^{-2}, λ=254 nm).

Results and Discussion

XRD measurements were carried out on the DSA using both "match2" software and the crystallography open database, as shown in Table 1. All three DSAs have in common the same RuO_2 phase, corresponding to a tetragonal crystalline structure (P42/mnm). In RuO_2-Bi, RuO_2-Co and RuO_2-Mn electrodes, all phases share a cubic crystalline structure (Pn-3, Fd-3m and Fd-3m, respectively). Likewise, ECSA was estimated using Randles-Sevcik equation through cyclic voltammetry in 5 mM $Fe(CN)_6^{4-}$ and 0.1 M KCl, at scan rates from 5 to 120 mV s^{-1} [6] (see table 1).

Iodometry results suggest that RuO_2-Mn exhibits greater chlorine production than RuO_2-Bi and RuO_2-Co, as corresponds to the estimated ECSA. SEM-EDS analysis (not shown) confirmed a mud-creaked surface with homogeneous dispersion of all elements involved over electrodes. Thus, RuO_2-Mn was selected to conduct degradation experiments.

HPLC was used to measure samples throughout 2-hour process with acid water/acetonitrile as mobile phase inside a C-18 column at 1.0 mL min^{-1}. This reveals that the EPA presented the best degradation results within the first hour of reaction. Complementary analysis confirmed the presence of formic acid and oxalic acid as main by-products (not shown), being the photo-assisted electrolysis the one with the highest conversions.

TOC results confirmed by far the outstanding synergy in EPA, 97.32% of mineralization, whereas photolysis and electrolysis reached 11.93% and 58.8%, respectively. This result was reached because of pH initial conditions, where HOCl is considerably predominant, and then, more •OH and •Cl are produced. Photolysis stills retains the pH change towards alkaline conditions.

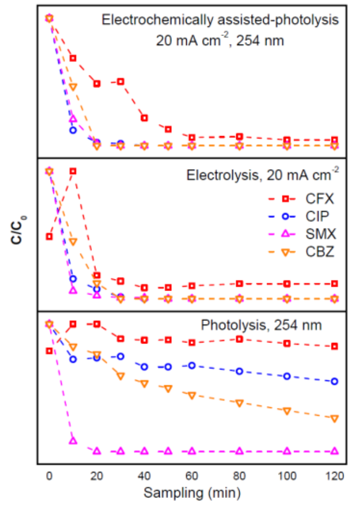

Figure 1. HPLC measurements C/C_0 of CFX, CIP, SMX and CBZ.

Table 1. DSA anodes characterizations.

DSA	Ru phase (COD)	Co-catalyst phase (COD)	ECSA
RuO_2-Bi	96-210-1931	96-100-4041	4.42
RuO_2-Co	96-210-1931	96-591-0032	3.91
RuO_2-Mn	96-210-1931	96-151-4106	5.29

Conclusions

RuO_2-Mn was the electrode with the greatest activity according to ECSA and iodometry measurements, since Mn doping produced large active sites enhancing ClER. Furthermore, this electrode in EPA achieved mineralization levels above 97%. Initial compounds were suppressed in the first hour as result of pH and radiation conditions, whilst unavoidably by-products as formic acid and oxalic acid were formed along 2-hour process as confirmed by HPLC results.

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