



Degradation of dipyrone via advanced oxidation processes using a cerium nanostructured electrocatalyst material



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ABSTRACT

This work studied the degradation of dipyrone, via electrochemical processes and via electro-Fenton reaction using a 4% CeO₂/C gas diffusion electrode (GDE) prepared via modified polymeric precursor method. This material was used to electrochemically generate H₂O₂ through oxygen reduction. The mean crystallite sizes estimated by the Scherrer equation for 4% CeO₂/C were 4 nm for CeO_{2-x} (0.44) and 5 nm for CeO₂ (1 1 1) while using transmission electron microscopy (TEM) the mean nanoparticle size was 5.4 nm. X-ray photoelectron spectroscopy (XPS) measurements revealed nearly equal concentrations of Ce(III) and Ce(IV) species on carbon, which contained high oxygenated acid species like CO and O=C=O. Electrochemical degradation using Vulcan XC 72R carbon showed that the dipyrone was not removed during the two hour electrolysis in all applied potentials by electro-degradation. Besides, when the Fenton process was employed the degradation was much similar when using cerium catalysts but the mineralization reaches just to 50% at –1.1 V. However, using the CeO₂/C GDE, in 20 min all of the dipyrone was degraded with 26% mineralization at –1.3 V and when the Fenton process was employed, all of the dipyrone was removed after 5 min with 57% mineralization at –1.1 V. Relative to Vulcan XC72R, ceria acts as an oxygen buffer leading to an increase in the local oxygen concentration, facilitating H₂O₂ formation and consequently improving the dipyrone degradation

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1. Introduction

Pharmaceuticals are used in large quantities throughout the world in both human and veterinary medicine, but their environmental effects have long been neglected [1]. Currently, however, the presence of pharmaceuticals and related compounds in aquatic environments has been recognized as problematic because these compounds, which generally enter the environment through sewage treatment plants after domestic use, and if they are not first eliminated, they are discharged into rivers and lakes that are used as sources of drinking water [1–3].

Analgesics are among the most commonly detected pharmaceuticals [3] and dipyrone is one of the most popular substances in this class (also known as metamizol) [1]. Dipyrone is a widely used analgesic and antipyretic that, after intake, is non-enzymatically hydrolyzed by the intestine to 4-methylaminoantipyrine (MAA), which is absorbed from the gastrointestinal tract and further

biotransformed via enzymatic demethylation to 4-aminoantipyrine (AA) and oxidation to 4-formylaminoantipyrine (FAA) in the liver. AA undergoes polymorphic acetylation to 4-acetylaminoantipyrine (AAA). These compounds are not completely eliminated by biological treatment and are found in large quantities in both wastewater and surface water [1,3–7].

Since the presence of pharmaceuticals in wastewater became a serious problem, a notable increase in research activity concerning the identification and treatment of industrial effluents has occurred, and possible determination and degradation pathways have been suggested [8–13]. Many technologies, including biological, physical and chemical processes, have already been proposed for the remediation of these effluents [14–17].

Among the various degradation methods, advanced oxidation processes (AOPs) using strong oxidizing agents, such as O₃ and H₂O₂, to generate the powerful and non-selective hydroxyl radical (OH[•]) oxidizing agent for the destruction of hazardous pollutants [18–21] demonstrate certain advantages for various reasons. Compared to other methods [22], the AOP either completely mineralizes [23] or oxidizes several compounds to very low concentrations [24,25] and generates environmentally friendly byproducts [26,27].

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Both hydrogen peroxide and the hydroxyl radical are environmentally friendly chemicals that leave no hazardous residuals. Hydrogen peroxide can be produced from acidic solutions via the two-electron reduction of oxygen on a cathode surface [28–31] and the hydroxyl radical can be obtained from the Fenton reaction by adding Fe(II) to an H₂O₂ solution [31]. It is well known that the 2-electron reduction of oxygen on a three-dimensional carbon-based cathode occurs with a high yield because of the low solubility of oxygen in aqueous solution [14], [32–34].

Many studies have reported the use of gas diffusion electrodes (GDEs) as cathodes, with the goal of increasing hydrogen peroxide generation. This technique is quite promising for the electrogeneration of H₂O₂ via the oxygen reduction reaction (ORR) [27], and recent investigations indicate that the two-electron ORR is enhanced by GDEs containing organic redox electrocatalysts, noble metals or metal oxides [27], [35,36].

In the case of a metal oxide GDE, the presence of low quantities of metal oxide nanoparticles can facilitate the 2-electron transfer in the ORR because of their unique electronic and catalytic properties, as demonstrated by our group [37–39]. Ceria in particular can act as an oxygen buffer and lead to an increase in the local oxygen concentration [40] that facilitates H₂O₂ formation.

Because of the environmental impact of pharmaceuticals from wastewater, this work reports on the degradation of dipyrone via electrochemical methods, such as the electro-Fenton process, using a 4% CeO₂ gas diffusion electrode prepared by the modified polymeric precursor method (PPM) as a cathode to enhance hydrogen peroxide production through the ORR.

2. Materials and methods

2.1. CeO₂ preparation

A PPM was used to prepare 4% CeO₂/C (w/w) as described by our group De Souza et al. [41–44]. This concentration was used based on our previous results [38] where we analyzed 3 mass proportions of cerium electrocatalysts (4%, 9% and 13%) for H₂O₂ electrogeneration. The precursor solution was obtained by dissolving citric acid in ethylene glycol at 60 °C and adding cerium chloride to produce a viscous resin. The electrocatalyst was prepared by mixing the required amount of Vulcan XC-72R carbon (Cabot Corporation) into the previously prepared resin and adding sufficient ethylene glycol to cover the carbon powder. This mixture was homogenized in an ultrasonic bath and thermally treated at 400 °C for 2 h under an N₂ atmosphere.

2.2. Physical characterization

The cerium oxide electrocatalysts were previously physically characterized by X-ray diffraction (XRD) [38] using a D8 Focus diffractometer (Bruker AXS) with a Cu K α radiation source and operating in the continuous scan mode (2° min⁻¹) from 20° to 90°. For TEM analysis a TECNAI F20 FEI microscopy was used, operating at 200 kV.

XPS analysis was performed at a pressure of less than 10⁻⁶ Pa using a commercial spectrometer (UNI-SPECS UHV). The Mg K α line was used ($h\nu = 1253.6$ eV) and the analyzer pass energy was set to 10 eV. The inelastic backgrounds of the C_{1s}, O_{1s}, and Ce_{3d} core-level electron spectra were subtracted using the Shirley method. The composition of the near surface region was determined to an accuracy of $\pm 10\%$ from the ratio of the relative peak areas corrected by the Scofield sensitivity factors for the corresponding elements. The spectra were fitted without constraints using multiple Voigt profiles. The full width at half maximum (FWHM) varied between 1.2 and 2.1 eV and the accuracy of the peak positions was ± 0.1 eV.

2.3. Gas diffusion electrodes

After preparing the 4% CeO₂ material, GDE were prepared with a diameter of 2.5 cm and used in an electrochemical cell to determine the real quantity of H₂O₂ produced by exhaustive electrolysis at different potentials as proposed by Forti et al. [27]. H₂O₂ was quantified by reacting 500 μ L of the electrolyte containing the H₂O₂ with 4 mL of 2.4×10^{-3} mol L⁻¹ of (NH₄)₆Mo₇O₂₄ and 0.5 mol L⁻¹ H₂SO₄ to produce a pale-yellow peroxymolybdate complex, which can be detected by UV-vis at 350 nm, as proposed by Chai et al. [45] and Forti et al. [46]. The H₂O₂ concentration was determined from a previously constructed analytical curve using a Varian Cary 50 spectrophotometer equipped with a 10 mm polystyrene cell (3.5 mL).

2.4. Dipyrone degradation

After determining the real quantity of H₂O₂ produced during exhaustive electrolysis with the 4% CeO₂/C GDE and Vulcan Carbon, the best potentials for H₂O₂ electrogeneration were chosen for the degradation of 350 mL of 100 mg L⁻¹ dipyrone in 0.1 mol L⁻¹ H₂SO₄ and 0.1 mol L⁻¹ K₂SO₄. The electro-Fenton process was employed by adding 3×10^{-3} mol L⁻¹ of iron sulfate (Fe II) to the 100 mg L⁻¹ dipyrone solution to be degraded. The reaction was performed in the same electrochemical cell used to quantify the H₂O₂ concentration.

All of the degradation reactions were monitored by high performance liquid chromatography (HPLC) and a total organic carbon (TOC) analyzer. For the HPLC analysis, the samples were first filtered through a Millipore 0.45 mm Durapore PVDF filter (13 mm diameter) and then analyzed immediately after removal from the electrochemical cell. The dipyrone concentration was monitored using a Shimadzu 20A HPLC equipped with a C-18 column (250 mm \times 4.6 mm, i.d. \times 5 μ m particle size), a mobile phase composed of methanol:phosphate buffer at pH 7 (50:50, v/v) at a flow rate of 1 mL min⁻¹. The injection volume was 20 μ L and the detection wavelength was 254 nm (UV-vis SPD-20A). The dipyrone concentration was evaluated during the electrolysis using a previously constructed analytical curve. The TOC content was analyzed via the direct injection of the samples into a Shimadzu TOC-VCPN analyzer.

3. Results and discussion

3.1. Physical characterization

The XRD analysis presented at our previous work [38] showed that the three mass proportions of cerium materials containing two different phases CeO₂ and CeO_{2-x}, depending on the ceria content and it was also possible to observe that for the 4% CeO₂/C the peaks attributed to CeO₂ and CeO_{2-x} are in almost equal intensities. The average crystallite sizes estimated from our prior XRD data [38] for the 4% CeO₂/C electrocatalyst was 4 nm in the ceria phase (CeO_{2-x} (0 4 4)) and 5 nm in the ceria phase (CeO₂ (1 1 1)).

The mean nanoparticle size was also measured using TEM by counting more than 100 particles from different regions. TEM images of 4% CeO₂/C are shown in Fig. 1(a) which illustrate that the nanoparticles are dispersed on carbon support. Fig. 1(b) shows the histogram of the catalyst particle mean diameter distribution. The nanoparticles are with average sizes of 5.4 nm, value much similar to that obtained by XRD analysis and 100% of the particles measured are among 2 and 11 nm.

The local bonding structure of the electrocatalyst was investigated through the deconvolution of the C_{1s}, O_{1s} and complex Ce_{3d} core level spectrum. Fig. 2 shows the XPS C_{1s} spectra for both the electrocatalyst and Vulcan XC-72R carbon support. The C_{1s}

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