Hydrogen Peroxide Electrogeneration by Gas Diffusion Electrode Modified with Tungsten Oxide Nanoparticles for Degradation of Orange II and Sunset Yellow FCF Azo Dyes

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In this work, the gas diffusion electrode (GDE) cathode of Vulcan XC72 carbon modified with nanoparticles of WO$_{2.72}$ (WO$_{2.72}$/Vulcan XC72) was used for H$_2$O$_2$ electrogeneration and degradation of 350 mL of Orange II (OII) and Sunset Yellow FCF (SY) azo dyes by electro-Fenton (EF) and photoelectro-Fenton (PEF) processes with different Fe$^{2+}$ initial content (1.00, 0.50 and 0.25 mmol L$^{-1}$). The WO$_{2.72}$/Vulcan XC72 GDE electrolyzed approximately 3 times more H$_2$O$_2$ than the Vulcan XC72 GDE. Decolorizations and mineralizations of the dye solutions were more efficient at higher concentrations of Fe$^{2+}$. The decolorization decay showed pseudo-first-order kinetics. The most promising decolorization results obtained at processes of WO$_{2.72}$/Vulcan XC72 cathode combined with Pt anode (100% color removal of OII and SY at 30 and 20 min of electrolysis with 1.00 mmol L$^{-1}$Fe$^{2+}$, respectively). The best mineralization achieved in trials of WO$_{2.72}$/Vulcan XC72 cathode combined with boron-doped diamond (BDD) anode (82% total organic carbon (TOC) removal of OII by PEF / 1.00 after 3 h and 90% TOC removal of SY by PEF / 0.50 after 4 h). It was found that SY decolorization was faster and mineralization showed a similar yield independent of oxidized dye.

Keywords: WO$_{2.72}$/Vulcan XC72, H$_2$O$_2$ electrogeneration, decolorization, mineralization, azo dyes

Introduction

The discharge of large volumes of azo dye industrial effluents into water bodies is a concerning practice because it can generate serious environmental and health problems, such as highly colored dyes being a dramatic source of aesthetic pollution, as well as being toxic, carcinogenic and mutagenic. Azo dyes are characterized by one or more –N=N– bonds, usually conjugated with benzene and/or naphthalene systems. Among different types of dyes, azo dyes are more versatile and represent approximately 70% of the world’s dye production. Orange II (OII) (Figure 1a) and Sunset Yellow FCF (SY) (Figure 1b) were used as model azo dyes. OII is very stable and widely used in the textile, food and cosmetic industries. SY is extensively used in food, pharmaceuticals and cosmetic products.

Therefore, the removal of color from aqueous effluents is of remarkable environmental and health importance. Recently, electrochemical advanced oxidation processes (EAOPs) are promising alternatives to conventional methods. These processes can lead to a complete mineralization (transformation into CO$_2$, H$_2$O and inorganic ions) of persistent organic pollutants in aqueous systems via the in situ generation of reactive oxygen species (ROS),
such as hydroxyl radicals (•OH), a powerful oxidizing agent.\textsuperscript{5,12,14}

Hydroxyl radicals can be produced directly by anodic oxidation (AO) of water (equation 1).\textsuperscript{5,15} When active anodes such as Pt, IrO\textsubscript{2} and RuO\textsubscript{2} are employed, the M(•OH) radicals have a weaker oxidizing ability because they are chemisorbed.\textsuperscript{1} In contrast, non-active anodes, like PbO\textsubscript{2} and boron-doped diamond (BDD), favor the electrochemical incineration of organics because they generate physiosorbed M(•OH) with very weak M–•OH interactions, resulting in a greater O\textsubscript{2}–overpotential and a quicker destruction of organics.\textsuperscript{1,14}

\begin{equation}
M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \quad (1)
\end{equation}

Hydroxyl radicals can also be produced indirectly via electrogenerated Fenton’s reagent (H\textsubscript{2}O\textsubscript{2} / Fe\textsuperscript{2+}).\textsuperscript{5,6,16} In this case, the H\textsubscript{2}O\textsubscript{2} is produced by the oxygen reduction reaction (ORR) two-electron pathway in carbonaceous cathodes (equation 2).\textsuperscript{15,17,18} The H\textsubscript{2}O\textsubscript{2} can be produced by gas diffusion electrode (GDE) cathodes, which are advantageous due to the large contact areas among the cathode, oxygen and water.\textsuperscript{19}

\begin{equation}
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)
\end{equation}

Most recently, there have been increased efforts in developing EAOPs based on \textit{in situ} hydrogen peroxide production, such as the electro-Fenton (EF) and photoelectro-Fenton (PEF) processes.\textsuperscript{20,21} In EF, the electrogenerated H\textsubscript{2}O\textsubscript{2} reacts with externally added Fe\textsuperscript{2+} ions to produce hydroxyl radicals and Fe\textsuperscript{3+} ions, according to Fenton’s reaction (equation 3).\textsuperscript{5,15,22} The generated Fe\textsuperscript{3+} ions are reduced to Fe\textsuperscript{2+} at the cathode (equation 4).\textsuperscript{16,21} EF can be improved by the incidence of UV light into the reaction medium. This process is called PEF, in which the radiation facilitates the degradation of organic compounds due to the faster regeneration of Fe\textsuperscript{2+} and increased •OH production induced by the photoreaction of Fe(OH)\textsuperscript{2+} species (equation 5) and the photolysis of complexes of Fe\textsuperscript{III}-carboxylate (equation 6).\textsuperscript{20,23} in which carbon-centered radicals (R*) are also formed.\textsuperscript{24}

\begin{equation}
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (3)
\end{equation}

\begin{equation}
Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)
\end{equation}

\begin{equation}
Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot OH \quad (5)
\end{equation}

\begin{equation}
Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^* \quad (6)
\end{equation}

At this point, our group has worked to develop new electrocatalytic materials with high performance in the peroxide electrogeneration for environmental applications. In our previous work, we demonstrated the physical and electrocatalyst properties of WO\textsubscript{2.72} supported on Vulcan XC72 carbon.\textsuperscript{25} The material showed high performance in H\textsubscript{2}O\textsubscript{2} electrogeneration, with good current efficiency (CE) and lower energy consumption (EC).\textsuperscript{25} For this reason, in this work, this new material (WO\textsubscript{2.72} / Vulcan XC72) was used to produce a GDE cathode. This cathode was combined with the Pt and BDD anodes for decolorization and mineralization of OII and SY azo dyes by EF and PEF processes. The effect of the initial concentrations of Fe\textsuperscript{2+} ions (0.25, 0.50 and 1.00 mmol L\textsuperscript{-1}) was studied with the intention of elucidating how the mediated electrolytic process affects dye oxidation. All these trials had the main objective of determining the best parameters for application of the WO\textsubscript{2.72} / Vulcan XC72 cathode in the degradation of the dyes. In addition, to evaluate the influence of the structure of the dyes in the oxidation processes by Fenton’s reaction.

**Experimental**

**Preparation of GDE electrode**

First, the WO\textsubscript{2.72} / Vulcan XC72 electrocatalyst was prepared. The WO\textsubscript{2.72} nanoparticles (NPs) anchored on Vulcan XC72 carbon (Cabot Corporation) without any previous treatment were prepared by the modified polymeric precursor method (PPM) at the mass ratio of 1:100 (W:C).\textsuperscript{25-27} All reagents used were purchased from Sigma-Aldrich (St. Louis, USA). The GDE cathode was prepared by the hot pressing procedure using WO\textsubscript{2.72} / Vulcan XC72 and Vulcan XC72 with 20% (m/m) of a 60% aqueous dispersion from Sigma-Aldrich. A sintered 3-mm-thick GDE was obtained after 2 h at 290 °C, under load of 18 MPa, as proposed by other works.\textsuperscript{25,28,29}
Physical characterization

Physical characterizations were performed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS) and contact angle measurements.

XRD was conducted on a Rigaku-MiniFlex X-ray diffractometer with a continuous Cu Kα radiation source (2° min⁻¹) at intervals of 20-60°. XPS spectra were measured at a pressure of less than 10⁻⁷ Pa using a commercial spectrometer (UNI-SPECS UHV). The Al Kα line was used (hν = 1486.6 eV), and the analyzer pass energy was set to 10 eV. The inelastic background of the W 4f, O 1s and C 1s high-resolution core-level spectra were subtracted using Shirley’s method. The spectra were fitted without placing constraints using multiple Voigt profiles in the CasaXPS software. TEM images were collected with a JEOL JEM-2100 electron transmission microscope operating at 200 kV. The samples for the TEM studies were prepared by placing nanodispersion droplets on a carbon-coated copper grid and evaporating the solvent at room temperature. EDS analyses were performed using an EDS chemical microanalysis module coupled to a JEOL JSM-6010LA compact sweep electron microscope. Contact angle was determined on a goniometer (GBX Digidrop) by dropping a water droplet (5 μL) onto the electrocatalyst surface. Windrop++ software was used.

Electrochemical measurements

Hydrogen peroxide electrogeneration in GDE cathode

H₂O₂ was generated by electrolysis performed with a 3.0 cm² exposed area GDE cathode supplied with O₂ at 0.2 bar. An undivided cell was used containing 350 mL aqueous electrolyte (0.1 mol L⁻¹ H₂SO₄ and 0.1 mol L⁻¹ K₂SO₄ at 20 °C and pH 3.0), with Ag / AgCl (analyzer) and 7.5 cm² Pt electrodes as the reference and auxiliary electrodes, respectively. The distance between the cathode and anode was 1.0 cm. Ag / AgCl was used as the reference electrode. All processes evaluated were conducted potentiostatically at ~1.9 V vs. Ag / AgCl. The EF and PEF trials were performed at pH 3.0 and with the addition of 0.25, 0.50 or 1.00 mmol L⁻¹ Fe²⁺. The photodegradation was carried out using a mercury UV lamp of 𝜆ₘₐₓ = 254 nm immersed in the solution, positioned at 2 cm from the GDE cathode.

Analytical procedures

The hydrogen peroxide was quantified via UV-Vis by reacting 0.5 mL of the electrolyte containing H₂O₂ with 4 mL of a solution containing 2.4 × 10⁻¹ mol L⁻¹ (NH₄)₆Mo₇O₂₄ and 0.5 mol L⁻¹ H₂SO₄, with the absorption measured at 350 nm. The H₂O₂ concentration was determined from a previously constructed analytical curve using a Varian Cary 50 Scan UV-Vis spectrophotometer. The limit of detection (LOD) was 34.6 mg L⁻¹.

The decolorization of OII and SY solutions was determined by the decrease of their absorbance (A) at the maximum visible wavelength of 𝜆ₘₐₓ = 484 and 482 nm, respectively. This procedure was conducted employing a UV-Vis spectrophotometer (Varian Cary 50 Scan). Dye solution aliquots of 0.5 mL were diluted in 4 mL electrolyte (0.1 mol L⁻¹ H₂SO₄ and 0.1 mol L⁻¹ K₂SO₄) and analyzed between 200 and 800 nm at 20 °C.

All samples extracted from electrolyzed solutions were treated with sodium sulfite to stop the mineralization process and filtered through 0.45 μm polytetrafluoroethylene (PTFE) filters from Analítica before analysis. The TOC concentration was monitored using a TOC-V CPN Shimadzu analyzer.

Results and Discussion

Physical characterization

The results of the physical characterization of the WO₂₋₂₋ / Vulcan XC72 electrocatalyst were presented in detail in the article published previously by our group. Briefly, XRD analysis showed the presence of the monoclinic crystalline phase WO₂₋₂₋ (W₁₈O₄₉). The XPS analysis showed that the material modified with the WO₂₋₂₋ nanoparticles presented a high content of oxygenated acidic groups. The micrographs obtained by TEM showed the dispersion and shape of the nanometer structure of the WO₂₋₂₋ phase anchored on Vulcan XC72 carbon. The EDS analysis presented the W:C estimated content to be approximately 0.8% (m/m), close to the nominal value of 1.0% (m/m). The contact angle values showed that the WO₂₋₂₋ / Vulcan XC72 material is more hydrophilic than pure Vulcan XC72.
Hydrogen peroxide electrogeneration in GDE cathode

The H₂O₂ electrogeneration was performed using unmodified Vulcan XC72 and WO₂.₇₂ / Vulcan XC72 GDEs over a wide range of applied cathodic potential (−0.7 to −2.5 V vs. Ag / AgCl). Figure 2 shows the H₂O₂ electrogeneration as a function of electrolysis time for different values of applied potentials obtained with unmodified Vulcan XC72 and modified Vulcan XC72 (WO₂.₇₂ / Vulcan XC72) GDEs. As can be observed, an increase in cathodic applied potential caused an improvement in the H₂O₂ electrogeneration in both GDEs studied. This was a surprise, as there is usually a reduction of H₂O₂ generation when high cathodic potentials are applied during electrolysis. Such behavior of the studied GDEs can be justified by the attenuation or absence of parallel reactions, such as the reduction of H₂O₂ to H₂O, H₂ evolution and the ORR four-electron pathway, which can occur in electrolysis at higher potentials.  

Table 1 shows the accumulated H₂O₂ from the Vulcan XC72 and WO₂.₇₂ / Vulcan XC72 GDEs after 120 min of electrolysis. The WO₂.₇₂ / Vulcan XC72 GDE accumulated more H₂O₂ than the Vulcan XC72 GDE at all studied potentials (1.5, 2.9, 2.8 and 2.8 times higher at −0.7, −1.3, −1.9 and −2.5 V vs. Ag / AgCl, respectively). These results show how much the modification with the WO₂.₇₂ nanoparticles improved the electrocatalytic activity of Vulcan XC72 carbon for H₂O₂ electrogeneration and, consequently, for application in the degradation of organic pollutants by EF processes and derivatives. We attributed the improved electrocatalytic to the higher hydrophilicity of WO₂.₇₂ / Vulcan XC72 due to the increase of acid oxygen groups resulting from the modification of Vulcan XC72 carbon with the nanoparticles of WO₂.₇₂.  

Hydrophilic materials favor the adsorption of O₂ according to the Pauling model. This allows the ORR by two-electron pathway resulting in the formation of H₂O₂.  

Additionally, it is important to know the EC and the CE for the H₂O₂ electrogeneration. The EC (in kWh kg⁻¹) and the CE (in %) for the H₂O₂ electrogeneration were determined from equations 7 and 8 respectively.

\[
EC = \frac{\eta E_{\text{cell}} t}{1000 m} \tag{7}
\]

\[
CE = \frac{z F [H_2O_2] V}{M_{H_2O_2} t_s} \tag{8}
\]

where I represents the current (A), E_{cell} is the cell potential (V), t is the time (h), m is the mass of hydrogen peroxide formed (kg), z is the number of electrons transferred for the oxygen reduction to H₂O₂, F is the Faraday constant (96,485 C mol⁻¹), [H₂O₂] is the concentration of H₂O₂ (g L⁻¹), V is the solution volume (L), M_{H_2O_2} is the molar mass of H₂O₂ (34.01 g mol⁻¹), and t_s is the electrolysis time (s).

The EC and the CE for the H₂O₂ electrogeneration for 120 min by Vulcan XC72 and WO₂.₇₂ / Vul...
Vulcan XC72 GDEs are shown in Figure 3. As seen, the WO\textsubscript{2.72} / Vulcan XC72 GDE consumed less power than the Vulcan XC72 GDE (1.7, 2.6, 3.1 and 3.1 times lower at −0.7, −1.3, −1.9 and −2.5 V vs. Ag / AgCl, respectively). In addition, the EC increased in both GDEs due to the increase of the applied potential. The CE of WO\textsubscript{2.72} / Vulcan XC72 GDE was superior to the CE of Vulcan XC72 GDE at all potentials. The values were 1.6, 2.7, 3.0 and 2.9 times higher at −0.7, −1.3, −1.9 and −2.5 V vs. Ag / AgCl, respectively. Contrary to the EC, CE decreased as the applied potential was increased, from 38.1 and 62.7% at −0.7 V to 15.3 and 44.8% at −2.5 V for modified and unmodified Vulcan GDE, respectively. Higher EC and lower CE for the H\textsubscript{2}O\textsubscript{2} electrogeneration at higher potentials can be justified by parasitic reactions such as H\textsubscript{2}O\textsubscript{2} reduction on the cathode to H\textsubscript{2}O, its oxidation in the anode and H\textsubscript{2} evolution reactions. In addition, other works have demonstrated that the decomposition of H\textsubscript{2}O\textsubscript{2} is favored in smaller volumes, and, at higher potentials, the process can be controlled by mass transfer from dissolved oxygen.

The results of H\textsubscript{2}O\textsubscript{2} electrogeneration show that the WO\textsubscript{2.72} / Vulcan XC72 GDE is a very promising cathodic material, particularly when it is compared to other cathodic materials published in the literature recently, as seen in Table 2.36

### Table 2. Comparisons of H\textsubscript{2}O\textsubscript{2} generation rate between this work and representative published data obtained from cathode materials

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>H\textsubscript{2}O\textsubscript{2} generation rate / (mg L\textsuperscript{-1} h\textsuperscript{-1} cm\textsuperscript{-2})</th>
<th>Reference or applied potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy / lig-GF</td>
<td>10.1</td>
<td>36</td>
</tr>
<tr>
<td>GF-Co</td>
<td>13.9</td>
<td>37</td>
</tr>
<tr>
<td>NCNT / NF / CNT</td>
<td>42.2</td>
<td>38</td>
</tr>
<tr>
<td>CoPc / Px</td>
<td>64.9</td>
<td>34,36-38</td>
</tr>
<tr>
<td>WO\textsubscript{2.72} / Vn</td>
<td>54.2 at −0.7 V vs. Ag / AgCl\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>WO\textsubscript{2.72} / Vn</td>
<td>125.8 at −1.3 V vs. Ag / AgCl\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>WO\textsubscript{2.72} / Vn</td>
<td>162.8 at −1.9 V vs. Ag / AgCl\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>WO\textsubscript{2.72} / Vn</td>
<td>187.5 at −2.5 V vs. Ag / AgCl\textsuperscript{a}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Applied potential during the electrolysis of this work. lig-GF: lignin-graphite felt; NCNT / NF / CNT: N-doped multi-walled carbon nanotubes / nickel foam / multi-walled carbon nanotubes; CoPc / Px: cobalt(II) phthalocyanine / Printex 6L carbon; Vn: Vulcan XC72.

### Decolorization of OII and SY solutions

Treatments of 350 mL solutions containing 50 mg L\textsuperscript{-1} of TOC of OII (91.2 mg L\textsuperscript{-1}) or SY (117.8 mg L\textsuperscript{-1}) in the presence of 0.1 mol L\textsuperscript{-1} K\textsubscript{2}SO\textsubscript{4} at pH 3.0 were carried out at −1.9 V vs. Ag / AgCl (3 mol L\textsuperscript{-1}) and 20 °C. Figure 4 shows percentage of OII and SY removal by EF and PEF processes as a function of time for different values of Fe\textsuperscript{2+} initial concentrations equal to 1.00, 0.50 and 0.25 mmol L\textsuperscript{-1}, employing a WO\textsubscript{2.72} / Vulcan XC72 GDE cathode and Pt or BDD as the anode. The decolorization efficiency for EF and PEF processes was calculated from equation 9:

\[
\text{% Color removal} = \frac{A_0 - A_t}{A_0} \times 100
\]

where \(A_o\) and \(A_t\) are the absorbance at initial time and time t, respectively, at \(\lambda_{max} = 484\) and 482 nm for OII and SY, respectively.\textsuperscript{6,22,25}

For the processes using Pt as anode, 100% of decolorization was attained in approximately 30, 40 and 105 min for OII and 20, 40 and 90 min for SY at 1.00, 0.50 and 0.25 mmol L\textsuperscript{-1} Fe\textsuperscript{2+}, respectively (Figure 4). In processes with BDD, the complete decolorization was attained after approximately 60 min of electrolysis for OII (Figure 4a) and after 30, 60 and 75 min, 98-100% of the SY had been removed at 1.00, 0.50 and 0.25 mmol L\textsuperscript{-1} Fe\textsuperscript{2+}, respectively (Figure 4b). The decolorizations increased at higher Fe\textsuperscript{2+} concentrations at all processes because of the higher amount of hydroxyl radicals generated according to Fenton’s reaction (equation 3).\textsuperscript{1,5,15} A similar pattern of color removal was found for OII e SY using Pt and BDD anodes. However, the decolorizations with 1.00 and 0.50 mmol L\textsuperscript{-1} Fe\textsuperscript{2+} with the Pt anode were faster than processes with the BDD anode. These results can be justified by the faster oxidation of Fe\textsuperscript{2+} to Fe\textsuperscript{3+} on the surface of the anode of BDD (equation 4) and by the consumption of Fe\textsuperscript{2+} that reacts with the S\textsubscript{2}O\textsubscript{8}\textsuperscript{2–} formed on the surface of the BDD (equation 11).\textsuperscript{19,39} Such reactions
reduce the concentration of *OH produced by the Fenton reaction (equation 3). 5,19,39

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad (10)
\]

\[
\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+} \quad (11)
\]

The determination of decolorization EC is an important parameter because it provides information for selecting the best cost-benefit process. The decolorization EC per volume unit (in kWh m\(^{-3}\)) for the trials made with 350 mL solution were obtained from equation 12:\(^8\)

\[
\text{EC} = \frac{E_{\text{cell}} \cdot I \cdot t}{V_s} \quad (12)
\]

where \(E_{\text{cell}}\) is the average potential difference of the cell (V), \(I\) is the applied current (A), \(t\) is the electrolysis time (h) and \(V_s\) is the solution volume (L).

Figure 5 shows the EC of decolorization of OII and SY. It can be observed that the EC in the processes using the Pt anode was inversely proportional to the \(\text{Fe}^{2+}\) concentration. This observation can be explained taking into account the effect on conductivity of the production of protons and hydroxyl ions caused by Fenton’s reactions, which lead to faster decolorization. The decolorization with the BDD anode showed similar EC in the most processes, which was higher than the EC of the decolorization with Pt anodes. This tendency may be attributed to the fact that parasite reactions are consuming hydroxyl radicals and other significant oxidants, limiting the action of the radicals on the dye oxidation. In this way, decolorization with Pt was faster, and smaller potential differences between the electrodes are provided to the Pt / GDE cell at the same current density.\(^{22}\) From these results, it can be inferred that the decolorizations of OII and SY with Pt anode in 1.00 mmol L\(^{-1}\) \(\text{Fe}^{2+}\) presented the best cost-benefit.

The kinetics of decolorization of OII and SY solutions can be described as a pseudo-first-order reaction by: \(^8,40\)

\[
A = A_0 e^{-k_1 t} \quad (13)
\]
\[
\ln(A_0/A) = k_1 t \quad (14)
\]

where \(A_0\) and \(A\) are the absorbance at initial time and time \(t\), respectively, at \(\lambda_{\text{max}} = 484\) nm for OII and SY, respectively; \(k_1\) (min\(^{-1}\)) is the pseudo-first-order kinetic constant and \(t\) (min) is the decolorization time.

The absorbance decays were well-fitted to a pseudo-first-order kinetic equation, as seen in the inset of Figure 4. This suggests the constant production of oxidant \(\cdot \text{OH}\) in the systems that accelerates the oxidation rate of both dyes. Table 3 shows the pseudo-first-order kinetic constants (\(k_1\)) and the corresponding squares of the correlation coefficients (\(R^2\)) for the decolorization of OII and SY. The \(k_1\) values of OII and SY increased by increasing Fe\(^{2+}\) concentrations. The \(k_1\) increased from 0.021 to 0.223 min\(^{-1}\) when the Fe\(^{2+}\) concentration increased from 0.25 to 1.00 mmol L\(^{-1}\) for the decolorization of SY by EF with Pt, for example. The decolorization of OII and SY with Pt is very low at the lower Fe\(^{2+}\) concentration. This indicate that this Fe\(^{2+}\) content is insufficient to propagate Fenton’s reaction, and thus, it diminishes the oxidation efficiency of the dye. In addition, the \(k_1\) values were higher in the SY decolorizations compared to OII decolorization under similar conditions.

Considering the decolorizations of OII and SY dyes under same conditions (anode and Fe\(^{2+}\) initial concentration), it was observed that: (i) the EF and PEF processes showed similar decolorization efficiency, indicating that the color removal process was controlled mainly by Fenton’s reaction (equation 3)\(^1\) and direct anodic oxidation (equation 1);\(^5\) and (ii) the color removal of SY was faster than OII. We believe that to be due to the chemical structure of SY because it contains two sulfonic groups (Figure 1), which are negative and repel each other, leaving the azo group (–N=N–) more exposed and susceptible to the attack of hydroxyl radicals.

Mineralization of OII and SY solutions

Solutions of 350 mL of the OII or SY dye were submitted to mineralization by EF and PEF processes with different Fe\(^{2+}\) initial concentrations (0.25, 0.50 and 1.00 mmol L\(^{-1}\)). The GDE cathode of WO\(_{2.72}\) / Vulcan XC72
was combined with Pt or BDD anode. Figure 6 show results of mineralization of OII and SY as a function of time. In general, (i) the processes with the highest Fe²⁺ initial concentration obtained higher mineralization rates of the dyes employing Pt anode and, (ii) in the experiments with BDD anode, the highest TOC removals occurred in the processes at 0.5 mol L⁻¹ Fe²⁺.

Comparing the mineralizations of the OII and SY under the same conditions (i.e., same anode and initial Fe²⁺ concentrations), the mineralization efficiency of the PEF process was superior to the EF process (Figure 6). This behavior was expected as the incidence of UV radiation in the system allows the photolytic reactions (equations 5 and 6) to produce more hydroxyl radicals that have oxidative action on stable intermediates, which is not possible solely by EF process.¹² Then, with the exception of OII mineralization by PEF / 1.00 and PEF / 0.50 processes, the other processes with Pt showed a stagnation of TOC removal after a certain time. This means that if the electrolysis time were extended, the total mineralization of the dyes OII and SY would not be achieved. In contrast, when BDD was used, almost complete mineralization was attained at 240 min, showing a clear trend for total decay even for SY by PEF / 1.00 and EF / 1.00, which showed slower decay (Figure 6).

From TOC decay, the EC per unit TOC mass (EC_{TOC}, in kWh (kg TOC)⁻¹) and the mineralization CE (MCE, in %) were obtained from equations 15 and 16, respectively:²²

\[
EC_{TOC} = \frac{1000E_{cell}I t}{V_s\Delta(A(TOC))_{exp}} \quad (15)
\]

\[
MCE(\%) = \frac{n F V_s\Delta(A(TOC))_{exp} \times 100}{4.32 \times 10^7 m \ I t} \quad (16)
\]

where 1000 is a conversion factor (mg g⁻¹), E_{cell} is the average potential difference of the cell (V), I is the applied current (A), t is the electrolysis time (h), V_s is the solution volume
(L), $\Delta$(TOC)$_{exp}$ is the experimental TOC decay (mg L$^{-1}$), $n$ is the theoretical number of electrons consumed per dye molecule for overall mineralization, $F$ is the Faraday constant (96,487 C mol$^{-1}$), $4.32 \times 10^7$ is a conversion factor to homogenize units ($3600$ s h$^{-1} \times 12,000$ mg mol$^{-1}$) and $m$ is the number of carbon atoms of the azo dye.

Studies have shown that the mineralization of N present in azo dyes by EF processes can generate NO$_3^-$, NO$_2^-$ and NH$_4^+$. Normally, NO$_3^-$ is formed in the greatest quantity. Thus, we consider the mineralization of OII and SY as their conversion into CO$_2$ with the release of NO$_3^-$ and SO$_4^{2-}$ as major inorganic ions, according to equations 17 and 18, respectively. Then, the theoretical number of electrons consumed per dye molecule ($n$) for overall mineralization is 84.$^{22,44,45}$

$$C_{16}H_{11}N_2O_4S^- + 38H_2O \rightarrow 16CO_2 + 2NO_3^- + SO_4^{2-} + 87H^+ + 84e^- \quad (17)$$

$$C_{16}H_{10}N_2O_7S_2^{2-} + 39H_2O \rightarrow 16CO_2 + 2NO_3^- + 2SO_4^{2-} + 88H^+ + 84e^- \quad (18)$$

Table 4 shows values of EC and MCE of combustions of OII and SY by EF and PEF processes with different initial concentration of Fe$^{2+}$ using WO$_{2.72}$/Vulcan XC72 GDE cathode and Pt or BDD anode. In general, the incinerations of OII and SY presented increasing EC and decreasing MCE at longer electrolysis times for both EF and PEF processes. This can be explained since in the long time of electrolysis, there was a reduction of organic matter available for oxidation and the formation of more recalcitrant byproducts, probably oxidized more slowly by Pt(•OH) or BDD(•OH), limited by their transport towards anode surface.$^7$

In the processes with BDD anode, the mineralizations at lower concentrations of Fe$^{2+}$, especially at 0.50 mmol L$^{-1}$
Fe\textsuperscript{2+}, presented lower EC and higher MCE. This is desirable because it enables the incineration of this compound under more environmentally friendly conditions, including a lower Fe\textsuperscript{2+} ion content. It seems that higher Fe\textsuperscript{2+} content interfered negatively with the performance of BDD. In this case, the excess Fe\textsuperscript{2+} may have favored the residual reaction (equation 19),\textsuperscript{46} which can reduce the oxidation power of the process due to the consumption of hydroxyl radicals and the inhibition of the production of hydroxyl radicals by the Fenton reaction (equation 3).\textsuperscript{46}

Fe\textsuperscript{2+} + •OH \rightarrow Fe\textsuperscript{3+} + OH\textsuperscript{-} (19)

The trials of cathode WO\textsubscript{2.72} / Vulcan XC72 combined with the BDD anode showed the highest TOC removals: 82% TOC removal of OII by PEF / 1.00 after 3 h and 90% TOC removal of SY by PEF / 0.50 after 4 h. The results of mineralization also indicate that the electrochemical system (cathode: WO\textsubscript{2.72} / Vulcan XC72 and anode: BDD) employed in these experiments can become a good choice for dye removal. Both EF and FEP processes show superior or equal efficiency when compared to many other published studies, as shown in Table 5.

Table 4. Energy consumption and mineralization current efficiency for EF and PEF combustions of OII and SY at different initial concentrations of Fe\textsuperscript{2+} and different anodes

<table>
<thead>
<tr>
<th>Dye</th>
<th>Anode</th>
<th>Process</th>
<th>time / min</th>
<th>EC / (kWh per kg TOC)</th>
<th>MCE / %</th>
<th>Fe\textsuperscript{2+} / (mmol L\textsuperscript{-1})</th>
<th>Fe\textsuperscript{2+} / (mmol L\textsuperscript{-1})</th>
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<tr>
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<td>Fe\textsuperscript{2+} / (mmol L\textsuperscript{-1})</td>
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<td>Fe\textsuperscript{2+} / (mmol L\textsuperscript{-1})</td>
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<tr>
<td>Orange II</td>
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</table>

Conclusions

Modification of Vulcan XC72 carbon by incorporating WO$_{2.72}$ nanoparticles resulted in increased H$_2$O$_2$ electrogeneration. The faster decolorization of SY can be attributed to its structure. Decolorizations with Pt anode were faster. However, mineralization with BDD anode showed higher yield. The Fe$^{2+}$ initial concentration was determinant: 1.0 and 0.5 mmol L$^{-1}$ Fe$^{2+}$ were the most adequate concentrations for decolorization with Pt anode and mineralization with BDD anode, respectively. Thus, depending on the purpose, one should choose the most suitable anode to match it with the WO$_{2.72}$/Vulcan XC72 cathode. The study showed the limitation of Pt anode to mineralize the studied dyes and allowed to identify the best parameters for application of the cathode of WO$_{2.72}$/Vulcan XC72 at the combustion of OII and SY. The PEF process at 0.5 mol L$^{-1}$ Fe$^{2+}$ with BDD anode was shown to be more promising because it presented greater TOC removal and indicated a tendency of complete mineralization of the dyes. In addition, the study opens up possibilities to evaluate other parameters in order to obtain greater efficiency of the degradation process of dyes, considering that the cathode presented significant H$_2$O$_2$ electrogeneration.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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Table 5. Comparative EF and PEF treatments of OII and SY dyes with GDE cathodes

<table>
<thead>
<tr>
<th>Material</th>
<th>Process</th>
<th>Dye: C$_0$ (mg C L$^{-1}$) (V$_0$/mL)</th>
<th>TOC removal / % (time / h$^a$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTF@CF</td>
<td>EF</td>
<td>OII: 19.2 (200)</td>
<td>28 (4)</td>
<td>$^a$</td>
</tr>
<tr>
<td>PPy / lig-GF</td>
<td>EF</td>
<td>OII: 5.5 (200)</td>
<td>60 (3)</td>
<td>$^a$</td>
</tr>
<tr>
<td>Air-diffusion cathode-BDD</td>
<td>PEF</td>
<td>SY: 100 (100)</td>
<td>95 (4)</td>
<td>$^a$</td>
</tr>
<tr>
<td>WO$_{2.72}$/Vn-BDD</td>
<td>EF</td>
<td>OII</td>
<td>72 (3)</td>
<td>this work$^b$</td>
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<tr>
<td>WO$_{2.72}$/Vn-BDD</td>
<td>PEF</td>
<td>SY</td>
<td>82 (3)</td>
<td>this work$^b$</td>
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<td>WO$_{2.72}$/Vn-BDD</td>
<td>EF</td>
<td>SY</td>
<td>83 (4)</td>
<td>this work$^b$</td>
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</table>

$^a$Electrolysis period; $^b$C$_0$ = 50 mg C L$^{-1}$ and V$_0$ = 350 mL. C$_0$: total organic carbon (TOC) initial concentration of dye; V$_0$: initial volume of solution; CNTF@CF: carbon nanotube fiber deposited on carbon fiber; EF: electro-Fenton; OII: Orange II; lig-GF: lignin-graphite felt; BDD: boron-doped diamond; PEF: photoelectro-Fenton; SY: Sunset Yellow FCF; Vn: Vulcan XC72.