Development of a TiO₂ modified optical fiber electrode and its incorporation into a photoelectrochemical reactor for wastewater treatment

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Abstract
Electrochemical advanced oxidation processes (EAOPs) are used to chemically burn non-biodegradable complex organic compounds that are present in polluted effluents. A common approach involves the use of TiO₂ semiconductor substrates as either photocatalytic or photoelectrocatalytic materials in reactors that produce a powerful oxidant (hydroxyl radical) that reacts with pollutant species. In this context, the purpose of this work is to develop a new TiO₂ based photoanode using an optic fiber support. The novel arrangement of a TiO₂ layer positioned on top of a surface modified optical fiber substrate, allowed the construction of a photoelectrochemical reactor that works on the basis of an internally illuminated approach. In this way, a semi-conductive optical fiber modified surface was prepared using 30 μm thickness SnO₂:Sb films on which the photoactive TiO₂ layer was electrophoretically deposited. UV light transmission experiments were conducted to evaluate the transmittance along the optical fiber covered with SnO₂:Sb and TiO₂ showing that 43% of UV light reached the optical fiber tip. With different illumination configurations (external or internal), it was possible to get an increase in the amount of photo-generated H₂O₂ close to 50% as compared to different types of TiO₂ films. Finally, the electro-Fenton photoelectrocatalytic Oxidation process studied in this work was able to achieve total color removal of Azo orange II dye (15 mg L⁻¹) and a 57% removal of total organic carbon (TOC) within 60 min of degradation time.

1. Introduction

Advanced oxidation processes (AOPs) have been identified as a successful alternative for the elimination of some toxic organic compounds in water. These processes are chemical, photochemical, photocatalytic or electrochemical methods characterized by the generation of the hydroxyl radical species (OH⁻) (Yu et al., 2008; Tomovska et al., 2007; Lou and Huang, 2008; Lapertot et al., 2008; Bandala et al., 2008; Orozco et al., 2008; Guinea et al., 2008). The hydroxyl radical is a strong oxidant with a standard potential of 2.8 V vs NHE (pH 0) capable of destroying most of the organic matter present in water.

Recently, there has been an increasing interest in the use of the so-called Electrochemical Advanced Oxidation Processes (EAOPs) (Martínez-Huitle and Brillas, 2009; Skoumal et al.,...
which consist on electrochemical methods that result in the generation of hydroxyl radicals (OH/C15) or its precursor, hydrogen peroxide. In this way, while the OH/C15 radical can be directly generated on the surface of an anode M (see Eq. (1)), its production can be achieved indirectly by generation of H2O2 (through the reduction of dissolved oxygen in water under slightly acidic conditions according to Eq. (2) (Brillas et al., 2003; Boye et al., 2003)).

\[
M + H_2O \rightarrow M(OH^+) + H^+ + e^- \quad (1)
\]

\[
O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)
\]

Hydrogen Peroxide, as can be seen in Eq. (3), can react with Fe2+ ions (pH 2–3) to produce OH radicals in an arrangement known as the Electro-Fenton process (Peralta-Hernández et al., 2007; Özcan et al., 2009; Virkutyte and Jegatheesan, 2009; Serra et al., 2008).

\[
H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^- \quad (3)
\]

Reaction 3 is propagated by Fe3+ regeneration, resulting from reduction of Fe3+ at the cathode (Flox et al., 2007a, b; Oturan et al., 2008).

A feasible alternative is the use of the photoelectro-Fenton process where the application of UV light promotes the photo-decomposition of complexes of Fe3+ with generated carboxylic acids (Boye et al., 2002; Sirés et al., 2006) and the regeneration of Fe2+ from photoreduction of Fe(OH)2+, which is the predominant form of the Fe3+ species in aqueous solution (Eq. (4)):

\[
Fe(OH)_2^+ + h\nu \rightarrow Fe^{2+} + OH^+ \quad (4)
\]

Advanced oxidation technology studies often have included semiconductor photocatalyst as well and in this regard, titanium dioxide (TiO2) has been proven to be an effective catalyst for oxidation and mineralization of organic pollutants (Wang et al., 2007). Previous works in our research group (Peralta-Hernández et al., 2007, 2008) as well as in others (Li et al., 2006; Jiang et al., 2006; Zhao et al., 2007) have focused on the use of TiO2 electrodes showing that it can be efficiently used as anodes in a photoelectrochemical reactor. The use of the TiO2 in this approach involves the light induced promotion of an electron (e−) from the valence band (VB) into the conduction band (CB), thus creating a hole (h+) in the later according to Eq. (5) (Gumy et al., 2008; Fujishima et al., 2000). The e−/h+ pair can be separated under the influence of an applied potential forcing the electron to travel through the electric circuit towards the cathode favoring at the same time, the reaction of the positively charged vacancy, h+, with either adsorbed water or hydroxyl ions to produce the powerful OH oxidant (Eqs. (6) and (7)).

\[
TiO_2 + h\nu \rightarrow e_{cb} + h_{vb} \quad (5)
\]

\[
h_{vb} + H_2O \rightarrow OH^+ + H^+ \quad (6)
\]

\[
h_{vb} + OH^- \rightarrow OH^+ \quad (7)
\]

The effectiveness of the oxidation process can also be enhanced through the direct oxidation of the organic compound, R, by the positively charged vacancy (hvb, Eq. (8))
\[ h_{\text{aq}}^+ + R \rightarrow R_{\text{aq}}^{+} \]  

Under typical conditions however, illumination of the semiconductor electrode in these reactors is not optimized due to the absorption and scattering of the radiation by the reaction medium (Danion et al., 2004a, b, 2006, 2007). As proposed and theoretically evaluated by Marinangeli and Ollis (1977, 1980, 1982), a feasible solution for this problem is the use of an optical fiber as a light distributor and support of the photocatalyst. Several works have developed, characterized, and modelled an optical fiber reactor (OFR) system for water treatment (Peill and Hoffmann, 1998; Choi et al., 2001; Wang and Ku, 2003) and others have demonstrated that the covered optical fiber with TiO2 films can be used for the photocatalytic oxidation of organic compounds (Miller et al., 1999).

So far however, the use of a TiO2 modified optical fiber as photomode in a photoelectrochemical wastewater treatment reactor has not been published. Therefore, in this work we report the construction of an optical fiber-based electrode covered with TiO2 and its use for the oxidation of the model textile dye Orange II.

Since the optical fiber carries light along its length and is made from a nonconducting material (SiO2), it was necessary to previously modify the fiber by promoting holes or cracks along its surface (so that light could escape) and later, deposit a semiconductor material (SnO2:Sb) on which the formation of the photocatalytically active TiO2 film could be carried out by electrophoretic deposition (see Fig. 1). As a part of this work, we evaluated the physicochemical characteristics of the SnO2:Sb and TiO2 films and the influence of the coating thickness and fiber length on the light transmission and on the photocatalytic production of H2O2.

2. Materials and methods

2.1. Optical fiber treatment

Optical fiber O.F. P600-12-UV/VIS (Ocean Optics, USA) with a 600 µm silica core and a polymer optical cladding was used. Each optical fiber was cut into pieces of 20 cm in length and 10 cm of optical cladding was removed by heating at 500 ºC. Fiber ends were polished with abrasive paper. The fibers were pre-treated with HF (48–51%, J.T. Baker) solution and later rinsed with deionized water. Scanning electron microscopy (SEM) and emission diffraction X-ray (EDX) analysis were completed using a JEOL JSM-5400L microscope with an accelerating voltage of 25 kV.

2.2. Antimony tin oxide (SnO2:Sb) film

These films were prepared on top of the pre-treated optical fiber material to provide a rough and conducting surface on which the TiO2 films could later be grown by electrophoretic deposition. The ATO (Antimony Tin Oxide) material was chosen for its conductive properties and for its optical transparency in the visible spectral region. The films were prepared using the painting technique. The solution was prepared using 11 g of SnCl4 (98% Strem Chemicals) dissolved in 5 mL hydrochloric acid (HCl, 36.5–38.0% J.T. Baker) and heated at 90 ºC for 30 min. Afterwards, 10 mL of methanol were added to the SnCl4 solution in order to prepare the starting mixture. Finally, to prepare the doped solution, SbCl3,(99% Strem Chemicals) was dissolved in 2-propanol (2-Propanol 99.97% J.T. Baker) and added to the starting solution to form a 2 % w/w solution (Elangovan and Ramamurthi, 2003).

The SnO2:Sb films were heated at 450 ºC for 10 min in a tubular furnace (Thermoline model 21100) in order to promote the formation of the oxidized species of tin and antimony (SnO2, Sb2O3 and Sb2O5). The SnO2:Sb films were characterized by SEM, EDX, X-ray diffraction (XRD), light transmission and profilometry.

2.3. TiO2 film

TiO2 films were deposited on the pre-treated fibers using the electrophoretic deposition method in which the fiber was immersed for 60 s at room temperature in a sonicated 250 mL colloidal suspension (12.5 gr P25 Degussa TiO2 powder in 5% v/v 2-propanol, J.T. Baker 99.97% in deionized water) under a 4 V potential difference applied between a stainless steel sheet and the optical fiber previously coated with SnO2:Sb. The electrodes were then placed in an oven at 450 ºC to sinter the TiO2 film (Manriquez and Godinez, 2007).

2.4. Light transmission across the SnO2:Sb–TiO2 films

The measurement of light transmitted by the coated fiber was made with a light sensitive photo-resistance semiconductor (CdS) with a maximum detection limit of 15 MΩ. The photoresistance semiconductor was connected to a multimeter (Fluke Model 45) to measure the electrical resistance. The fraction of light transmitted, \( I_{\text{trans}} / I_{\text{input}} \), was obtained by calculating the ratio of the electrical resistance between the value obtained placing the resistance at the specific point of analysis, \( R_{\text{trans}} \), and the value obtained at the illumination source, \( R_0 \) (Eq. (9), Pallas, 2005). All the measurements were performed in a darkroom.

\[
\frac{I_{\text{trans}}}{I_{\text{input}}} = \frac{R_{\text{trans}}}{R_0}
\]

2.5. H2O2 photocatalytic generation

To measure the influence of the illumination arrangement mode (internal or external) and the effect of the number of TiO2 layers deposited on the light conducting substrate on the production of hydrogen peroxide, a bundle of 25 fibers was placed in a 0.05 M Na2SO4 (Karal, 7039) solution at pH 3 (adjusted with sulfuric acid, 98%, J.T. Baker) previously saturated with oxygen (O2 99.99%, Infra). For externally illuminated sources, \( I_{\text{trans}} / I_{\text{input}} \), was obtained by using an internal illumination arrangement mode, the same electrode was illuminated from one end of the fiber bundle.
using the same lamp under similar experimental conditions. The hydrogen peroxide production was also measured using the titanium (IV) oxysulfate method.

2.6. Electrochemical generation of H₂O₂

Hydrogen peroxide was simultaneously produced at the cathode and the anode in an electrochemical arrangement. In the former electrode, it was produced by the electrochemical reduction of the dissolved oxygen on a carbon cloth cathode (ElectroChem, Inc.) characterized by 69 cm² of geometric area (Eq. (2)). In the anodic side, a bundle of 25 optical fibers coated with SnO₂:Sb and TiO₂ (13 cm² geometric area) worked as an anode producing H₂O₂ through the electrochemical oxidation of water. The electrolyte consisted of a sulphate buffer (Na₂SO₄) solution at pH 3. The experimental system included a fiberglass electrochemical reactor with three individual chambers of 9 cm length and 5.5 cm inner diameter. The reactor volume was 640 mL and the recirculation flow rate was maintained at 80 L h⁻¹ using a diaphragm pump (Shurflo Model 2088-594-154). The experiments were performed under galvanostatic conditions applying 1 mA cm⁻² cathodic current density using a GW Model GPR-1820HD power supply.

2.7. Electrochemical advanced oxidation processes (EAOPs)

Four different processes were evaluated by measuring the color removal of a 15 mg L⁻¹ Orange II (C₁₆H₁₁N₂NaO₄S, ALDRICH) solution using the electrochemical reactor:

(i) Anodic electrooxidation; which consists on electron transfer from the dye molecule to the anode. In this case, hydroxyl radicals can also be produced from the Electrolytic-Oxidation of water on the anode surface (Eq. (1) (Xie and Li, 2006).

(ii) Electro-assisted photocatalytic oxidation; which is a process that involves the photocatalytic oxidation reaction of the dye on a polarized photo excited TiO₂ electrode. While the applied potential favors charge carrier separation (Selcuk et al., 2004; Wang et al., 2008; Neelavannan and Basha, 2008; Hou et al., 2009; Yang et al., 2009), UV illumination of the anodic material (Eqs. (5)-(8)) was conducted under internal and external arrangement modes.

(iii) Electro-Fenton; that combines the reactions that occur in the Fenton system (Eq. (3)) and those described in (i).

(iv) The electro-Fenton photoelectrocatalytic Oxidation process that considers the combination of the photoelectrocatalytic reactions of TiO₂ (ii) and the photoelectro-Fenton reactions shown in Eqs. (3) and (4) (Xie and Li, 2006).

The photo assisted processes were performed with the UV lamp used in the H₂O₂ generation studies. In the case of the electro-Fenton and electro-Fenton photoelectrocatalytic Oxidation processes, 0.2 mM of FeSO₄ was added as the Fe²⁺ ion source (98% J.T. Baker). The removal of color was evaluated by determining the absorbance of the solution at λ = 487 nm in a UV-vis spectrophotometer (Agilent Technologies). Total organic carbon (TOC) data was obtained using a TOC VSCN analyzer (Shimadzu Co.).

3. Results and discussion

3.1. Optical fiber treatment

Fig. 2 shows the SEM image of the optical fiber without the cladding (2a) and after it was pre-treated with HF (2b). As can
be observed, the morphology changed due to the formation of pores over the surface of the optical fiber. The EDX test indicated the presence of Si and O and the absence of F, so pore formation was only due to chemical attack by HF as no other species were found on the surface (Fig. 2c). It is important to note that while the pre-treatment of the fiber was carried out to produce a light escaping path on the fiber surface (see Fig. 1), it also resulted in a rough surface on which adherence of the SnO2:Sb and TiO2 films could be favored.

3.2. Antimony tin oxide (SnO2:Sb) film

A homogeneous deposit of tin oxide doped with antimony was obtained after repeating 10 times the painting process described in the experimental section (SEM images not shown). Although the electrical resistance of the SnO2:Sb film was high (0.1 Ω), a more aggressive thermal treatment to increase the conductivity was not tried since the optical transparency of the film could be affected (Russo and Cao, 2008). Despite the fact that the conductivity obtained with these films was relatively low, the adherence of the TiO2 films that were later grown by electrophoretic deposition was favored by the presence of the transparent SnO2:Sb film. The XRD patterns obtained from the SnO2:Sb deposits on the other hand indicated the presence of tin and antimony oxides (Sb2O5 and Sb2O3). The profilometer experiments indicated that the thickness of the deposit is about 30 μm.

UV light transmission along the optical fiber was determined as received without the cladding and using the fiber treated with HF. The measurements were made with various lengths of the optical fiber. When a complete fiber was used, a loss of almost 30% of the UV radiation was measured in the first 10 cm due to refraction and reflection phenomena (Fig. 3a). When the polymer optical cladding was removed and the core was exposed, the UV light transmission decreased to 45% in the first 2 cm of the fiber caused by the abrupt change of the refraction index between the SiO2 and air (n = 1.5 vs n = 1) (Wang and Ku, 2003). The UV light transmittance in the HF treated fiber decreased to 5% in the first 2 cm of the fiber.

The measurement of the UV light transmittance along the SnO2:Sb covered fiber as a function of the number of deposits shows that 20 % of the UV light is absorbed or refracted by the chemical and structural properties of SnO2:Sb films (Fig. 3b), and this percentage remains constant for the various numbers of films. According to these results, the thickness of the SnO2:Sb does not affect the absorbance percentage, so the number of deposits do not limit the transmittance of the fiber.

3.3. TiO2 coating

To reduce the electrical resistance in the SnO2:Sb film in order to be able to carry out the electrophoretic deposition of TiO2, carbon cloth threads were placed around the optical fiber already covered with SnO2:Sb; thus obtaining an electrical resistance of the optical fiber surface of 50 Ω. Fig. 4 shows SEM images of the TiO2 films deposited on the carbon cloth thread and on the optical fiber after electrophoretic deposition layers were carried out. Under these conditions, the TiO2 films have a homogenous and porous surface. However, when applying the deposition procedure from 3 to 10 times, the texture of the surface becomes compact and the deposits tend to crack and fall apart. The results obtained with the profilometer indicate that the thickness of the film ranged between 2.5 and 70 μm.

The transmittance in the optical fiber is affected by the thickness of the TiO2 film that covers the external surface, so it was necessary to assess the effect of the TiO2 deposit thickness on the global efficiency of light transmission. This effect was evaluated by measuring the light fed to the fiber (Iinput) and the light transmitted throughout the optical fiber coated with TiO2 (Itrans). According to the results obtained, the relationship Itrans/Iinput decreases exponentially from 1.0 when there is no TiO2, to 0.47 when the thickness of the TiO2 film is 70 μm (Fig. 5).

The mathematical expression of Beer’s law predicts that the fraction of refracted or absorbed light by the TiO2 deposit...
should increase proportional to the increase of the deposit thickness. Choi et al. (2001) and Peill and Hoffmann (1995), adapted Beer’s Law to the specific case of coated optical fibers:

\[ \frac{I_{\text{trans}}}{I_{\text{input}}} = e^{-\varepsilon_{\text{app}} \delta} \quad (10) \]

\[ \frac{I_{\text{trans}}}{I_{\text{input}}} = (1 - f_b) + f_b e^{-\varepsilon_{\text{app}} \delta} \quad (11) \]

where \( I_{\text{input}} \) is the input light intensity (W cm\(^{-2}\)); \( I_{\text{trans}} \) is the residual light intensity transmitted (W cm\(^{-2}\)); \( \varepsilon_{\text{app}} \) and \( \delta \) are the apparent extinction coefficient and thickness of the coating respectively; \( f_b \) is the fraction of incident light with \( \theta < 90^\circ \) refracted and absorbed by the TiO\(_2\) coating and \((1 - f_b)\) represents the fraction of near-parallel incident light that is not absorbed by the TiO\(_2\) film.

The fitting of the experimental data to Eqs. (10) and (11) shows that the relationship \( I_{\text{trans}}/I_{\text{input}} \) decreases exponentially with the TiO\(_2\) thickness and that the light transmitted through the semiconductor material reaches values near 0.5 for a TiO\(_2\) thickness value of about 35 \( \mu \)m. The fitting of the data also allows the estimation of: 1) the fraction of near-parallel incident light \((1 - f_b)\) that is not absorbed by the TiO\(_2\) coating (0.5261), 2) the fraction of incident light \( (f_b) \) with \( \theta < 90^\circ \) refracted and absorbed by the TiO\(_2\) coating (0.4739) and 3) the value of the apparent extinction coefficient \( (\varepsilon_{\text{app}}) \) for the TiO\(_2\) film (0.088 \( \mu \)m\(^{-1}\)).

### 3.4. Photocatalytic generation of H\(_2\)O\(_2\)

Once the TiO\(_2\) modified optical fiber electrode was prepared and characterized, its performance as a photocatalytic material (under no polarization conditions) using UV radiation was tested. In these experiments, the difference between internal (light travelling and escaping along the optical fiber path, see Fig. 1) and external (from a source located outside the reaction cell) illumination modes on the TiO\(_2\) modified fiber was evaluated by measuring the photocatalytic production of H\(_2\)O\(_2\) in the presence of oxygen. Upon illumination of the TiO\(_2\) modified substrate, hydrogen peroxide is assumed to be produced by reactions 5–7,12 and 13 (Bauer et al., 1999; Peralta-Hernández et al., 2006; Gianluca et al., 2008). This is supported
by the data presented in Fig. 6 in which a control experiment without UV radiation does not result in H₂O₂ generation.

\[
\text{OH}^*_\text{ads} + \text{OH}^*_\text{ads} \rightarrow \text{H}_2\text{O}_2 \quad (12)
\]

\[
2\text{H}_2\text{O} + 2h^*_\text{VI} \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ \quad (13)
\]

Additional information presented in Fig. 6 indicates that in the case of one and two TiO₂ coatings, there is approximately 50% more peroxide production with internal than with external illumination. In the case of five TiO₂ coatings however, the radiation feeding mode has no effect on the quantity of H₂O₂ generated since in both cases the concentration of H₂O₂ in solution is approximately 6 mgL⁻¹. The production of H₂O₂ on the other hand, decreases for both internal and external illumination when the number of deposits is more than six. This observation is likely due to the loss of TiO₂ film caused by a poor adherence of thick films of TiO₂.

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**Fig. 5** – UV light transmission ratio (experimental and fitted data) of a TiO₂ modified optical fiber as a function of the coating thickness.

**Fig. 6** – Photocatalytic production of H₂O₂ as a function of the number of deposits of TiO₂ on an optic fiber-based electrode under different illumination conditions, visible light (■), UV external illumination (○) and UV internal illumination (△). Illumination time, 60 min. Na₂SO₄ 0.05 M pH 3 solution saturated with oxygen and without applied electric current.

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**Fig. 7** – Photoelectrochemical reactor scheme. As cathode is used carbon cloth and as anode the TiO₂/modified optical fiber electrode. UV lamp \( \lambda = 254 \text{ nm} \), \( P = 21 \text{ W cm}^{-2} \) in both illumination configuration. Reactor volume 640 mL and flow rate 80 L h⁻¹.
In the case of the Anodic electrooxidation process. In the removal of color in the different electrochemical processes (EAOPs), the removal of color related to the discoloration of the solution. As can be seen in Fig. 5, the iron containing solution due to the UV light (see Eq. (4)) that, in the case of the internal illumination, the decrease of this ratio is possible at the negatively polarized cathode surface because, as can be seen in Fig. 7, the iron containing solution is continuously passing through the two electrodes during the process. In addition, reduction also takes place in solution due to the UV light (see Eq. (4)) that, in the case of the internal illumination mode, goes through the SnO2:Sb and TiO2 modified optical fiber. Note for instance that, as has been previously described, 50% of the incident light is not absorbed by the SnO2:Sb and TiO2 layers (See Sections 2.4 and 3.3 and Fig. 5).

In terms of color removal rates (calculated from the simple linear correlation employing the first two points of the experimental response for each system), Anodic electro-oxidation shows a value \( k = 0.0122 \text{ min}^{-1} \) that is very similar to that obtained for the Electro-assisted photocatalytic oxidation process when the external illumination arrangement is used \( k = 0.0126 \text{ min}^{-1} \) and slightly lower to that

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**Fig. 8** – Color removal data for Azo orange II dye by different EAOPs. [OG II] 15 mg L\(^{-1}\). Electrolyte 0.05 M Na2SO4 solution pH 3. 0.2 mM Fe\(^{2+}\) in the Fenton processes. Degradation time 60 min. \( [\text{H}_2\text{O}_2] 80 \text{mg L}^{-1}\). UV lamp \( \lambda = 254 \text{nm}, P = 21 \text{W cm}^{-2} \) in both illumination configurations. \( j = 1 \text{mA cm}^{-2} \). Anodic electrooxidation (■), Electro-assisted photocatalytic oxidation (external (○) and internal illumination (△)), electro-Fenton (△), electro-Fenton photoelectrocatalytic Oxidation (external (○) and internal illumination (△)).

**Fig. 9** – Total Organic Carbon removal data for Azo orange II dye by different EAOPs. [OG II] 15 mg L\(^{-1}\). Electrolyte 0.05 M Na2SO4 solution pH 3. 0.2 mM Fe\(^{2+}\) in the Fenton processes. Degradation time 60 min. \( [\text{H}_2\text{O}_2] 80 \text{mg L}^{-1}\). UV lamp \( \lambda = 254 \text{nm}, P = 21 \text{W cm}^{-2} \) in both illumination configuration. \( j = 1 \text{mA cm}^{-2} \). Anodic electrooxidation (■), Electro-assisted photocatalytic oxidation (external (○) and internal illumination (△)), electro-Fenton (△), electro-Fenton photoelectrocatalytic Oxidation (external (○) and internal illumination (△)).

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3.5 Electrochemical advanced oxidation processes (EAOPs)

So far, it has been shown that the novel optical fiber supported TiO2 film has photocatalytic activity for \( \text{H}_2\text{O}_2 \) production and that the internal illumination mode suggested in Fig. 1 works just as well as the external mode of illumination. To verify however that the modified optic fiber could also be polarized and used as a photoanode in EAOPs, the removal of color and the TOC of a model pollutant compound (azo Dye Orange II) were evaluated using a photoelectrochemical reactor (see Fig. 7) that, as described in the experimental part, incorporated a carbon based cathode and a TiO2 modified optical fiber-based electrode as an anode. The electrodes in this reactor were polarized three hours before the addition of the dye to assure a suitable concentration of \( \text{H}_2\text{O}_2 \) (the \( \text{H}_2\text{O}_2 \) was electro-generated on the cathode by oxygen reduction and by water oxidation on the anode, see Eqs. (2) and (13) and Section 2.6). In all cases, after 180 min of polarization, the hydrogen peroxide concentration reached approximately 80 mg L\(^{-1}\).

The removal of color in the different electrochemical advanced oxidation processes studied is shown on Fig. 8. The relationship \( A_{0}/A_{t} \) corresponds to the ratio of the absorbance of the solution at 487 nm at the time \( t, A_{t} \), and at the beginning of the process \( A_{0} \). The decrease of this ratio is related to the discoloration of the solution. As can be seen from this data, it is possible to remove nearly 50% of the color in the case of the Anodic electrooxidation process. In the Electro-assisted photocatalytic oxidation, the color removal is similar to the previous treatment using either internal or external illumination. The similarity between the results using the two illumination configuration modes, also suggest that the photo-induced decomposition of \( \text{H}_2\text{O}_2 \) by UV radiation in solution does not play an important role in the process. On the other hand, when the iron salt in form of \( \text{Fe}^{2+} \) is added to the reactor (electro-Fenton and electro-Fenton photoelectrocatalytic Oxidation), it is possible to achieve a color removal above 98% due to the rapid concentration increase of the \( \text{OH}^- \) species in solution (Peralta-Hernández et al., 2007, 2008, Abdelmalek et al., 2008). At this point, it is important to note that although the electrochemical or photoelectrochemical regeneration of \( \text{Fe}^{2+} \) from \( \text{Fe}^{3+} \) is not possible at the positive charged anode, however the reduction is possible at the negatively polarized cathode surface because, as can be seen in Fig. 7, the iron containing solution is continuously passing through the two electrodes during the process. In addition, reduction also takes place in solution due to the UV light (see Eq. (4)) that, in the case of the internal illumination mode, goes through the SnO2:Sb and TiO2 modified optical fiber. Note for instance that, as has been previously described, 50% of the incident light is not absorbed by the SnO2:Sb and TiO2 layers (See Sections 2.4 and 3.3 and Fig. 5).

In terms of color removal rates (calculated from the a simple linear correlation employing the first two points of the experimental response for each system), Anodic electro-oxidation shows a value \( k = 0.0122 \text{ min}^{-1} \) that is very similar to that obtained for the Electro-assisted photocatalytic oxidation process when the external illumination arrangement is used \( k = 0.0126 \text{ min}^{-1} \) and slightly lower to that
computed when the reactor was operated under internal illumination conditions \(k = 0.0131 \text{ min}^{-1}\). The electro-Fenton process on the other hand, shows a color removal rate substantially higher \(k = 0.1956 \text{ min}^{-1}\) that, as expected, is lower than that obtained if UV light is incorporated into the reaction system. In this case, (electro-Fenton photoelectrocatalytic Oxidation process) the color removal rate \(k = 0.2303 \text{ min}^{-1}\) was the same for the two illumination arrangements surveyed.

The results of TOC removal on the other hand, are shown in Fig. 9. Inspection of the curves indicates that when the electro-Fenton photoelectrocatalytic Oxidation process is used, it is possible to achieve a relatively high partial mineralization of the Orange II compound. In this way, using internal illumination (see Fig. 1) it is possible to reach TOC removal values of 57% after 60 min of treatment \(\text{TOC}_0\) value 12.3 ppm and \(\text{TOC}_f\) value 5.3 ppm. The lowest percentage of TOC removal on the other hand (of only 15%) was obtained with the Anodic electrooxidation approach. In terms of TOC removal rates (calculated from a simple linear correlation employing the first two points of the experimental response for each system), the electro-Fenton photoelectrocatalytic Oxidation process shows similar \(k\) values (0.013 and 0.0109 min\(^{-1}\)) for the internal and external illumination arrangements. As expected, these constants are higher than those measured for the Electro-assisted photocatalytic oxidation process for which it is also interesting to note that a similar value was found for external and internal illumination modes \(k = 0.0049\) and 0.0055 min\(^{-1}\). The lowest \(k\) value corresponds to the Anodic electrooxidation \(k = 0.0035 \text{ min}^{-1}\). Despite the relatively low percentages of TOC removal found, it is possible to predict better results using longer degradation times.

4. Conclusions

This work has shown that optical fibers previously treated with HF, SnO\(_2\)-Sb and electrochemically covered with TiO\(_2\) films can be used as internally illuminated photo anodes to produce OH\(^+\) radicals in the presence of Fe\(^{2+}\) ions. Although an exploratory study, these results are of relevance because the proposed approach can improve the light illumination efficiency in photoelectrochemical reactors; particularly in those designed for water treatment processes. The photoelectrochemical reactor considered in this study is for instance capable of removing 98 % of the color of Azo orange II dye and 57% of TOC in the presence of iron (II) ions using an internal illumination arrangement.

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