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Combination of Photoelectrocatalysis and Ozonation as a Good Strategy for Organics Oxidation and Decreased Toxicity in Oil-Produced Water

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The oil-produced water generated during drilling of oil wells and gas extraction has been a cause for great concern since it contains a complex mixture of different organic and inorganic compounds, large amount of CO_2, grease, salts, minerals, oils, and many hazardous compounds. The present work investigates the efficiency of photocatalysis (PC), photoelectrocatalysis (PEC), ozonation (O_3), and photoelectrocatalysis coupled with ozonation (PEC+O_3) in the removal of organic and inorganic contaminants in the oil-produced water monitored by Gas Chromatography-Mass Spectrometry (GC-MS) and Ionic Chromatography (IC) techniques. Parameters such as toxicity, which was investigated using Zebrafish embryos, color, turbidity, pH, quantity of dissolved solids, conductivity, chemical oxygen demand (COD), and concentrations of organic and inorganic carbon were also investigated. The best results were obtained by coupling PEC and O_3 techniques, which presented superior reduction in color (98%), turbidity (100%), inorganic carbon (99%), COD (73%), and a decrease of 96% in the fluoride and 35% in the chloride detected previously in the real oil-produced water. Among the 12 organic compounds identified in the oil-produced water, the PEC+O_3 treatment reached complete oxidation in eight of them and a lower Zebrafish embryo mortality occurred with 12.5% of dilution after 2 h treatment.

Petroleum is one of the most important energy sources in the modern world.[1] However, it is also responsible for the generation of high concentrations of greenhouse gases, originating not just from its burning but also from its extraction and processing.[2] During petroleum extraction, water is used to pump the oil from the oil well to the surface.[3] This kind of extraction generates three barrels of water for each barrel of oil produced.[4] Moreover, another complex challenge is in avoiding contamination of sea water or soil with the oil during its extraction.[5]

Diverse pollutants can be found in the water produced from the petroleum extraction and the type of the pollutant can change according to the composition of the petroleum,[1] which is intimately banded to the location of the oil well, and the age and geologic factors that influence the characteristics of the oil. However, it is possible to point out some commons pollutants that cause concern. The major pollutants of oil-produced water are: benzene, toluene, phenol, xylene, and organic aromatic compounds.[6] A high concentration of ions, such as Na^+, K^+, Mg^+, Cl^-, SO_4^{-2}, CO_3^{-2}, and HCO_3^-, is also observed, along with dissolved gases such as CO_2. In addition, traces of heavy metals, such as Cd, Cr, Cu and Hg, have also been reported.[4,7]

The methods normally used to treat the oil-produced water are filtration, flotation, and separation membrane,[3] which involve only phase transfer but not the elimination or degradation of the compounds. However, recently some authors have been investigating advanced oxidative technologies such as photocatalytic and electrochemical treatment of the organic compounds present in the oil-produced water.

Some works have reported electrochemical oxidation (EC) of oil-produced water using metal oxide anodes,[5,8] photocatalytic oxidation,[9] and photoelectrocatalytic oxidation using TiO_2 semiconductors.[6,10] Jaramillo-Gutiérrez and coworkers[6] used a simulated effluent and a TiO_2 semiconductor prepared by sol-gel method to evaluate photoelectrocatalysis (PEC) oxidation under 1.24 V and light incidence of 370 W. The author obtained 80% of phenol removal, however, with a poisoning of the semiconductor after 2 h of reaction. Li et al.[10]

employed TiO_2 nanoparticles prepared by sol-gel for the oil-produced water treatment by PEC under 30 V and UV light. After 2 h, the author reached 87% of chemical oxygen demand (COD) removal, a higher value compared with photocatalysis (PC) and EC techniques.

Photocatalytic oxidation of organic compounds is based on the use of *n*-type semiconductors irradiated by light with wavelengths higher than the energy of its band gap. Thus, electrons are excited from the valence band to the conduction band, generating holes that can oxidize water to hydroxyl radicals, potent oxidants ($E° = 2.7$ V vs NHE) that can degrade organic compounds.[11] The application of an electrochemical potential to an irradiated semiconductor, known as photoelectrocatalysis, has been explored in the last 20 years.[11–16] Photoelectrocatalysis decreases the electron-hole pair recombination controlling band bending, thereby increasing the transference rate of electrons and holes to their respective receptors.[11,17,18]

TiO_2 nanotube arrays are well known catalysts for oxidation of organic compounds.[19,20] It presents a combination of high catalytic activity and good electrical properties with an excellent stability in many solvents over a wide pH range.[21,22] Its band gap, when crystallized in the anatase phase, is around 3.2 eV,[21,23] causing photoactivation by UV irradiation ($\lambda \leq 387$ nm) with an efficient electron-hole pair separation.[12] However, although photoelectrocatalysis has proven to be more efficient than photocatalysis, it is still not appropriated under some conditions, such as in highly concentrated, turbid, and colored solutions, showing low mineralization efficiency.[24,25] Under these conditions, much of the radiation emitted by the light source does not reach the surface of the photoanode, creating few electron-hole pairs.

Recently, it has been demonstrated that the combination of photoelectrocatalysis with ozonation is an excellent alternative to circumvent these limitations.[25–27] Ozone is a powerful oxidant (2.07 V, while 2.7 V for ˙OH) and can react with organic pollutants via direct molecular ozone oxidation reaction (which is selective and relatively slow) and/or via indirect pathway (˙OH radicals are produced, called catalytic ozonation, which is fast and non-selective). Ozone decomposition is dependent on pH, catalysts, and UV irradiation and usually

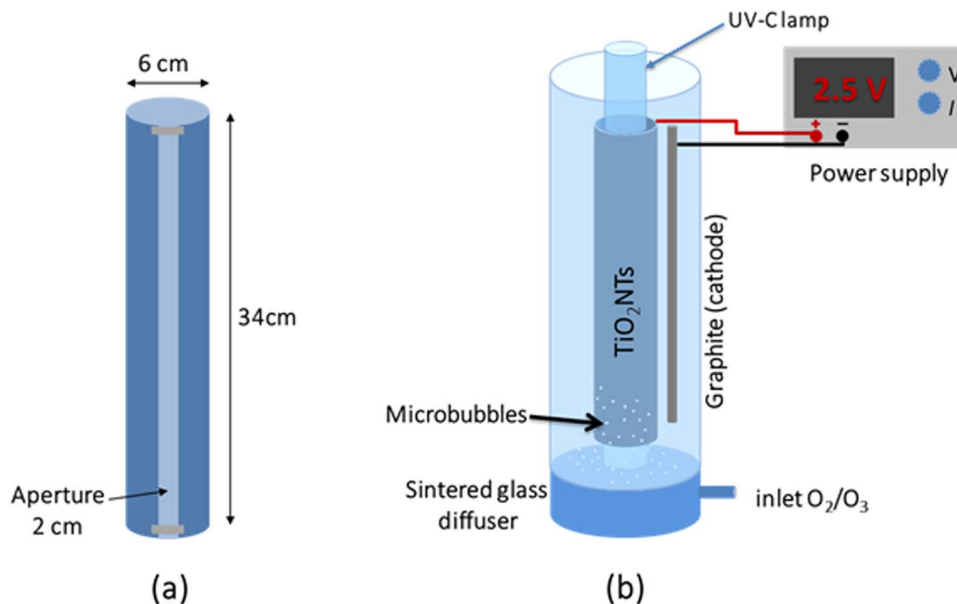z E-mail: jfbrito@ymail.com; boldrinv@iq.unesp.br

Figure 1. Schematic representation of (a) the Ti/TiO$_2$NTs anode with a lateral aperture of 2 cm for the flow of solution; and (b) the annular bubble reactor, with injection of microbubbles through a sintered glass diffuser. In the center, one can find a cylindrical electrode of Ti/TiO$_2$NTs internally irradiated by a 36 W UV-C lamp and polarized under 2.5 V using a power supply vs two graphite rods.

promotes the formation of more recalcitrant compounds in the end of the treatment.[28,29]

Within this context, this work shows an extensive chemical characterization study of oil-produced water using chromatographic methods and the assessment of different oxidation processes for the treatment, such as photocatalysis, photoelectrocatalysis, ozonation, and photoelectrocatalysis coupled with ozonation, using a cylindrical TiO$_2$ nanotube arrays electrode inserted in an annular bubble reactor.[25,27] The efficiency of treatment was also monitored by measuring the reduction of several analytical parameters such as color, COD, turbidity, and selected inorganic and organic compounds identified by Ionic Chromatography (IC) and Gas Chromatography-Mass Spectrometry (GC-MS). Lastly, assays with Zebrafish embryos were performed to assess the acute toxicity of the samples treated by the different techniques.

Experimental

Preparation of TiO$_2$ nanotube arrays cylindrical anode.—For the photoelectrocatalytic and photocatalytic experiments, a cylindrical TiO$_2$ nanotube array electrode (TiO$_2$NT) was constructed. The electrode was constituted of 600 cm^2 geometric area with a lateral opening for solution flow (Figure 1a). A Ti foil (35 × 17 cm and 0.5 mm thickness) was shaped into cylindrical form, chemically polished (using a 5% HNO$_3$ + 10% HF solution), and ultrasonically cleaned for 15 min in acetone, isopropanol, and water. Then, TiO$_2$ nanotubes were grown by electrochemical anodization (30 V for 50 h using Minipa MPL-1303 power supply with a ramp of 2.0 V min^{-1}) in a two-electrode cell using a dimensionally stable anode (De Nora) sheet as a counter electrode. The electrolyte was composed of 0.25% NH$_4$F in glycerol (90%)/water (10%). The Ti/TiO$_2$NT electrode was annealed at 450°C for 30 min (heating rate of 2°C min^{-1}).[30] A small sample of a TiO$_2$NT electrode prepared using the same protocol was characterized by X-ray diffraction (XRD) on a SIEMENS D5000, DIFFRAC PLUS XRD Commander X-ray diffractometer with Cu Kα radiation. The morphological characterization was carried out by Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) on a JEOL 7500F Microscope.

Treatment of the petroleum wastewater by photocatalysis, photoelectrocatalysis, ozonation, and photoelectrocatalytic ozonation.— Real wastewater samples were supplied by Petrobras (a plant in Rio

Grande do Norte, Brazil) and stored in polypropylene bottles, which were kept at 3°C. The following physicochemical parameters of the collected wastewater were measured: conductivity (multiparameter pHtek CD-8B), turbidity (portable turbidimeter Quimis Q279P), color (mg PtCo/L units; colorimeter Hanna Instruments HI83200), chemical oxygen demand, and carbon contents (total organic and inorganic carbon; Shimadzu TOC-V$_{CPN}$ model).

Treatments of petroleum wastewater were performed in an annular bubble reactor (ABR) 63.5 mm in diameter with just two electrodes (Figure 1b). The reactor was equipped with a sintered glass bubbler at its bottom for injecting O$_2$/O$_3$ and operated with 1.0 L wastewater.[25] An UV-C 36 W lamp (Osram) was used for the experiments involving light, which was directly inserted at the center of the reactor, and the cylindrical Ti/TiO$_2$NT anode was placed around the lamp. Two graphite rods (diameter 1.0 cm) were used as cathodes. The bias voltage of 2.5 V was controlled using a Tectrol TC 60-02XA1A power supply. Ozone was generated by an O$_3$R ozonator model ID-05 (Brazil) using dry oxygen as the feed gas (99.9% purity). The ozone input rate of 3.85×10^{-4} mol min^{-1} was delivered at an O$_2$ flow rate of 3.0 L min^{-1} monitored with a Cole-Parmer flowmeter (0.4–5.0 L min^{-1}). The amount of ozone generated was determined by an ozone analyzer, Anseros GM-OEM (254 nm). All the experiments were performed in an isolated laboratory and inside a fume cupboard with good exhaustion. In the experiments performed without O$_3$ production, O$_2$ was bubbled in the same flow to provide the mass transport.

A sample of the petroleum wastewater diluted with distilled water 1:1 was transferred to the ABR and subjected to 90 min of treatment based on ozonation (O$_3$), photocatalysis, photoelectrocatalysis, and photoelectrocatalytic ozonation (PEC+O$_3$). For all the experiments, aliquots of 20 mL solution were taken out at a pre-determined time and subjected to the different analyses described hereafter.

Chemical analysis of wastewater.—The treated samples were analyzed by gas chromatography-mass spectrometry (GC-MS) and ion chromatography using an Agilent (GC model 7890B and MS model 5977A) and a Dionex model ICS 1100 reagent-free ion chromatograph, respectively. The analysis of GC-MS was performed after volatilization of organic compounds present in 5 mL of petroleum wastewater and the samples after the treatments for 10 min at 100°C. The headspace of the samples was analyzed in a HP5 column with injector at 280°C and detector at 300°C, carrier gas flow of 1.0 mL min^{-1},
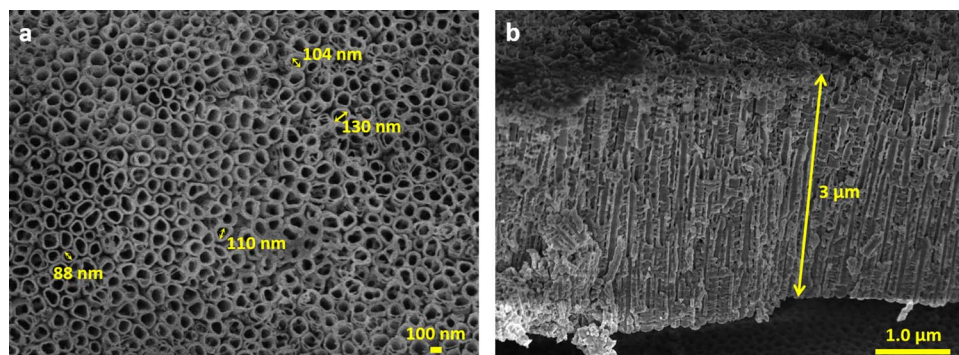
Figure 2. FEG-SEM images of a) top view and b) cross section of the well-organized TiO_2 nanotubes grown in the Ti substrate by electrochemical anodization.

and heating ramp starting at 60°C for 5 min, heating 5°C min^{-1} until 290°C, and keeping this temperature for 10 min. The IC analysis was performed in a Dionex IonPac AS23 column for 25 min using as mobile phase 4.5 mmol L^{-1} Na$_2$CO$_3$ + 0.8 mmol L^{-1} NaHCO$_3$ with a current of 7 mA, flow of 0.25 mL min^{-1}, temperature of 30°C, and volume of 5 μL. The ion concentrations were determined by the standard addition method.

The physical parameters of color, turbidity, pH, quantity of dissolved solids, and conductivity were analyzed by a photometer multiparameter Hanna instruments HI3200 and a CD-8B-220 Phtek conductivity meter, respectively. Carbon inorganic, organic, and total quantity were analyzed using a TOC-V$_{CPN}$ da Shimadzu. The COD was inferred by UV-Vis spectrometry (BEL photonics).[31]

Toxicity analysis of wastewater.—Toxicity tests with Zebrafish embryos were used for the toxicological analysis, according to OECD Guideline for testing of chemical n°366. Zebrafish (*Danio rerio*) adults were obtained from the facility at the School of Pharmaceutical Sciences of Ribeirão Preto at the University of São Paulo (Ribeirão Preto, Brazil). Adults were kept in a ZebTEC (Tecniplast, Italy) recirculating system using water obtained by a reverse osmosis system at standard conditions (pH 7.5 ± 0.5, temperature 26 ± 1°C, dissolved oxygen at 95% saturation, conductivity 750 ± 50 μs cm^{-1}, and a 14h:10h light/darkness photoperiod). The fish were fed twice a day with commercial feed Early Life Stage (ELS) (TetraMin Tropical Flakes).

Briefly, newly fertilized eggs were used for the test at the blastula stage, collected from the reproduction of a two-to-one male to female ratio. The tests were performed in triplicate for all samples at dilutions of 2.5%, 5.0%, 7.5%, 12.5%, and 25%. Before the test, samples were autoclaved and filtered to remove impurities before the dilution process. In addition, two separate plates were used, one containing the negative control (OECD standardized water) and the other the 4.0 mg L^{-1} 3,4-dichloroaniline positive control (standard solution causing deleterious effects). In a 24 well plate, we used one embryo per well, totalizing 20 organisms exposed to 2 mL of each solution. The other 4 wells were used for the standard OECD water, as a plate control. After the distribution of eggs, the plates were incubated for a photoperiod of 14 h of light and 10 h of darkness, at a temperature of 26 ± 1°C. Embryos were observed daily in stereomicroscope (Stemi 508, Zeiss) and photographed with a coupled camera (AxioCam IC Zeiss, Germany). The endpoints assessed were lethality coagulation, tail not detached, malformation of somites, no heartbeat, sub-lethality (development of eyes, spontaneous movement, pigmentation, and edemas) and teratogenicity (malformation of head, tail and otoliths, scoliosis, deformity of yolk sac, and retarded growth).

GraphPad Prism 5.01 software (GraphPad Software, San Diego, California, USA) was used for statistical analyses. After verifying normality and homogeneity (Kolmogorov-Smirnov test and Barlett's tests, respectively), a one-way analysis of variance (ANOVA) was performed and Dunnett's test was applied to verify significant differences among treatments and controls. In case the data failed the normality and/or homosdasticity test, the Kruskal–Wallis test was used. The

lowest observed effect concentration (LOEC) was determined when significant differences were found. All statistical analyses were performed with a significance level of 0.05.

Results and Discussion

TiO$_2$ nanotubes characterization.—TiO$_2$ nanotube arrays prepared by electrochemical anodization presented a self-organized morphological characteristic as shown in FEG-SEM images of Figures 2a and 2b. The TiO$_2$ nanotubes had an average diameter of 110 nm, tube wall of 35 nm, and length of 3 μm. TiO$_2$ nanotube morphology has received remarkable interest because they exhibit excellent stability, large internal surface area, and excellent electron percolation pathways for vectorial charge transfer.[32,33] These characteristics are critical for improvements in photoelectrocatalytic efficiency.

Figure 3 shows the XRD pattern of the TiO$_2$ nanotube arrays sample. The diffraction peaks can be indexed to the formation of the anatase phase (2θ = 25.3; 37.9; 48.0; 54.1 and 54.9) after the heat treatment of the TiO$_2$ at 450°C for 2 h, and the metallic titanium of the substrate (2θ = 35.1; 38.4; 40.2; 53.0; 62.9; 70.5; 76.3 and 77.4). It is known that the anatase phase exhibits higher charge carrier mobility compared to the rutile,[34] thereby contributing to the minimization of the electron-hole pairs recombination.

Advanced oxidation treatment of petroleum wastewater.—The physical-chemical parameters evaluated for the petroleum wastewater collected in the Northeast region of Brazil presented high conductivity
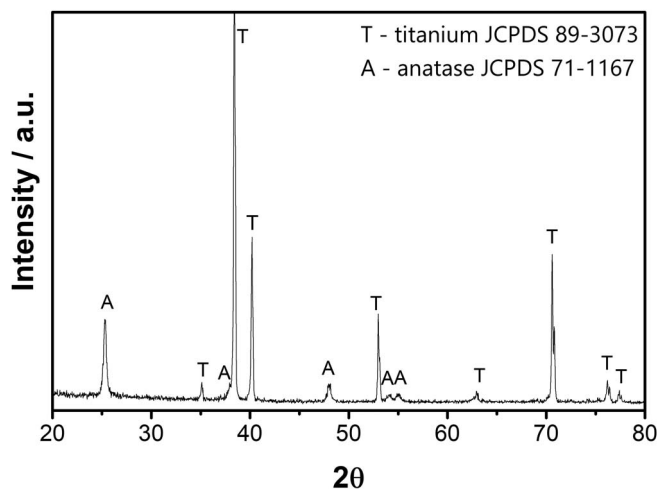

Figure 3. XRD spectrum of the well-organized TiO$_2$ nanotubes grown in the Ti substrate by electrochemical anodization and annealed at 450°C for 2 h. The peaks labeled with A are indexed to the anatase phase (JCPDS 71-1167) of TiO$_2$ and the peaks labeled T are indexed to titanium (JCPDS 89-3073).
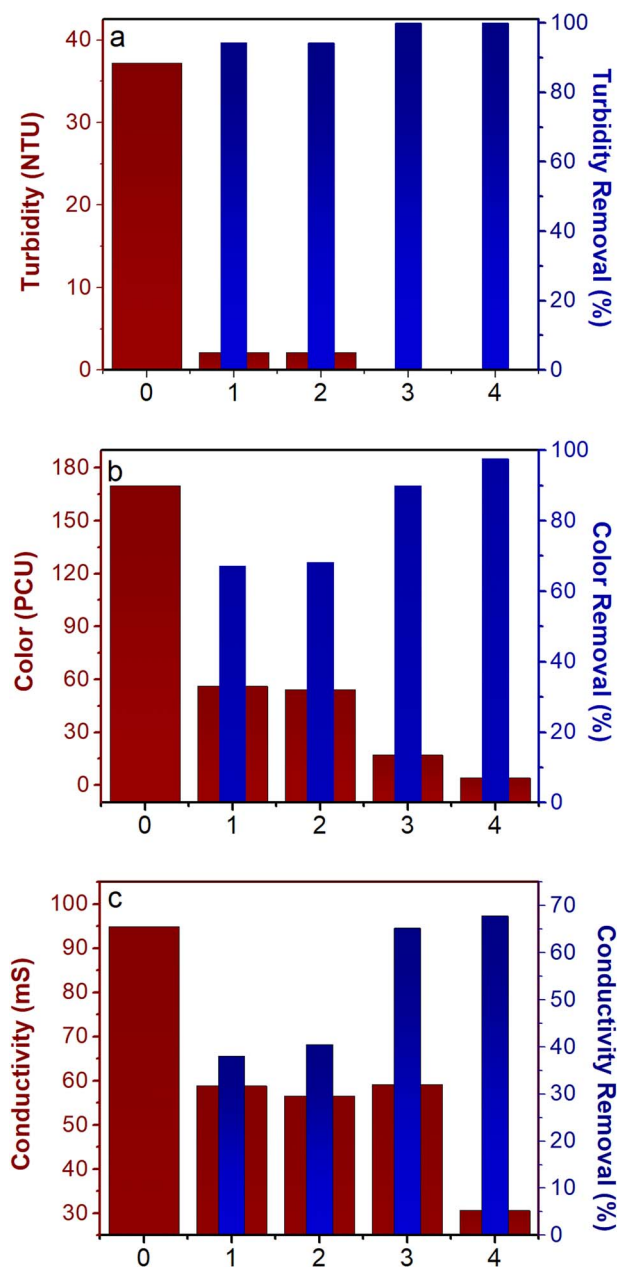
Figure 4. a) Turbidity and turbidity removal (NTU = nephelometric turbidity units), b) color and color removal, and c) conductivity and conductivity removal of the petroleum wastewater before treatment (refers to the '0' of the x-axis) and after 120 min treatment by PC (1), PEC (2), O_3 (3), and PEC+O_3 (4). Treatment conditions: irradiation of a 36 W UV-B lamp; TiO_2NT photoanode under 2.5 V *vs* two graphite rod cathodes; and ozone input rate of 3.85×10^{-4} mol min^{-1}, delivered at O_2 flow rate of 3.0 L min^{-1}.
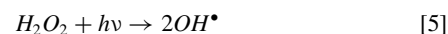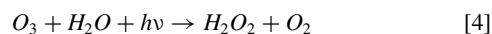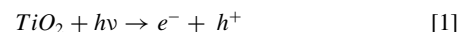
(164.0 mS), due to the high halide ion concentrations from sea water; pH close to neutral (7.31); intense color (170.0 PCU or mg Pt-Co L^{-1}) and high turbidity (37.2 nephelometric turbidity units, NTU); high levels of total carbon (224.2 mg L^{-1}), which was composed mainly of inorganic carbon (122.0 mg L^{-1}); and raised levels of COD (1104 mg L^{-1}). These results are shown in Figure 4, along with these parameters measured after 120 min of treatment by PC, PEC, O_3, and PEC+O_3.

The wastewater turbidity (Fig. 4a) decreased close to the same value of distilled water (0.04 NTU) after 120 min treatment with O_3 and PEC+O_3, reaching practically 100% reduction. On the other hand, PC and PEC oxidation treatments presented a decrease of 93%

in turbidity. The evaluation of the color removal in the wastewater (Fig. 4b) also shows higher efficiency using O_3 treatment when compared to PC and PEC techniques. The best color removal was reached by the coupling PEC and O_3 techniques, reaching 97% decolorization after 120 min of treatment. This behavior of the O_3 technique for turbidity and color reduction was presented in the literature.[25,26]

The efficiency of the O_3 technique in the removal of color and turbidity is a very valuable contribution in favor of PEC technique, justifying the coupling of both techniques. Some wastewater presents intense coloration that hinders the light incidence across the solution, making it difficult to activate the semiconductor by photons incidence and decreasing the electrons-hole pair generation and the hydroxyl radical.

This behavior is explained since O_3 in a solution contributes to the increase of PEC efficiency, in this case by synergic effects related to the formation of oxidant species:[28]

$$TiO_2 + h\nu \rightarrow e^- + h^+ \qquad [1]$$

$$h^+ + H_2O \rightarrow H^+ + OH^\bullet + e^- \qquad [2]$$

$$O_3 + e^- \rightarrow O_3^{\bullet-} + H^+ \rightarrow HO_3^\bullet \rightarrow O_2 + OH^\bullet \qquad [3]$$

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \qquad [4]$$

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \qquad [5]$$

Once PEC technique generates electrons in the TiO_2 surface and, some of these electrons may react with O_3 to form hydroxyl radicals ($^\bullet$OH); simultaneously, the absorption of UV photons by O_3 also generates $^\bullet$OH species and, the phogenerated holes at TiO_2 surface are capable to produce more $^\bullet$OH, thus, the combination of both techniques create a higher oxidative ambient, increasing the treatment efficiency in comparison to the use these techniques separated."

The conductivity of the oil-produced water after the treatments by PC, PEC, and O_3 present a similar reduction, reaching a decrease around 28% in all most the cases (Fig. 4c). However, applying PEC+O_3 technique, the reduction in the conductivity of the effluent reached 68%. This result shows the efficiency of the PEC+O_3 in the decrease of ions present in the solution. The chemical analysis presented contributes to the understanding of the conductivity decrease after the wastewater treatment.

The COD indicates the quantity of dissolved oxygen necessary to oxidize the organic matter present in the effluent.[35] The results obtained for PC, PEC, O_3, and PEC+O_3 (Fig. 5a) show that the treatment is more efficient using PEC+O_3, since the treatment reached 73% COD removal, a value similar to the O_3 treatment and higher than that obtained by PEC treatment (67% reduction).

The best results in relation to the reduction of the concentration of organic and inorganic carbon were obtained with the PEC+O_3 technique (Fig. 5b). The removal of organic carbon by the PEC and the O_3 techniques was similar; however, coupling both techniques made it possible to reduce the inorganic carbon to 1.0 mg L^{-1} (99% removal). In this case, the removal of organic carbon reached just 23% and the total carbon 64%. This effect can be linked to the removal of carbonate ions present in the effluent, which also involves the conductivity of the solution.

The concentration of inorganic ions in the oil-produced water was investigated by ion chromatography before and after each of the treatments (Fig. 6). The ions fluoride, chloride, chlorite, chlorate, sulfate, thiosulfate, iodide, thiocyanate, perchlorate, bromide, bromate, phosphate, nitrite, and nitrate were analyzed; however, just fluoride and chloride were identified in the samples. As observed for the others parameter evaluated, the best results for chloride removal were obtained by applying PEC+O_3 treatment. The fluoride concentration decreased by 96% (Fig. 6a) while chloride concentration decreased by 35%
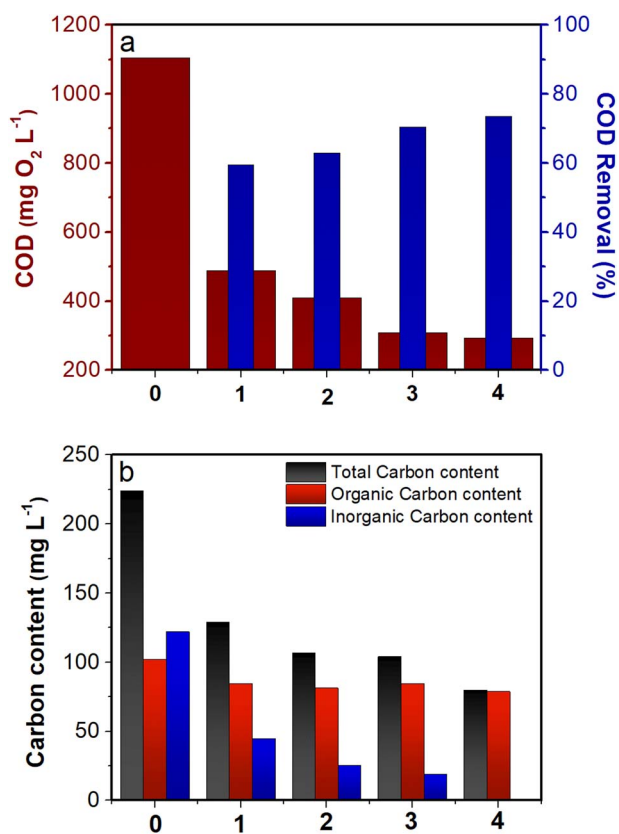
Figure 5. a) Chemical oxygen demand (COD) with COD removal and b) carbon content of the petroleum wastewater before (0) and after the treatments by PC (1), PEC (2), O_3 (3), and PEC+O_3 (4). Treatment conditions: irradiation of a 36 W UV-B lamp; TiO_2NT photoanode under 2.5 V *vs* two graphite rod cathodes; and ozone input rate of 3.85×10^{-4} mol min^{-1}, delivered at O_2 flow rate of 3.0 L min^{-1}.

Figure 6. Concentration of a) fluoride and b) chloride in the petroleum wastewater before treatment and after 120 min treatment by PC, PEC, O_3, and PEC+O_3. Conditions: irradiation of a 36 W UV-B lamp; TiO_2NT photoanode under 2.5 V vs two graphite rod cathodes; and ozone input rate of 3.85×10^{-4} mol min^{-1}, delivered at O_2 flow rate of 3.0 L min^{-1}.

(Fig. 6b). The fluoride concentration decrease was significant in all of the techniques employed for the treatment of the wastewater, obtaining at least 80% removal. However, the chloride was more recalcitrant; aside from the PEC+O_3 treatment, the reduction in the concentration of this ion reached just 13%.

According to Santos et al.,[36] the chloride removal occurs from the reaction of hydroxyl radicals forming hydroxides that adsorb into the counter electrode. Santos, Dezotti, and Dutra[8] identified some oxides adsorbed in the cathode surface after the electrocatalytic oxidation of oil-produced water. This behavior can also be assigned to the reaction between metals and nonmetals with the hydroxyl radicals in the solution. On the other hand, Jaramillo-Gutiérrez et al.[6] observed the poisoning of the electrode of TiO_2 thin film after 120 min of treatment of oil-produced water using the PEC technique and attributed that to the electropolymerizing of phenol in the electrode surface. However, EDS analysis of the electrode after the treatment revealed the presence of metals and nonmetals elements, as chlorine. In our experiments, the TiO_2 nanotubes electrode also presented poisoning after 120 min of treatment using PEC and PEC+O_3, which may be ascribed to the adsorption of the hydroxides. However, the semiconductor can be cleaned by performing a PEC+O_3 reaction in 0.1 mol L^{-1} Na_2SO_4 for around 2 h. This process generates •OH radicals at the TiO_2 surface, which can oxidize adsorbed contaminants, restoring the performance of photoanode for further experiments.

The organic compounds present in the oil-produced water were identified by CG-MS as the compounds that persisted after the treatments (Table I). Some of the compounds were not identified in the samples submitted to 120 min of treatment in all of the techniques studied: eucalyptol, bicyclo[2,2,1]heptan-2-one, 1,7,7-trimethyl, terpineol, cyclohexanone 4-(1,1-dimethylethyl), isobornyl acetate, diethyl phtha-
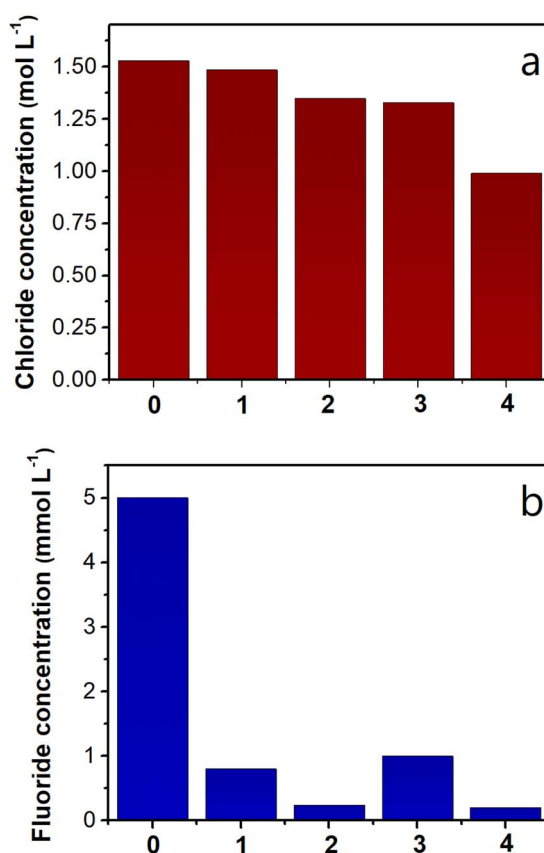
late, and octadecanoic acid. Oleic acid degraded just after PEC and PEC+O_3 treatment. Benzaldehyde, benzyl alcohol, octadecane, and hexadecanoic acid decreased in the abundance of molecular ions after the treatments. Benzyl alcohol and hexadecanoic acid degraded better under PEC treatment, while benzaldehyde and octadecane presented a higher decrease with the PEC+O_3 treatment.
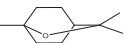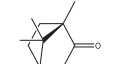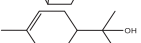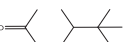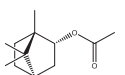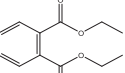
The photoelectrocatalysis minimizes the recombination of photogenerated electrons-holes pairs compared to photocatalysis, generating a higher concentration of hydroxyl radicals by water oxidation.[11,15,17] In the PEC+O_3 system, additional hydroxyl radicals can be generated (Eqs. 1–5),[25,26,37] which explains why this combined technique performed the best. The physical-chemical analyses performed in this work show the superior performance of the PEC+O_3 technique in the treatment of oil-produced water. The effluent reached color and turbidity similar to water after 120 min of treatment using PEC+O_3. The chemical parameters also presented better results after the treatment using PEC+O_3, mainly the COD and inorganic carbon removal.

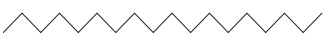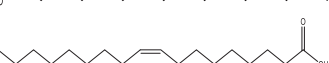***Toxicity of the oil-produced water before and after treatment.—*** In order to perform the toxicity tests, we prepared dilutions of each sample, as discussed in the material and methods section. Zebrafish embryos exposed to raw petroleum water (untreated) and products generated after PC, PEC, O_3, and PEC+O_3 presented different effects, from mortality to sublethal effects.

Table II shows the effects observed on the organisms exposed to the different dilutions, for the raw sample and after wastewater treatments. We observed that even after different treatments, all samples diluted at 25% induced the death of all exposed organisms, showing that the treated petroleum water still induced relevant acute toxicity.

Table I. Compounds identified by GC-MS chromatography and its respective peak area in the petroleum wastewater before and after 120 min of treatment by photocatalysis (PC), photoelectrocatalysis (PEC), ozonation (O_3), and photoelectrocatalytic ozonation (PEC+O_3). Treatment conditions: irradiation of a 36 W UV-B lamp; TiO$_2$NT photoanode under 2.5 V *vs* two graphite rod cathodes; and ozone input rate of 3.85 × 10^{-4} mol min^{-1}, delivered at O_2 flow rate of 3.0 L min^{-1}.

Ret. time (min)	Compound	Structure	molecular ion (m/z)	Area Waste-water	Area after PC	Area after O_3	Area after PEC	Area after PEC + O_3
7.78	Benzaldehyde		m/z 105	10653.8	5437.1	6193.2	8701.0	3012.8
10.19	Eucalyptol		m/z 108.1	133085.7	N/A	N/A	N/A	N/A
10.30	Benzyl alcohol		m/z 79.1	113631.5	48126.6	32162.9	21666.3	36281.0
13.89	Bicyclo [2,2,1] heptan-2-one, 1,7,7-trimethyl		m/z 95.1	207541.5	N/A	N/A	N/A	N/A
15.32	Terpineol		m/z 93.1	15313.5	N/A	N/A	N/A	N/A
16.42	Cyclohexanone 4-(1,1-dimethylethyl)		m/z 98.1	1483302.2	N/A	N/A	N/A	N/A
18.17	Isobornyl Acetate		m/z 93.1	51842.7	N/A	N/A	N/A	N/A
26.00	Diethyl phthalate		m/z 149	27604.6	N/A	N/A	N/A	N/A
30.42	Octadecane		m/z 57.1	26573.7	2037.0	4676.8	2170.5	9779.5
33.60	Hexadecanoic acid		m/z 73.1	22211.4	2457.8	5958.8	1065.0	15420.5
36.93	Oleic acid		m/z 55.1	8661.4	1250.0	2146.7	N/A	N/A
37.34	Octadecanoic acid		m/z 73.1	4894.4	N/A	N/A	N/A	N/A

*N/A – compounds that were not identified after the treatment.

Considering the dilutions of 12.5%, we observed that none of the samples reduced or significantly increased ($p \leq 0.05$) the effect of mortality when compared to the raw sample.

All samples diluted at 12.5% induced to sublethal effects with lower or higher intensity when compared to the raw sample. Regarding scoliosis, photoelectrocatalysis combined with O_3 was the most effective treatment compared to untreated petroleum water. According to Nagel,[38] Zebrafish eggs should hatch at up to 96hpf. As can be seen in Tables II, for raw sample and treatments, we observed failure in hatching of some organisms. PC treatment (at 12.5%) was the most efficient, significantly reducing ($p \leq 0.05$) hatching failure compared to raw sample in about 90%. Although PEC+O_3 (12.5%) did not reduce hatching failure, this combined treatment did not cause effects at the lowest dilutions, as occurred in the raw sample, showing a slight reduction. Carlsson et al.[39] studying crude AP of oil and gas / condensate production platforms of the North Sea of Norway also observed acute toxicity in zebrafish embryos. In the cited study, embryotoxicity of the water and particle / oil soluble fractions of AP effluents from various platforms of the region were evaluated, detecting different effects such as changes in movement, pigmentation, heart rate, hatching time, and embryonic malformations. Carlsson and coworkers[39] also observed a number of lethal and sublethal effects, such as mortality of 100% of organisms exposed in their highest concentration of effluent, as detected in our study.

Failure in swim bladder inflation was observed even after all treatments. Regarding the combination PEC+O_3, we observed that this effect (sample diluted at 12.5%) showed no significant difference when compared to raw water. However, the bladder inflammation was induced after exposure at 7.5% dilution in the untreated sample and not after 12.5% of dilution as occurred in the case of the sample treated by PEC+O_3. Inflating the swim bladder is essential for adult survival, because it maintains fish balance during swimming, allowing capture food. Considering that, failure in inflation or formation of this organ seriously impact in fish development.[40]

Therefore, considering the toxicological tests presented here, we conclude that PEC+O_3 and PC has been the more effective treatment for reducing both lethal and sublethal effects, although it has not been totally successful. Although it was not possible to achieve total organic carbon removal, an elimination of some organic compounds of environmental concern was achieved, besides was possible to suppress the toxicity of the wastewater. Therefore, our results are an important step in the investigation of effective treatments for oil-produced water. In addition, we provided important chemical, physical-chemical, and toxicological characterization results of wastewater before and after treatment by advanced oxidation processes.

Conclusions

The oil-produced water presents a diversified composition, with many long-chain organic compounds, high concentration of ions, high concentration of inorganic carbon, and an acute toxicity to Zebrafish embryos. The combination of PEC+O_3 has been shown to be a powerful technique for the treatment of this complex wastewater. The PEC+O_3 presented better removal of all parameters analyzed for the treatment of the real effluent. O_3 contributes to decreasing the effluent color, providing an easier way for the photons to reach the TiO$_2$

Table II. Effects observed after the exposure of Zebrafish embryos to different dilutions of the sample generated after the treatment of petroleum water by PC, PEC, O$_3$, and PEC+O$_3$. The results are expressed in mean ± standard deviation.

| | Raw petroleum water | | | |
| | Observed effect | | | |
% Dilution	% Mortality	% scoliosis	% Swimming bladder inflation defects	% Hatching failure
25	100	0	0	0
12.5	25.0 (±15)	29.44 (±14.56)	100 (±0)	77.21 (±12.94)
7.5	1.7 (±2.9)	0	6.92 (±8.06)	11.66 (±20.20)
5	1.7 (±2.9)	0	0	1.66 (±2.88)
2.5	0	1,66	0	1.66 (±2.88)
Treatment with photocatalysis				
25	100	0	0	0
12.5	35 (±30.4)	7.5 (±8.44)	100 (±0)	6.00 (5.88) *
7.5	0	0	0	0
5	1.7 (±2.9)	0	0	0
2.5	0	0	0	0
Treatment with photoelectrocatalysis				
25	100	0	0	0
12.5	43.3 (±34.0)	49.7 (±29.37)	100 (±0)	61.97 (±27.87)
7.5	0	0	6.66 (±11.54)	0
5	1.7 (±2.9)	0	0	0
2.5	6.7 (±7.6)	0	3,33 (±5,77)	1.66 (±2.88)
Treatment with O$_3$				
25	100	0	0	0
12.5	23.3 (±17.6)	50.26 (±30.78)	97.77 (±3.85)	50.99 (±21.63)
7.5	6.7 (±11.5)	5 (±8.66)	3.33 (±2.88)	1.66 (±2.88)
5	1.7 (±2.9)	0	0	0
2.5	0	0	1.66 (±2.88)	0
Treatment with PEC+O$_3$				
25	100	0	0	0
12.5	16.7 (±14.4)	1.66 (±2.88) *	100 (±0)	75.55 (±31.50)
7.5	0	0	0	0
5	3.3 (±5.8)	0	0	0
2.5	0	0	0	0

*=significant difference between raw sample (p≤0.05).

nanotubes cylindrical photoanode to improve the electron-hole pair generation, therefore increasing the concentration of hydroxyl radicals in the solution. The results presented show a decrease in color (98%), turbidity (100%), inorganic carbons (99%), COD (73%), fluoride concentration (96%), and chloride concentration (35%), oxidation of most of the long-chair organic compounds, and a reduction in both lethal and sublethal effects of the oil-produced water. Based on the results presented in this work and in the few reports presented in the literature, we believe that the combination of photoelectrocatalysis with ozonation could be a key to the treatment of real complex wastewater.

Acknowledgments

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