

Synthesis of Nb₂O₅/C for H₂O₂ electrogeneration and its application for the degradation of levofloxacin

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Abstract

The present work sought to investigate H₂O₂ generation using a gas diffusion electrode composed of carbon with niobium oxide for the degradation of levofloxacin. Results showed that the oxide formed was Nb₂O₅ (crystallographic structure was confirmed by XRD; chemical composition detected by XPS) and the increase in the Nb/C ratio led to more crystalline structure and higher crystallite size. The carbon with 5% Nb₂O₅ presented an average particle size of 5.6 nm and this material led to the generation of the highest amount of H₂O₂ (317.6 mg L⁻¹). The C/5% Nb₂O₅-modified GDE was applied for the degradation of levofloxacin in an acid medium, in the presence and absence of Fe²⁺ ions. Long-term experiments conducted for the analysis of the time required for the total removal of levofloxacin showed that 96% of levofloxacin and 66% of organic load were removed in 270 min of treatment at the current density of 100 mA cm⁻².

Highlights

- Nb₂O₅ on carbon increased the H₂O₂ generation by 236% compared to unmodified carbon
- In 90 min, 46% of the organic load was removed at 100 mA cm⁻²
- Levofloxacin degradation, in 270 min, reached 96% at 100 mA cm⁻²

1. Introduction

The rapid development of society in the last century has resulted in great advances in human activity, with huge progress in industrial, technological, medicine, and food production; these massive advances have at the same time caused significant impacts on the environment [1] showed that while the relationship between the economy, society, and the environment is not always evident, one factor is clear in this relationship: environmental degradation [1].

One of the visible aspects of societal development is population growth, which goes hand in hand with the increase of large urban centers [1]. Highly populated regions tend to suffer considerably from the depletion of natural resources, and water resources in these regions are especially impacted, where, the regions with high population density largely experience a decrease in both water supply and water quality [2].

The scenario for the coming years shows that a greater portion of the population will be living in large urban centers [1], and this may directly impact the availability and quality of water in these regions [2]; in this sense, it is essentially crucial to control the vectors of environmental contamination, know their origins, and understand the interaction of these contaminants [3–6].

It is undoubtedly clear that considerable attention needs to be paid when it comes to the disposal of medicine into the environment; this is because the exposure of humans and other living beings to natural waters contaminated by this class of compounds has been found to pose serious health risks, regardless of the low concentrations of the compounds (ng L⁻¹ or µg L⁻¹) [3–6].

In this context, public water and sewage treatment systems must account for the presence of emerging pollutants in raw water or sewage during the treatment processes, and it must be borne in mind that conventional techniques may not be efficient when it comes to the removal of certain emerging contaminants. Different works analyzed the presence of drugs in some Brazilian water supply systems; the authors detected the presence of 12 drugs in surface water used for public consumption, and out of these 12 drugs, 6 drugs were identified after the water treatment process [7, 8].

Becker et al. identified 43 drugs in the sewage of a hospital in the State of Rio Grande do Sul in Brazil as part of work to identify metabolites [6]. Pivetta et al. studied the degradation/removal of drugs in water samples from a sewage

treatment plant in the city of Campinas in Brazil; the authors analyzed 10 medications with psychotropic activity, out of which 8 were identified before and after the water treatment in the sewage treatment plant [8]. Based on the findings of Pivetta et al., the only drug that was totally removed after the water treatment process was sertraline. The authors recorded minimal removal rates or zero removal rates for the drugs investigated; in other words, the sewage treatment plant was incapable of removing the drugs from the water samples [8].

Epold, Trapido, and Dulova [9] and Hamdi El Najjar et al. [10] cited that many antibiotics have high resistance to biological treatment processes commonly used in cities, such as levofloxacin, indicating that these substances can cause long-term concerns due to toxicity in water bodies and cause bacterial resistance. Mustafa and Oladipo [11] cited the high solubility of some drugs and the consequent increase in their metabolites in the environment, which can cause serious problems associated with resistance to these drugs and toxicity in the environment [12, 13].

Considering the limitations of conventional water and sewage treatment processes, where drugs, among many other contaminants, are detected in sewage/wastewater before and after treatment, as well as in surface water and drinking water for human consumption [3–6], one does not need to overemphasize the importance of developing efficient treatment techniques which are capable of the following: i) maximizing the removal of these compounds in wastewater before they reach the sewerage system; ii) removing/degrading the compounds during the sewage treatment stage; or iii) effectively removing the compounds in the water treatment process.

Several works published in the literature have proposed different techniques for the removal or degradation of drugs, among these techniques include advanced oxidative processes [3–6]. According to Wu and Hu [14], advanced oxidative processes have enormous advantages over other techniques when it comes to the degradation of pharmaceutical compounds because they are capable of mineralizing drugs completely using small working areas [14–18]. Hassani et al., listed several processes for the degradation of organic pollutants, such as photo-Fenton, sono-Fenton, and electro-Fenton, and the latter process is indicated as very promising, mainly due to the in-situ generation of hydroxyl radicals [19].

Ighalo et al. showed that under advanced oxidative processes, the application of hydrogen peroxide (H_2O_2) with a small amount of Fe^{2+} ions leads to the efficient removal of drugs in water matrices [16].

In large-scale processes, the use of commercial H_2O_2 can be a serious problem, since the storage of large amounts of H_2O_2 requires controlled environmental conditions and careful handling procedures. In view of that, electrochemical techniques using gas diffusion electrode (GDE) are highly efficient H_2O_2 synthesis in situ [20] where the use of electrochemical technologies allows controlling the H_2O_2 generation in view of the real need in the process under study, this characteristic is highlighted by Hassani et al. [18].

H_2O_2 electrochemical synthesis is complex [21], the use of GDE allows one to perform the synthesis of H_2O_2 at room temperature/pressure and in direct contact with the pollutants[20]. A number of works published in the literature have demonstrated the efficiency of GDE when it comes to O_2 reduction in H_2O_2 synthesis [22–26]. GDE is a versatile electrode applied in H_2O_2 generation; this electrode can be constructed using a catalytic mass composed of carbon only [20], or carbon modified with different substances [25, 27]. The use of niobium to modify the carbon to obtain Nb_2O_5/C is of interest, as the use of this oxide is reported in the literature as having an effect of shifting the onset in the potential to fewer negatives potentials and also increasing the selectivity towards the 2-electrons pathway, increasing the generation of the H_2O_2 [28, 29].

Considering the importance of the removal of organic pollutants in water and environmental matrices and the need for the development of efficient techniques that are highly capable of decontaminating drug-contaminated water, the

present work seeks to investigate the electrogeneration of hydrogen peroxide in gaseous diffusion electrodes made up of carbon modified with niobium oxide and the application of the proposed technique for the degradation of levofloxacin.

2. Experimental

2.1. Preparation of Nb₂O₅/C Nanoparticles

Nb₂O₅ nanoparticles supported on Printex L6 carbon (Evonik Co.) were synthesized by thermal decomposition of a polymeric precursor using niobium ammonium oxalate (NH₄[NbO(C₂O₄)]·H₂O (purchased from Companhia Brasileira de Metalurgia e Mineração – CBMM, Brazil) was used as salt precursor. The salt was placed in a mixture containing ethylene glycol and citric acid in a molar ratio of 1:10:40, respectively, at 60°C. After homogenization, Printex L6 carbon was added to the mixture, and the suspension formed was subjected to magnetic stirring for 20 min. After that, the resulting dispersion was calcined in air at 500°C for 30 min. The mass proportion of niobium and carbon (Nb/C) applied was 0.5, 1.0, 3.0, 5.0, 8.0, 10 and 15% (w/w).

2.2 Physical characterization

X-ray fluorescence (XRF) measurements were carried out using MiniPal 4 apparatus model PW 4024 with a PANalytical B.V. rhodium X-ray tube (Almelo, the Netherlands). Powder X-ray diffraction (XRD) patterns were obtained from a Rigaku diffractometer operated under a Cu-K_α radiation source (λ = 1.54056 Angstrom) at a voltage power of 40 kV and current density of 80 mA. The compounds formed were identified based on a comparison with standard compounds using the International Center of Diffraction Data (JCPDS) database.

TEM analyses were carried out using a JEOL transmission electron microscope, model JEM-2100, operated at 200 kV.

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a commercial spectrometer at a pressure of less than 10⁻⁷ Pa (UNI-SPECS UHV System, Berlin, Germany). The analysis was performed using the Mg-K_α line (hν = 1253.6 eV) and analyzer pass energy of 10 eV. The inelastic background of the Nb 3d, C 1s, and O 1s electron core-level spectra was subtracted using Shirley's method. The composition (at. %) of the near-surface region was determined at an accuracy of ± 10% from the ratio of the relative peak areas corrected by Scofield's sensitivity factors for the corresponding elements. The binding energy scale of the spectra was corrected using the C 1s hydrocarbon component at a fixed potential of 285.0 eV. The spectra were fitted without constraints using multiple Voigt profiles. The full width at half maximum (FWHM) varied between 1.2 and 2.1 eV, and the accuracy of the peak positions was ± 0.1 eV.

2.3 Electrochemical characterization

The electrochemical experiments were conducted using an Autolab PGSTAT 128 N potentiostat/galvanostat (Metrohm) with a rotating ring-disk electrode (RRDE) (Pine Instruments). The RRDE consisted of a central glassy carbon disk and a platinum ring with a collection efficiency of N = 0.37. The working electrodes were prepared as described in [26]; the electrodes were prepared by dispersing 1 mg of each material studied and carbon with 20% Pt (ETEK) in 1 mL of water. After homogenization, 25 μL aliquots of the solution were placed on the glassy carbon disk and dried under N₂ flow. The experiments were performed using a supporting electrolyte which consisted of 0.1 mol L⁻¹ K₂SO₄, where the pH was adjusted to 2 using H₂SO₄. A platinum foil was employed as the auxiliary electrode and Ag/AgCl electrode was used as the reference electrode.

The microlayers were electrochemically characterized by cyclic voltammetry (CV) using the supporting electrolyte saturated with nitrogen gas in the potential range of +0.6 V to -0.6 V and at a scan rate of 10 mV s⁻¹. Subsequently,

linear voltammetry (LV) measurements were performed using the supporting electrolyte solution saturated with oxygen gas. The voltammograms were obtained in the potential range of +0.4 V to -0.8 V and at a scan rate of 5.0 mV s⁻¹. A potential of +1.0 V was applied to the Pt ring electrode, and this was used for the detection of H₂O₂ formed on the microlayer.

2.4. Electrochemical Generation of H₂O₂ on Gas Diffusion Electrode

The quantification of the H₂O₂ produced during the oxygen reduction reaction (ORR) was performed using either unmodified carbon or 5% Nb₂O₅/C (w/w) as a conductive matrix. The GDEs (20 cm²) were prepared based on the procedure described in previous studies [3–6]; under the procedure employed, polytetrafluoroethylene (PTFE) was used as a hydrophobic binder (20% (w/w) of a 60% aqueous dispersion – Dyneon TF 5035, 3M) and metallic screens were used for current collection. The GDEs were constructed by the hot-pressing mechanism as described in the literature [20].

The electrogeneration of H₂O₂ was performed in a conventional electrochemical cell using 0.1 mol L⁻¹ K₂SO₄, at pH 2 (adjusted by H₂SO₄), as a supporting electrolyte. A platinum plate was used as an auxiliary electrode and Ag/AgCl electrode (10 cm²) was used as the reference electrode. During the electrolysis, 0.5 mL of the electrolyte solution was added to 4 mL of 2.4 × 10⁻³ mol L⁻¹ (NH₄)₆Mo₇O₂₄ in 0.5 mol L⁻¹ H₂SO₄, and the absorbance of the resulting solution was measured at 350 nm. The electrolysis was carried out using Autolab PGSTAT 30 potentiostat/galvanostat (Metrohm) with a high current module at constant current density in the range of 10 to 150 mA cm⁻² for 90 min.

2.5. Levofloxacin Degradation Using Nb₂O₅/C-GDE

The degradation experiments were carried out using the same conditions applied for the H₂O₂ generation experiments (current density range: 10 to 150 mA cm⁻²; time: 90 min), with the application of 0.1 mol L⁻¹ K₂SO₄ at pH 2 (adjusted by H₂SO₄) as supporting electrolyte in the presence and absence of 0.1 mmol L⁻¹ FeSO₄ with 10 mg L⁻¹ of levofloxacin using a commercial compound.

The samples collected from the degradation experiments were analyzed by high-performance liquid chromatography (HPLC) using a Shimadzu Prominence LC 20 AT instrument fitted with a C-18 column (250 × 4.6 mm id; 5 μm) at 270 nm. The mobile phase employed consisted of the following: 0.5% formic acid applied in water (solvent A) and acetonitrile (solvent B) applied at a flow rate of 1 mL min⁻¹. The elution program employed was as follows: 0–0.5 min, 15% B (isocratic); 0.50–0.51 min, 15–30% B (step); 0.51–7.50 min, 30–75% B (linear gradient); and 7.5–12.00 min, 75–15% (linear gradient). A Shimadzu TOC-VCPH analyzer was used to monitor the removal of organic carbon.

3. Results and Discussion

- Structural morphological characterization

Figure SM1 shows the X-ray fluorescence emission spectra of the niobium incorporated into the Printex L6 carbon in lines K_a 16,529 keV and K_b 18,621 keV. Each metal has energy values that are typically characteristic of the fluorescence emission; for niobium, the values are in K_a 16,58 keV and K_b 18,62 keV [30]. As can be observed, the experimental values are in agreement with the tabulated values; this shows that the metal has been efficiently incorporated into the carbon support.

The XRD patterns obtained for the Printex L6 and 15% Nb/C electrocatalysts are shown in Fig. 1.

The XRD patterns show the typical crystalline characteristics of the Nb₂O₅ orthorhombic phase for Printex L6 carbon modified with niobium based on the JCPDS data 30–873. The intensity of the peaks related to the Nb₂O₅ phase was found to increase when the concentration of the metal was increased. It's also noted that peaks became well defined, with lower full width at half maximum (FWHM), indicating greater crystallization when the Nb₂O₅ concentration is increased in the material. The crystallite size was calculated using Rietveld analysis in the HighScore Plus software. The instrumental broadening was discounted by using a Si standard measured at the same instrument for the analysis. For the 15% Nb₂O₅/C electrocatalyst presented in Fig. 1, it was observed the crystallite size of 15.2 nm, is the largest crystallite amongst the studied compositions.

Using the polymeric precursor method under similar experimental conditions for the synthesis of niobium oxide, Carneiro et al. [31] obtained Nb₂O₅ through the application of graphene. Under similar synthesis conditions, Trevelin et al. [30] also produced Nb₂O₅ using carbon Printex 6L. Thus, the synthesis process presented in this work is efficient for obtaining Nb₂O₅ and is perfectly in line with the synthesis processes reported in the literature.

Figure 2 shows the TEM image of Nb₂O₅ supported on carbon. As can be observed, Nb₂O₅ nanoparticles are well distributed on the carbon support. Figure 2C shows the histogram with mean particle size distribution of 5.6 ± 0.7 nm (presented in Fig. 2B). This value reasonably agrees with XRD presented data, since XRD peaks with higher FWHM, ie. less crystalline material, should present smaller crystallite size.

The electron diffraction pattern shows the diffraction halos related to the main planes of Nb₂O₅; the interplanar distances of 3.93 Å, 3.14 Å, and 2.45 Å correspond to the (001), (180), and (181) planes, respectively. The interplanar distance presented in Fig. 2D agrees with the XRD pattern; furthermore, the diffuse ring observed in the electron diffraction pattern image is typically characteristic of the amorphous carbon support. The image in Fig. 2E related to the Nb₂O₅ overlayer is not entirely uniform; this is likely due to Bragg contrast effects caused by the differing orientations of the Nb₂O₅ crystallite planes which are associated with the incident electron beam.

The 5.0% Nb/C electrocatalyst presented a small average particle size, which is in agreement with the XRD data. This electrocatalyst exhibited a less intense broad peak pattern and a smaller average crystallite size compared to the 15% Nb/C electrocatalyst. The decrease in particle size contributed to an increase in the adsorption of oxygenated species on the catalyst surface [22, 30, 31], and this plays a major role in the kinetics of oxygen reduction reaction (ORR) in terms of electrocatalytic activity.

The atomic concentrations of the surface area of the particulate material obtained from the XPS high-resolution spectra are presented in Table 1. According to the XPS data, the electrocatalyst had 13.3% more oxygen than the Printex L6 carbon. A small fraction of the oxygen content was linked to niobium; in fact, the concentration of niobium was found to be lower than expected.

Table 1– Atomic concentration of the surface area of Printex L6 carbon and 5.0% Nb₂O₅/C (w/w) electrocatalyst obtained from XPS high-resolution spectra.

<i>Element</i>	Concentration (atomic %)	
	Printex L6	Nb/C
Carbon (C 1s)	90.5	77.0
Oxygen (O 1s)	9.5	22.8
Metal (Nb 3d)	---	0.2

The local bonding structure of the electrocatalyst was investigated through the deconvolution of the Nb 3d, C 1s, and O 1s core level spectrum. Figures 3B and 3D show the Nb 3d spectrum of the electrocatalyst composed of 5.0% Nb and Printex L6 carbon. The spectrum was fitted with good precision by only one spin-orbit doublet at a fixed separation of 2.7 eV with the area ratio of 3:2. The characteristic binding energy of 207.8 eV (Nb 3d_{5/2}) corresponds to the Nb₂O₅ oxidation state [30, 31]; this is in line with the XRD diffraction patterns.

Figure 3 shows the XPS C 1s and O 1s spectra of 5.0% Nb₂O₅/C electrocatalyst and Printex L6 carbon. Looking at Figs. 3B and 3C, one will observe that the C 1s spectra of 5.0% Nb/C and Printex L6 carbon are composed of four components. The main component of Printex L6 carbon is associated with the aromatic phase (C-C sp²) at 284.4 eV, and when niobium oxide is added to the Printex L6 carbon support, one notices a reduction in this phase due to the oxidation of the C-C group, which makes the structure more reactive toward ORR [31]. The spectra also show peaks related to the hydrocarbon phase (C-H sp³) at 285.7 eV and oxidized carbon phases in the form of alcohol/ether at 287.0 eV (C-O) and carboxyl at 289.5 eV (O-C = O).

The main components of the O 1s spectrum (Fig. 3D and 3E) related to Printex L6 carbon can be linked to the C-O and O-C = O groups at 532.7 eV and 534.0 eV, respectively; these groups are also identified in the analysis of the C 1s spectrum [22, 31]. A small component observed at high binding energy, 535.8 eV, is associated with molecular water on the surface of the particles. The O 1s spectrum of the 5.0 % Nb/C electrocatalyst shows an additional band at low binding energy which is related to Nb-O bonds at 530.9 eV.

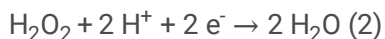
- Electrochemical characterization

The cyclic voltammograms obtained for Printex L6 carbon, 5.0% Nb₂O₅/C, and 15% Nb₂O₅/C electrocatalysts are shown in Figure SM2. The voltammetric behavior of Printex L6 carbon is characterized by a potential range limited by oxygen evolution reaction (anodic limit) and hydrogen evolution reaction (cathodic limit). One can observe a significant variation in the value of the current at more negative potentials (-0.4 to -0.6 V vs Ag/AgCl) at the beginning of the hydrogen evolution reaction; this variation is attributed to the reduction of H⁺ ions present in the solution. The absence of current peaks throughout the potential range studied indicates that the observed currents are of capacitive nature.

The 5.0% Nb/C electrocatalyst displays a blurred peak around 0.2 V vs Ag/AgCl (I), which is probably associated with Nb (V)/Nb (IV) redox transition - i.e., Nb₂O₅/NbO₂ [31]. The voltammogram obtained for the 15 % Nb/C electrocatalyst shows the occurrence of an additional oxide reduction process around - 0.5 V vs Ag/AgCl (II), which is probably related to redox transition from Nb(IV) to Nb(II) - i.e., NbO₂/NbO [22, 31]. The cathodic current associated with such process is not visible due to the variation of the current in this potential range at the beginning of the hydrogen evolution reaction.

The voltammogram shows a decrease in the loads associated with the redox transition, i.e. the active area. It can be assumed that electrocatalysts containing lower contents of modifier exhibit smaller crystallite sizes since the intensity of the peaks related to the metal oxide in the XRD decreases when the concentration of the metal is decreased; thus, these electrocatalysts exhibit poor lattice arrangement - i.e., smaller crystallization.

Figure SM3 shows the rotating ring disk electrode curves related to the oxygen reduction reaction obtained from the application of carbon with different niobium loadings and Printex L6 carbon. Figure SM4 shows the result obtained from the application of carbon with 20% Pt (C/Pt - ETEK).





The ORR analysis was performed using carbon modified with Nb₂O₅ and two reference materials - Printex L6 carbon as a reference for the 2-electron ORR mechanism and C/Pt as a reference for the 4-electron ORR mechanism. Figure SM3 shows the linear sweep voltammograms obtained for the carbon-based materials investigated in the presence and absence of the modifiers. For all the materials investigated, the experiments were initiated at 0.4 V vs Ag/AgCl and proceeded toward more negative potentials. The ORR began at approximately 0.0V vs Ag/AgCl; this shows that the addition of any amount of Nb₂O₅ does not significantly interfere with the onset potential of ORR. Other studies reported in the literature which employed Nb₂O₅ as a carbon modifier under similar experimental conditions also noted that Nb₂O₅ does not modify the onset potential of ORR [22, 30, 31].

As can be noted in Figure SM3, while the incorporation of niobium oxide into carbon leads to an increase in the current of the disk, the values of the currents recorded for the materials containing Nb₂O₅ were found to be close to those of Printex L6 carbon. Regarding the ring current response, an increase in current is observed up to 5% Nb₂O₅ mass concentration. After that, one notices a reduction in the H₂O₂ oxidation current; this decrease in current shows that the application of higher concentrations of Nb₂O₅ yields less amount of H₂O₂.

Figure SM3 shows the results obtained from the application of 15% Nb₂O₅/C. As can be observed, when applied at the potential ranging from 0.0 to -0.4 V vs Ag/AgCl, the 15% Nb₂O₅/C electrocatalyst exhibited patterns of behavior, in terms of disk and ring currents, which were quite similar to the unmodified carbon material. However, when applied at the potential ranging from -0.4 to -0.8 V vs Ag/AgCl, the disk current of the 15% Nb₂O₅/C electrocatalyst was found to be greater than that of the unmodified carbon but the ring current of the former was found to be smaller than that of the latter. Interestingly, this behavior was not observed for the other materials investigated; essentially, this may be an indication that, at more negative potentials, the application of higher amounts of Nb₂O₅ (greater than 10% w/w) may push the ORR closer to a 4-electron mechanism (i.e., higher current in the disk (higher ORR) and lower current in the ring (lower H₂O₂ generation)).

Figure SM3 shows the current profiles of the materials investigated. As can be observed, 5% Nb₂O₅/C exhibited the highest H₂O₂ detection current at -0.5 V vs Ag/AgCl. It must be noted, however, that for a complete analysis, one needs to also take into account the current applied in ORR at the same potential. According to Valim et al., due to the complexity of ORR analysis when it comes to H₂O₂ formation using the disk and ring currents, the use of equations to calculate the fraction of H₂O₂ detection current in total disk current and the total number of electrons is a viable alternative for evaluating the quality of the materials for H₂O₂ generation [32].

Several studies reported in the literature have used equations to estimate the current efficiency of H₂O₂ formation ($eff_{\text{H}_2\text{O}_2} \%$) and the total number of electrons exchanged (n_t) for each studied material [32]. Based on the current values presented in Figures SM3 and SM4, the values obtained for $eff_{\text{H}_2\text{O}_2} \%$ and n_t are shown in Table 2.

Table 2

– Current efficiency of H_2O_2 formation ($eff_{H_2O_2}$ %) and the total number of electrons exchanged (n_t) during ORR using different nominal loadings (w/w) of niobium oxide in carbon and Pt/C.

	Printex L6 (-0.70 V)	0.5% Nb ₂ O ₅ /C (-0.57 V)	1.0% Nb ₂ O ₅ /C (-0.57 V)	3.0% Nb ₂ O ₅ /C (-0.45 V)	5.0% Nb ₂ O ₅ /C (-0.54 V)	8.0% Nb ₂ O ₅ /C (-0.47 V)	10.0% Nb ₂ O ₅ /C (-0.44 V)	15.0% Nb ₂ O ₅ /C (-0.49 V)	Pt/C (-0.05 V)
$eff_{H_2O_2}$ %	76.3	74.6	75.5	76.4	82.5	70.2	68.0	64.1	0.4
n_t	2.5	2.5	2.5	2.5	2.3	2.6	2.6	2.7	3.9

As can be observed in Table 2, Printex L6 carbon recorded a current efficiency for hydrogen peroxide electrogeneration of 76.3; in other words, the application of this material resulted in 76.3% of hydrogen peroxide generation and 23.7% of other reactions. Furthermore, Printex L6 carbon recorded a transfer of 2.5 electrons per oxygen molecule. Pt/C – which is the reference material for ORR via the four-electron pathway, recorded $eff_{H_2O_2}$ % of 0.4% and n_t of 3.9.

The 5.0% Nb₂O₅/C (w/w) electrocatalyst exhibited the highest rate of H₂O₂ electrogeneration (82.5%); this is consistent with the polarization curve in which this electrocatalyst recorded higher ring current and smaller disk current compared to the electrocatalyst composed of 3.0% Nb₂O₅/C. In addition, the 5.0% Nb₂O₅/C electrocatalyst exhibited the lowest number of electrons transferred during oxygen reduction.

The high catalytic activity of the electrocatalysts can be associated with the occurrence of redox transition in the cyclic voltammetry. According to previous studies reported in the literature [32], the catalytic activity of the transition oxides is related to the occurrence of redox reaction between the species, such as Nb (V)/Nb (IV), and this reduces the species with the largest number of oxidation, with the subsequent transfer of an electron to oxygen. Apart from the presence of redox species, ORR can be related to the weak strength of adsorption of oxygen to the metal due to the low center of the energy band or low density of occupied electron states in the electrocatalysts near the Fermi level [22, 31]. This adsorption hinders the breaking of the O-O bond, resulting in the formation of hydrogen peroxide as the final product of the reaction, as described in the Pauling model. It is also worth noting that, the acidic character of the carbon surface modified with 5 % niobium oxide can lead to an increase in the production of hydrogen peroxide due to conductivity and hydrophilic effects.

- Electrochemical Generation of H₂O₂ in Gas Diffusion Electrode

In previous results presented above, based on the values of the disk/ring current (Fig. 5), the modification of carbon with Nb₂O₅ was found to lead to significant improvements in H₂O₂ generation and the 5% C/Nb₂O₅ electrocatalyst was found to generate the highest amount of H₂O₂ among the materials evaluated. It should be noted, however, that the RRDE technique compares ORR currents (disk) and electrochemical detection of H₂O₂ (ring); as such, it points to the tendency for H₂O₂ generation for each material investigated.

Although the RRDE technique can provide us with reliable information regarding the tendency for the electrochemical generation of H₂O₂, one cannot use it to quantify the amount of H₂O₂ generated. Thus, the gas diffusion electrodes were constructed in the presence and absence of 5% Nb₂O₅ for the generation and quantification of H₂O₂ as a function of the applied current (see Fig. 4). For the analysis of H₂O₂ generation, experiments were performed at different current densities where H₂O₂ concentration was evaluated as a function of time. The results obtained from the experiments

showed that H_2O_2 concentration increased linearly as a function of time. The results obtained from the analysis involving H_2O_2 concentration as a function of time can be found in Figures SM5 and SM6 in the Supplementary Material.

Figure 4 - Variation in the final concentration of H_2O_2 as a function of applied current density based on the application of the unmodified GDE and 5% Nb_2O_5 -modified GDE. O_2 pressure applied in the GDE: 0.2 bar. Electrolyte employed: 400 mL of $0.1 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$ at pH 2.

The two main points observed in this experimental analysis were as follows: i) first, the incorporation of Nb_2O_5 in carbon (100 mA cm^{-2}) led to a significant increase in H_2O_2 generation, with the production of 317.6 mg L^{-1} of H_2O_2 ; this amount represents an increase of 136.8% in the amount of H_2O_2 generated in comparison with the H_2O_2 generated under the application of the unmodified GDE (134.1 mg L^{-1}) using the same experimental conditions. As pointed out by Valim et al. (2013) [32], the variation in H_2O_2 concentration between different electrodes of the same composition with the application of the same experimental conditions is $4.5 \pm 0.4\%$. The increase in H_2O_2 generation fueled by the incorporation of Nb_2O_5 is higher than the intrinsic variation of the GDE[20]; ii) secondly, the application of both the Nb_2O_5 -modified GDE and the unmodified GDE at the current density of 150 mA cm^{-2} led to a decrease in the final concentration of H_2O_2 ; this behavior may be associated with the amount of energy supplied to the system, which stimulated a greater occurrence of parallel reactions (Equations 2 to 4) and led to the detection of a lower concentration of H_2O_2 at the end of the experiments.

The results presented in Fig. 4 show a dependence between H_2O_2 generation and applied current density for the modified and unmodified electrodes. To gain a better understanding of the analytical efficiency of the electrodes, it is essentially crucial to evaluate the stability of the carbon modification process. Given that, relevant analytical tests were performed. The first test evaluated the reproducibility of H_2O_2 generation in three sequential electrolyzes using the same electrode and new electrolyte in each electrolysis (see Fig. 5A). The second test evaluated H_2O_2 generation in a long-term experiment (270 min) based on the application of new electrodes; the results obtained are shown in Fig. 5B.

One of the key characteristics of the process of H_2O_2 generation in porous electrodes is reproducibility [20]. Figure 5A shows the concentration of H_2O_2 obtained from the three electrolyzes conducted using the same GDE and new electrolyte for each electrolysis. As can be observed, the H_2O_2 concentration values obtained in the three experiments were quite similar, with a variation of $2.3 \pm 0.4\%$ under the treatment periods investigated. Interestingly, the variation in H_2O_2 concentration observed in this study is very close to the variation reported by Reis et al. (2012) [20]; this points to the reproducibility of the C/ Nb_2O_5 -modified GDE.

Figure 5B presents the results obtained from the long-term H_2O_2 generation experiments conducted using the unmodified GDE and the 5% Nb_2O_5 -modified GDE. The objective of these experiments was to evaluate the stability of H_2O_2 generation throughout the experiments with the modification of carbon. The results obtained from the experiments conducted using both electrodes showed that, after 150 min of experiment, the variation in H_2O_2 concentration as a function of time stabilizes, with a very small variation in H_2O_2 concentration observed after this period up to the end of the experiment. The 5% Nb_2O_5 -modified GDE and the unmodified GDE recorded final H_2O_2 concentrations of 309 mg L^{-1} and 161 mg L^{-1} , respectively, at the end of the experiments.

The results obtained from these experiments pointed to the reproducibility and stability of the process involving the modification of carbon and H_2O_2 generation in different experimental conditions; in addition, the results also showed that H_2O_2 generation occurred in both unmodified carbon and Nb-modified carbon. The reproducibility (Fig. 5A) and

stability (Fig. 5B) observed in the H₂O₂ generation process show that the physical structure and electrochemical property of the electrocatalyst play an effectively constant role in O₂ reduction for H₂O₂ generation; in essence, this points to the success of the process involving the modification of carbon with thermal oxide. For the analysis of the electrochemical activity of Nb in carbon, the global electrical efficiency for H₂O₂ generation was estimated; the results obtained from this analysis are shown in Fig. 5C.

Figure 5C presents the global electrical efficiency values for H₂O₂ generation obtained from the application of the unmodified GDE and Nb₂O₅-modified GDE. For the calculation of the electrical efficiency, both the theoretical and practical numbers of moles of H₂O₂ were considered. The number of theoretical moles was calculated based on the electric charge (applied current and treatment time) and considering that Eq. 1 theoretically occurs with 100% efficiency (thus, all the applied electric charge will be used for H₂O₂ generation). The practical number of moles was calculated based on the mass of H₂O₂ quantified in each sample.

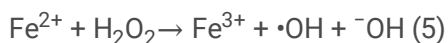
It is worth noting that the electrical efficiency values shown in Fig. 5C take into account only the quantified amount of H₂O₂; this is because, due to the structure of the electrochemical cell (single compartment), a certain amount of H₂O₂ generated may be degraded by the system itself, reduced by 2 electrons forming water and/or oxidized on the anode. Since these parallel reactions were expected to occur, the electrical efficiency was calculated taking into account only the quantified H₂O₂; thus, the global electrical efficiency was calculated for each collected sample. The results obtained from the calculation of the global electrical efficiency as a function of time are shown in Figures SM7 and SM8.

As can be observed in Fig. 5C, the increase in applied current density led to a decrease in electrical efficiency; this was possibly due to the excess of energy supplied to the system, which tended to increase the occurrence of secondary reactions parallel to H₂O₂ generation. Another point that deserves mentioning is the difference in efficiency between the electrodes investigated; as expected, the modified GDE presented a higher efficiency compared to the unmodified GDE; this behavior is associated with the activity of Nb₂O₅ which promoted greater H₂O₂ generation in the modified electrode (with maximum efficiency of 13.6%) compared to the unmodified electrode (8.7%), though both electrodes were applied under the same experimental conditions, with a current density of 20 mA cm⁻².

Considering the results obtained from the experiments conducted in this study, it is clear that the modification of carbon with Nb₂O₅ significantly enhanced H₂O₂ generation. However, the C/Nb₂O₅-GDE which generated the highest concentration of H₂O₂ (Fig. 4) also presented the lowest global electrical efficiency (Fig. 5C) due to the excess amount of energy consumed in the application of this electrode and the consequent intensification of parallel reactions.

- Levofloxacin (LEVO) degradation using C/Nb₂O₅-GDE

The analysis involving H₂O₂ generation using the modified and unmodified electrodes showed that the addition of Nb₂O₅ promoted a significant increase in H₂O₂ generation (see Fig. 4). As described by Silva et al. (2014), the amount of hydroxyl radical (Eq. 5) is directly associated with the degradation process, and in this sense, the amount of H₂O₂ available in the reaction medium can directly interfere with the process involving the degradation of levofloxacin (LEVO) and the reduction of the organic load. To evaluate the exact relation between the amount of H₂O₂ available in the solution and the degradation process, two experiments were carried out using either pressurized N₂ or O₂ in the GDE.



The use of pressurized N₂ in the GDE prevents the formation of H₂O₂; as such, the degradation process is linked to anodic (platinum screen) oxidation. The use of pressurized O₂ in the GDE promotes H₂O₂ formation; here, the

degradation process is the sum of anodic degradation and hydroxyl radical-induced degradation (hydroxyl radical is derived from H_2O_2 in the presence of Fe^{2+}) - this summation occurs due to the single compartment of the electrochemical cell.

- Degradation Process without H_2O_2

The use of pressurized N_2 in the GDE inhibited H_2O_2 formation in the reaction medium and the degradation process was restricted on the surface of the anode; in this sense, the samples were previously taken and no H_2O_2 concentrations were detected under the current densities investigated.

With regard to the degradation experiments conducted under all the current densities investigated, the results obtained showed that there was no significant decrease in LEVO concentration. A maximum LEVO removal rate of less than 1% was obtained from the application of a current density of 150 mA cm^{-2} ; this extremely low removal rate is associated with the small anode area. Based on the results obtained in these experiments, it is clear that the degradation process in the absence of H_2O_2 is irrelevant to the removal of LEVO; thus, a thorough analysis was conducted in order to evaluate the percentages of LEVO and organic load removal in the presence of H_2O_2 with and without Fe^{2+} ions.

- Degradation Process in the Presence of H_2O_2

To perform the degradation experiments in the presence of H_2O_2 , the same parameters employed for the experiments involving H_2O_2 generation were used (Fig. 4). First, the removal of LEVO was evaluated using electrolytes in the presence and absence of Fe^{2+} ions at different current densities; the values obtained from this analysis are shown in Fig. 6.

Figure 6A shows the values obtained in terms of LEVO removal based on the application of different current densities. Here, two distinct patterns of behavior can be observed. First, the experiments conducted in the presence of Fe ions resulted in a significant increase in LEVO removal under all the current densities investigated in comparison to the experiments performed in the absence of Fe ions; the experiments conducted in the presence of Fe ions yielded LEVO removal rates between 83% and 91% at current densities of 10 and 150 mA cm^{-2} , respectively. By contrast, as can be observed in Fig. 6, the experiments performed in the absence of Fe ions resulted in relatively lower removal rates of LEVO, where values between 30% and 71% were obtained based on the application of current densities ranging from 10 to 150 mA^{-2} .

A further interesting point that merits mentioning in Fig. 6A has to do with the behavior of the removal rates obtained from the experiments conducted in the presence and absence of Fe^{2+} . For the experiments carried out in the presence of Fe^{2+} , the removal rates obtained at all the current densities applied were found to be close to one another (minimum of 83% and maximum of 91%); this behavior is associated with the availability of hydroxyl radicals since hydroxyl radicals are immediately formed during the process involving H_2O_2 generation in the presence of Fe^{2+} . Essentially, this may explain why 83% of the LEVO removal rate was obtained in the experiment that involved lower H_2O_2 generation (10 mA cm^{-2}). A different pattern of behavior was observed for the experiments performed in the absence of Fe^{2+} ; there was a considerable increase in the removal rate when the applied current density was increased, with a maximum removal rate of 71% obtained from the application of a current density of 150 mA cm^{-2} .

Looking at the values shown in Fig. 6A, one will notice that, in general, high removal rates of LEVO were recorded, especially for the experiments conducted in the presence of Fe^{2+} ; however, one needs to point out that these high removal rates are only associated with the monitoring of the levofloxacin molecule without taking into account the other

compounds present in the commercial products. For this reason, a thorough analysis was conducted in order to evaluate the organic load removal in the degradation experiments; the results obtained from this analysis are presented in Fig. 6B.

The commercial compound Levofloxacin (LEVO) (acquired from Sandoz Brasil) was used for performing the experiments involving LEVO degradation; this product contains 500 mg of LEVO per unit, in addition to various incipient compounds, including lactose, sodium starch glycolide, glycerol dibehenate, hypolose, and macrogol. Due to the presence of these incipient compounds, the organic load of the samples was monitored during the degradation process conducted in the presence and absence of Fe^{2+} ions using the current densities investigated.

The experiments performed in the presence of Fe^{2+} ions led to a significant increase in organic load removal. This behavior, which has already been described in the literature[9, 10, 34–36], was expected and it is associated with the formation of hydroxyl radicals in the H_2O_2 reaction medium. Figure 6B shows the values obtained for total organic removal (TOC) as a function of the applied current density. As can be observed, an increase in applied current density promoted an increase in TOC removal up to 100 mA cm^{-2} ; organic load removal rates of 20% and 45% were obtained for the experiments conducted in the absence and presence of Fe^{2+} ions, respectively.

With regard to the experiments conducted using the applied current density of 150 mA cm^{-2} , the TOC removal rates obtained were 46% and 20% for the experiments carried out in the presence and absence of Fe^{2+} ions, respectively. These results show that a 50% increase in energy applied to the system did not promote greater removal of TOC; this outcome may be associated with the following factors: i) the amount of organic matter originally present in the samples (initial TOC value of 965 mg L^{-1}); ii) the amount of H_2O_2 generated in the experiment at 150 mA cm^{-2} (Fig. 6B); and iii) the duration of the experiment (90 min). In view of that, an experiment was carried out for a period of 270 min in order to gain a better understanding of the process involving the degradation of LEVO and the removal of organic load; the results obtained are shown in Fig. 7.

Figure 7 shows the values obtained in terms of the removal of LEVO and organic load for the experiment conducted at the current density of 100 mA cm^{-2} in the presence of Fe^{2+} . The aforementioned parameters were chosen because the application of these parameters yielded the best results (see Figs. 6A and 6B) in terms of LEVO and organic load removal; in fact, although the application of a current density of 150 mA cm^{-2} involved the use of a higher amount of energy, it yielded the same results as the application of current density of 100 mA cm^{-2} .

The results obtained from this experiment showed that 92% of LEVO removal was obtained after 90 min of treatment (See Fig. 7), with a maximum removal rate of 96% after 270 min of treatment. Regarding TOC removal, 46% and 66% (maximum) of TOC removal rates were obtained after 90 min (see Fig. 7) and 270 min of treatment. These results show that the limitations observed in terms of LEVO and TOC removal (as observed in Figs. 6A and 7) were associated with the duration of the experiment; the increase in degradation time led to a slight increase in LEVO removal (from 91–96%) and a considerable increase in TOC removal (from 46–66%). Clearly, the results obtained point to a direct relation between a decrease in organic load and the duration of the experiment; this relation can be attributed to the different types of organic structures that constitute the incipient compounds present in the commercial compound.

The results obtained from the experiments involving H_2O_2 generation (Fig. 4) and LEVO degradation (Figs. 6 and 7) showed that the proposed gas diffusion electrode is efficient when applied in H_2O_2 generation, as well as in the degradation of LEVO and the removal of organic load in the samples investigated. Furthermore, while a maximum LEVO removal rate of 92% was obtained after approximately 90 min of degradation, a longer experiment time was required (270 min) to reach a maximum TOC removal of 66%; this outcome was found to be linked to the time of experiment and

not to H_2O_2 concentration, since the results obtained from a longer period of the experiment (Fig. 7) showed that H_2O_2 concentration varied very little after 150 min onwards while the rate of TOC removal continued to increase up to the end of the experiment period (270 min). Essentially, the results obtained from the experiments conducted in this study point to the following: i) the amount of H_2O_2 present in the reaction medium was sufficient, and ii) more time was needed to oxidize the different chemical structures of the incipient compounds present in the commercial product investigated.

4. Conclusion

The present study showed the successful modification of Printex L6 carbon with niobium oxide; this modification allowed us to obtain the $\text{C-Nb}_2\text{O}_5$ phase, confirmed by the presence of (001) and (180) crystallographic planes (main), confirmed in the TEM analysis by the interplanar distances 3.93Å and 3.14Å, respectively. The results obtained from the analysis of H_2O_2 generation using carbon-based materials modified with different amounts of Nb_2O_5 showed that maximum amounts of H_2O_2 were obtained at the current density of 100 mA cm^{-2} ; the application of unmodified GDE and 5% Nb_2O_5 -modified GDE led to the generation of 134 mg L^{-1} and 317 mg L^{-1} of H_2O_2 , respectively after 90 min.

Based on the results obtained from the H_2O_2 generation process, experiments were carried out with the aim of degrading levofloxacin in the samples investigated. The application of $\text{Nb}_2\text{O}_5/\text{C}$ -based GDE resulted in levofloxacin removal of approximately 91% and TOC removal of 46% after 90 min of experiment in the presence of 0.1 mmol L^{-1} FeSO_4 . In experiments with longer duration, levofloxacin removal of approximately 96% and TOC removal of 66% were obtained after 270 min of treatment.

The results obtained in this study show that carbon can be successfully modified with niobium oxide, and this niobium oxide/carbon-based material can be used for the generation of H_2O_2 and for the efficient degradation of pharmaceutical compounds.

Declarations

Acknowledgments

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Ricardo Bertholo Valim: Investigation, Methodology, Validation, Formal analysis, Writing. **Jussara Fernandes Carneiro:** Investigation, Methodology, Validation, Formal analysis. **Fernando Lindo Silva:** Methodology, Formal analysis. **Julio César Lourenço:** Methodology, Formal analysis, Writing. **Peter Hammer:** Methodology, Formal analysis. **Mauro Coelho dos Santos:** Methodology, Formal analysis. **Rodnei Bertazzoli:** Conceptualization, Formal analysis, Resources, Supervision. **Marcos Roberto de Vasconcelos Lanza:** Conceptualization, Resources, Supervision. **Robson da Silva Rocha:** Conceptualization, Validation, Resources, Writing, Supervision.

Data availability

Data will be made available upon request.

Conflict of Interests

The authors have no competing interests to declare that are relevant to the content of this article.

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Figures

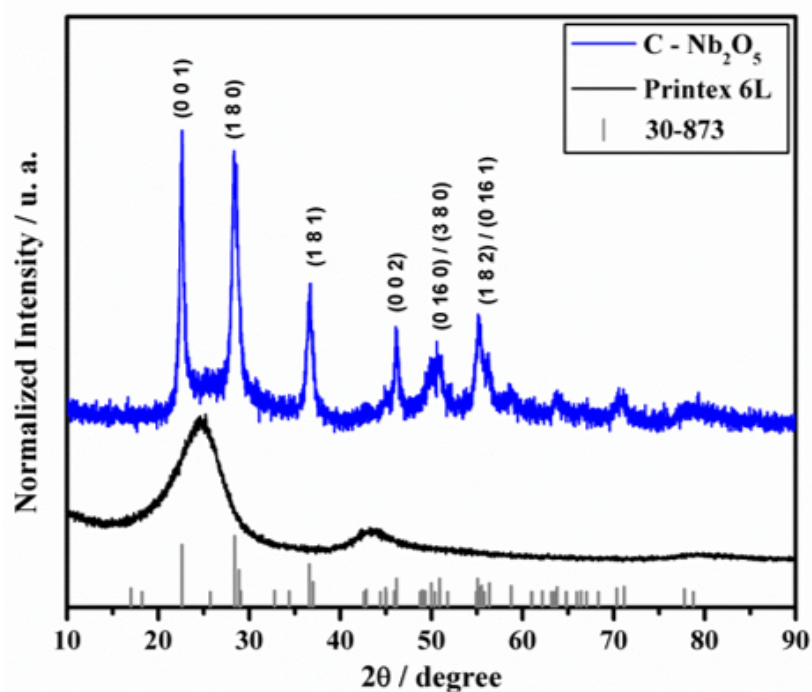


Figure 1

JCPDS characteristics of the Nb₂O₅ phase and XRD patterns of Printex L6 and 15% Nb/C electrocatalyst.

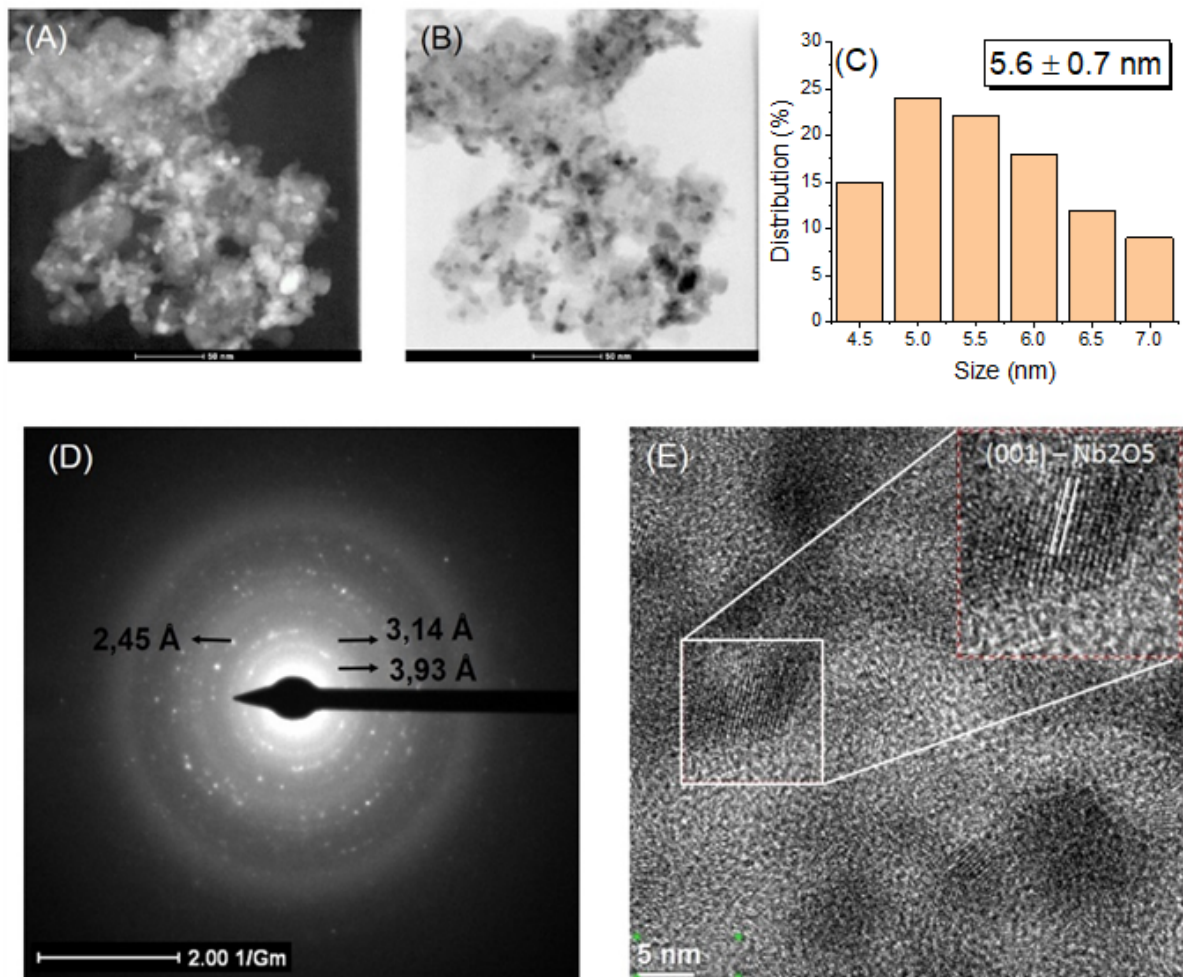


Figure 2

Transmission electron microscopic image of the Nb₂O₅/C catalyst (5.0 (m/m) Nb/C) in (A) dark field and (B) bright-field; (C) Histogram of the estimated mean particle size; (D) Electron diffraction pattern related to the main crystal planes of the Nb₂O₅ structure; and (E) Transmission electron microscopic image with high resolution and Fourier transform refinement.

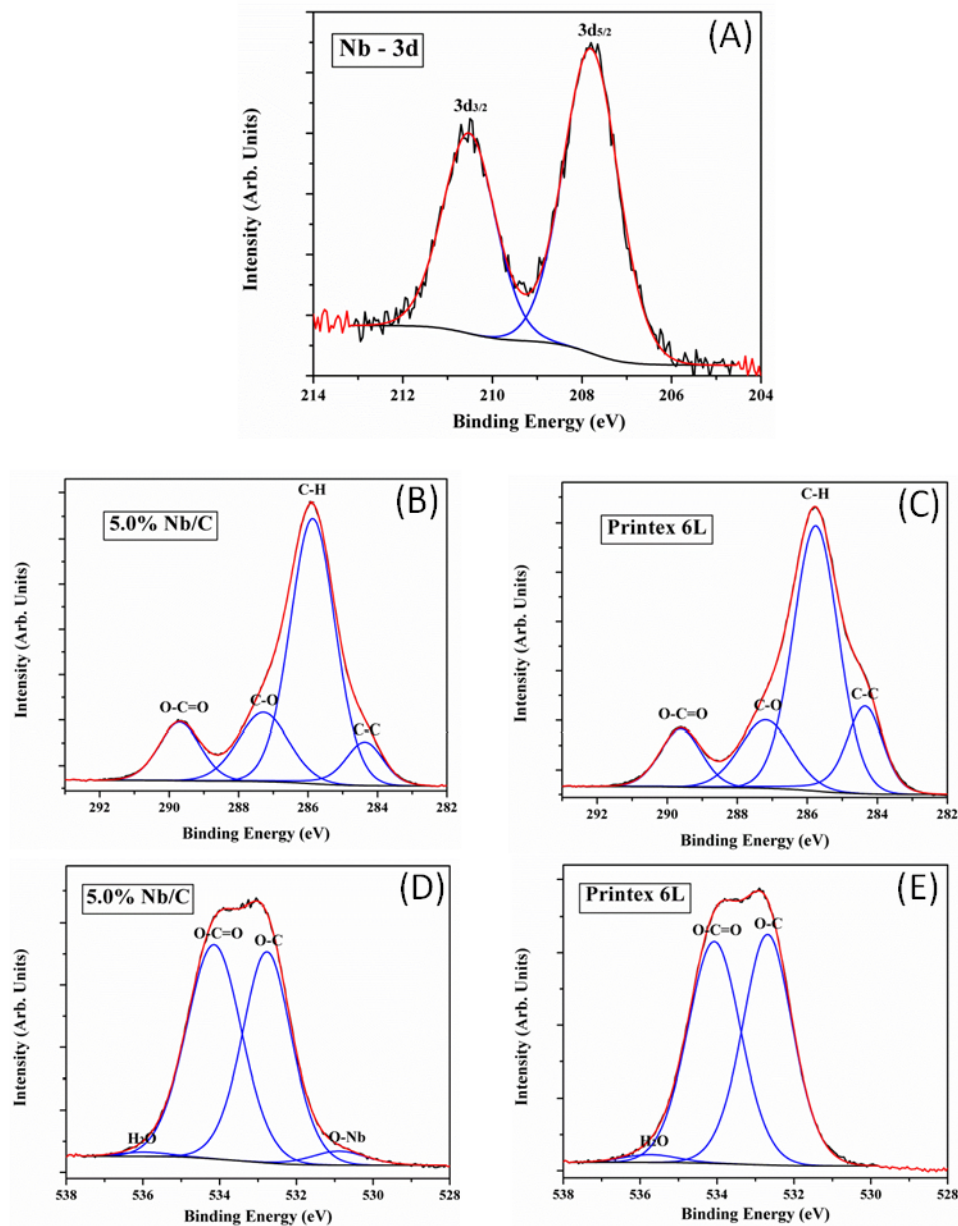


Figure 3

(A) Deconvoluted XPS Nb 3d spectra of niobium oxide nanoparticles composed of 5.0 % Nb₂O₅/C (w/w). Deconvoluted XPS C 1s spectra of (B) 5.0 % Nb₂O₅/C (w/w) electrocatalyst and (C) Printex L6 carbon. Deconvoluted XPS O 1s spectra of (D) 5.0 % Nb₂O₅/C electrocatalyst and (E) Printex L6 carbon.

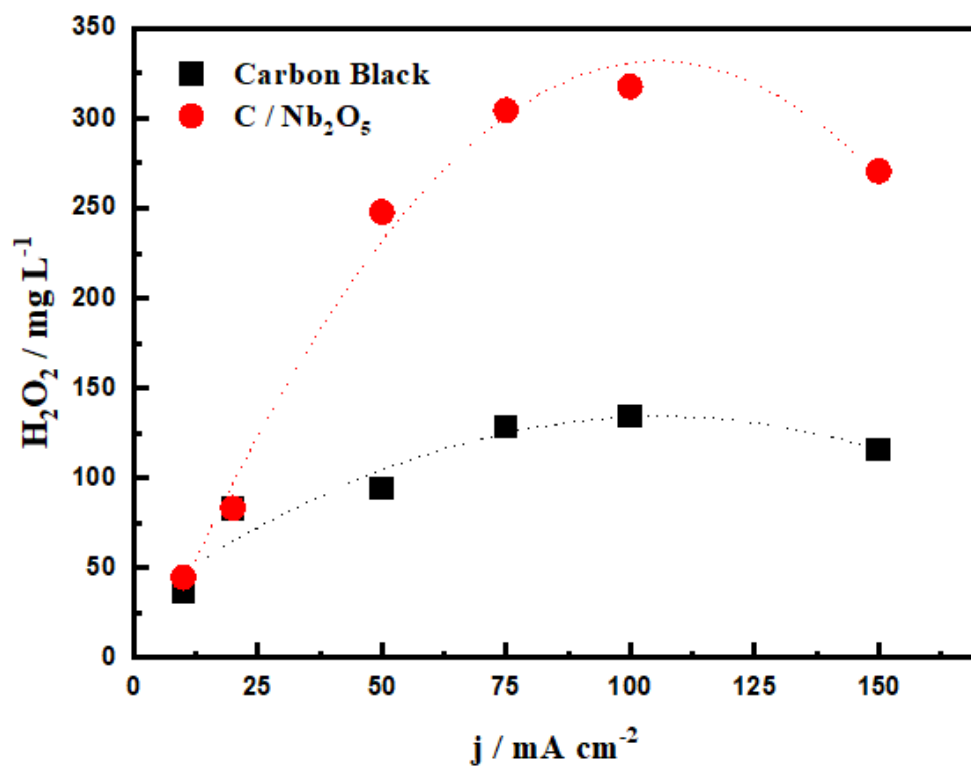


Figure 4

Variation in the final concentration of H₂O₂ as a function of applied current density based on the application of the unmodified GDE and 5% Nb₂O₅-modified GDE. O₂ pressure applied in the GDE: 0.2 bar. Electrolyte employed: 400 mL of 0.1 mol L⁻¹ K₂SO₄ at pH 2.

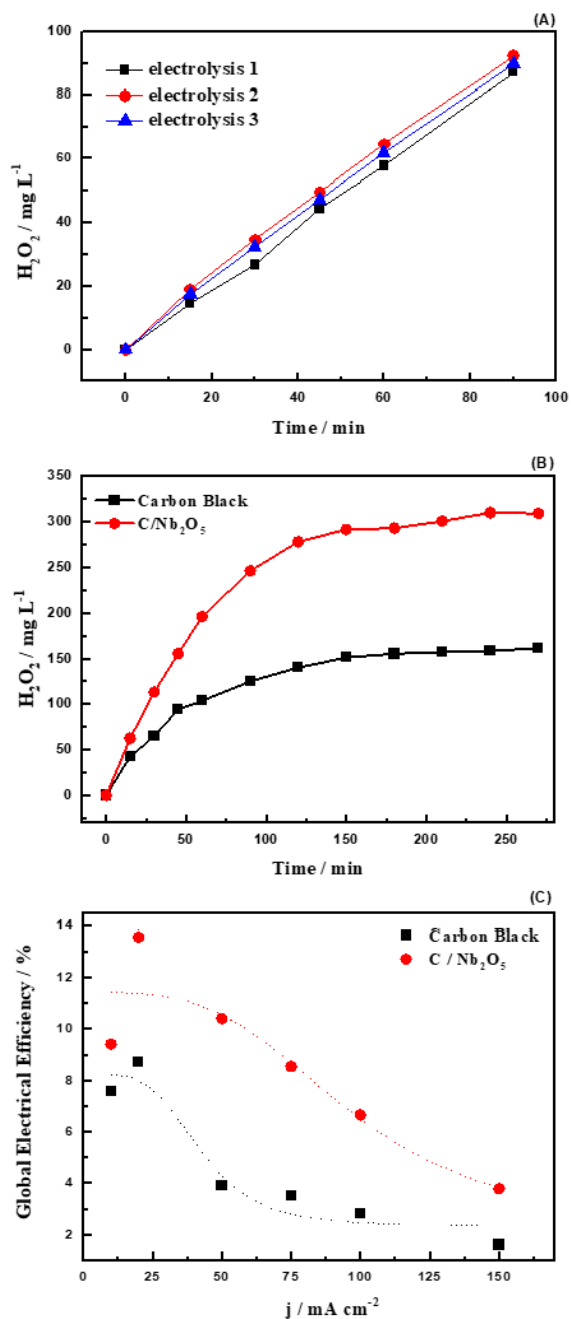


Figure 5

Stability of the carbon modifier. (A) A sequence of three electrolyses conducted at the current density of 20 mA cm⁻² using the same modified GDE. (B) Long-term electrolysis (270 min) conducted using unmodified GDE and 5% Nb₂O₅-modified GDE, both applied at the current density of 100 mA cm⁻². (C) Variation in global efficiency of H₂O₂ generation as a function of applied current density based on the application of unmodified GDE and 5% Nb₂O₅-modified GDE after 90 min of electrolysis. O₂ pressure applied in GDE: 0.2 bar. Electrolyte employed: 400 mL of 0.1 mol L⁻¹ K₂SO₄ at pH 2.

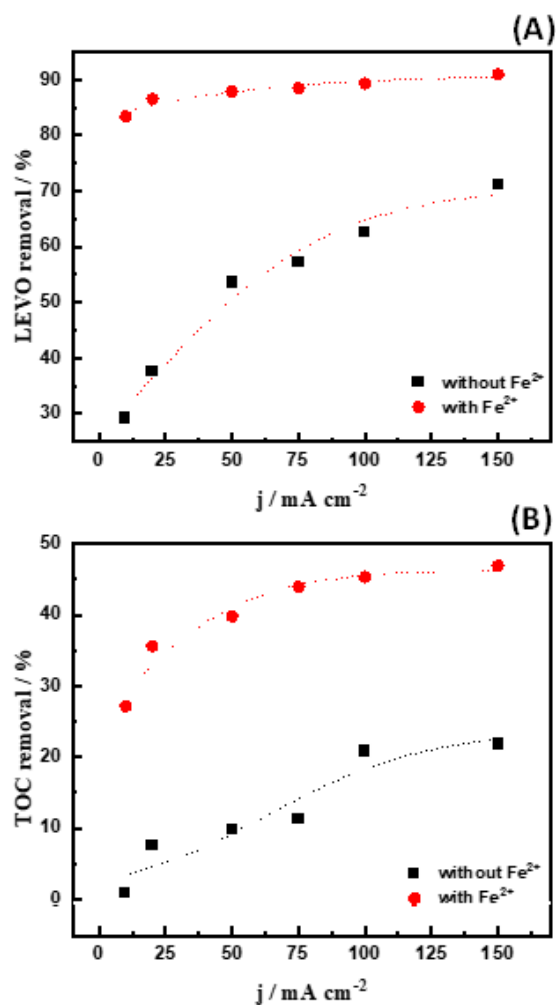


Figure 6

(A) Variation in LEVO removal; and (B) Variation in TOC removal. Both LEVO and TOC removal percentages were evaluated as a function of applied current density based on the application of unmodified GDE and 5% Nb₂O₅ – modified GDE using electrolytes in the presence and absence of ions Fe²⁺. The results shown here were based on experiments conducted for 90 min.

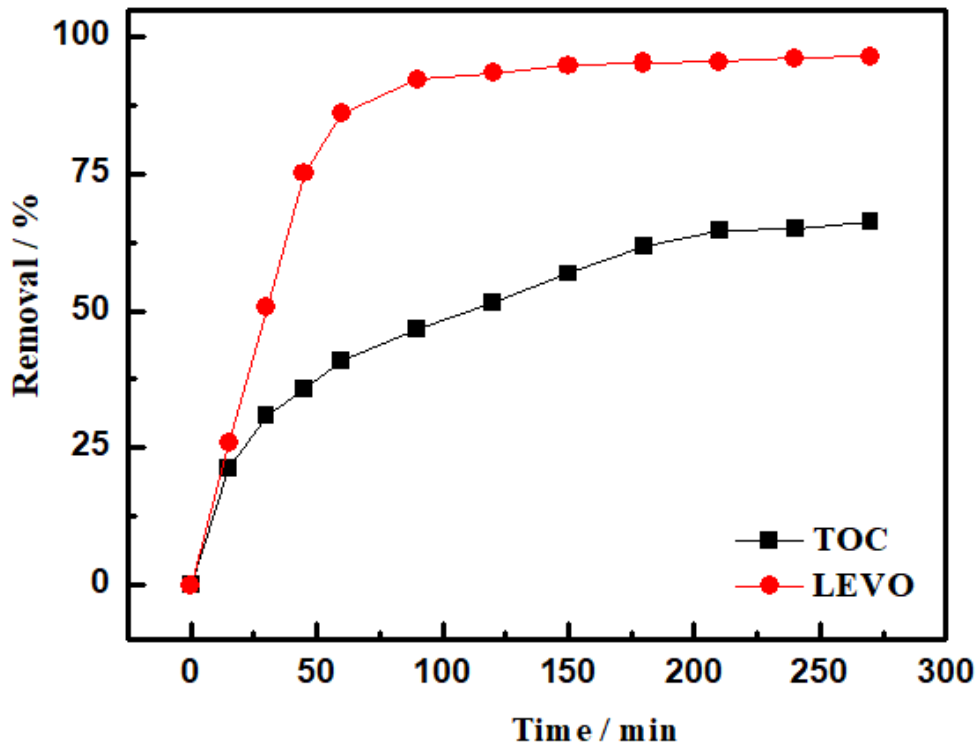


Figure 7

Long-term electrolysis (270 min) based on the application of 5% Nb₂O₅ –modified GDE at a current density of 100 mA cm⁻². O₂ pressure in GDE: 0.2 bar. Electrolyte: 400 mL of 0.1 mol L⁻¹ K₂SO₄ (at pH 2) in the presence of Fe²⁺ and 10 mg L⁻¹ of LEVO.