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Improvement of the Degradation of Methyl Orange Using a TiO₂/BDD Composite Electrode to Promote Electrochemical and Photoelectro-Oxidation Processes

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Electrophoretic deposit of titanium dioxide (TiO₂) was carried out over a boron doped diamond plate of 2 cm², annealing at 350 °C to produce binary TiO₂/BDD composite electrode. The composite was characterized by scanning electron microscopy (SEM) and linear sweep voltammetry (LSV) response. N,N-dimethyl-p-nitrosoaniline (RNO) was used as a probe molecule for the detection of free radicals (°OH) during the oxidation of water in phosphate buffer (pH 4) solution; at the TiO₂/BDD/*hv* composite, an apparent first-rate kinetic constant of $k_{obs} = 0.1314 \text{ min}^{-1}$ was observed. Afterwards, the composite electrode was applied to degrade 40 and 100 mg L⁻¹ of a typical azo dye methyl orange (MO) via electrochemical process, such as: electro-oxidation (EO) and photoelectro-oxidation (PEO) under 25, 75 and 125 mA cm⁻² current density (*j*); the PEO tests were performed using a UVA lamp at 365 nm. Results showed that the discoloration in the PEO process was larger than in the EO process, 96 and 100 %, respectively. Chemical Oxygen Demand (COD) was tested to evaluate the degradation. Hydroxylated derivatives were identified by means of mass spectroscopy during the PEO of MO in a TiO₂/BDD/*hv* composite electrode.

Keywords: TiO₂/BDD composite, hydroxyl radical formation, electrochemical process, water treatment, azo dye.

1. INTRODUCTION

Throughout the world, every day, a great amount of wastewater is discharged, which comes from different economic activities, such as: the textile industry, pharmaceutics, food, automotive and agricultural industries; as well as from different domestic activities, such as: showering, washing dishes, washing clothes, cleaning home, etc. [1]. In Mexico, for example, the textile and clothing industry employs a large number of synthetic dyestuffs to dye cloth; this activity generates large volumes of colored water, which most of the time is discharged without previous treatment by the municipal plants to rivers and lakes, causing a big problem for the surrounding places and the biodiversity that surrounds them. However, the local authorities feel relaxed about this industry, as it represents a very important source of growing economic means; for example, in 2017 it grew 6.8% above the inflation [2].

To resolve this serious problem of water pollution because of the use of dyes, throughout time, different alternatives of water treatment have been tried. It is worth mentioning that biological processes are usually ineffective, owing to the high concentrations of organic matter or due to a change in the pH value of the solution, which considerably affects the habitat of the microorganisms that are responsible for degrading the pollutants in this method. The separation processes, such as filtration or adsorption, have also been applied; however, with little efficiency, because they fail a phase shift of the colorants [3, 4, 5].

In the last 15 years, the advanced oxidation processes (AOPs) have been widely applied to remove several organic pollutants in wastewaters; the principal characteristic was the in situ generation of free hydroxyl radical (•OH), which has a high standard redox potential (2.80 V vs SHE) and can react with a great variety of organic pollutants, achieving its mineralization. The versatility of the AOPs allows the free radical (•OH) to be generated via chemical or electrochemical processes [6,7,8].

There is a wide variety of electrochemical methods, however, the electro-oxidation (EO) is undoubtedly the most popular to carry out the treatment of wastewater containing organic pollutants, such as dyes [9]. In this method, the pollutants are transformed into an anode material with a high oxygen evolution potential, which favors the formation of hydroxyl radicals (•OH) [10]. Among the anode materials, the best is the boron doped diamond (BDD), which can generate free radicals hydroxyl physisorbed BDD (•OH) on the surface of BDD (Eq. 1) [11]. Therefore, BDD is powerful enough to activate the mineralization of pollutants and their degradation intermediates, including carboxylic acids; and it has a much greater oxidation power than other common anodes [12].

$BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^-$

(1)

Another possibility to produce free hydroxyl radicals is via photochemical process, such as the photocatalysis method (PC), using semiconductor materials, from which the most popular is the titanium dioxide (TiO₂). In this way, TiO₂ has been widely used because of its ability to degrade organic contaminants; this coupled with its good properties, such as corrosion resistance, nontoxicity, durability, acceptable band gap and low cost [13]. The catalytic process begins when the TiO₂ undergoes a photoexcitation with light at a wavelength of λ =365 nm, followed by the absorption of photons with energy, equal to or greater than its energy gap (Eg). It stimulates the promotion of some electrons from the valence band (V_b) towards the conduction band (C_b) of semiconductor. Afterwards, it produces in the positive valence band a hole (h⁺_{Vb}) and in the negative conduction band an electron (e⁻_{Cb}) [13].

Then, over the (h^+_{Vb}), the water oxidation and hydroxide ion (OH⁻) take place to produce the free hydroxyl radical •OH, while the reducer (e^-_{Cb}) reduces oxygen to form superoxide radical anion (O₂^{-•}), what is shown in the Eq. 2-4 [14]:

$$TiO_2(h_{Vb}^+) + H_2O \to TiO_2 + H^+ + OH$$
⁽²⁾

$$TiO_2(h_{Vb}^+) + OH^- \to TiO_2 + OH$$
(3)

$$TiO_2(\bar{e_{Cb}}) + O_2 \to TiO_2 + O_2^{\bullet}$$
(4)

Recently, studies related to the combination of these two techniques with the aim of increasing the production of hydroxyl free radicals on the surface of an electrode, which in its turn will carry out the degradation of organic pollutants, increasing the efficiency of the process, have taken a relevant and special attention [15, 16, 17]. In this context, carrying out the combination between the processes of electro-oxidation (EO) and photocatalysis (PC), using as a substrate a semiconductor film electrode, such as BDD, and coated with titanium dioxide, has shown great potential for the destruction of organic pollutants, compared to EO and PC in their individual forms [18]. The main advantage of carrying out the process of immobilization of TiO₂ in a conductive substrate is to avoid the post-recovery process, thus, enabling the use of recycling of catalyst and allowing to improve the photocatalytic efficiency by suppressing the recombination of (h^+/e^-) pairs.

In this research, we show the preparation of TiO₂ monolayers, electrophoretically deposited on BDD substrates to form a TiO₂/BDD composite, whose structure resolves the potential origin of the capacitive effect. In our previous work [19], we concluded that the electrophoretic deposits of TiO₂ on the BDD could provide important benefits to the improvement of the production of heterogeneous hydroxyl radicals **•**OH and their potential application in the degradation of organic compounds. The detection of radicals was followed by the spin-trap technique, by using RNO. The degradation of MO by EO, PEO was followed by bulk electrolysis. The intermediaries during the oxidation of MO were followed by the chromatographic techniques.

2. EXPERIMENTAL

2.1. Chemical reagents.

Methyl orange (MO) sodium salt $C_{14}H_{14}N_3NaO_3S$, 327.33 g mol⁻¹ of 99% purity was supplied by Karal S.A. de C.V. (Mexico). The solutions were prepared with ultrapure water from a Millipore Milli-Q system (resistivity>18 M Ω cm, 25 °C). The solution pH was adjusted to 3.0 with analytical grade H₂SO₄, supplied by J.T. Baker. Solvents and other chemicals used were either of analytical or HPLC grade, and N,N-dimethyl-p-nitrosoaniline (RNO) was purchased from Sigma-Aldrich. Nanoparticulated TiO₂ (P25, 80% anatase, 20% rutile, average particle diameter 20 nm) was purchased from DegussaTM. Boron doped diamond (BDD) electrodes supported on Nb of 2 cm² geometric area were purchased from MetakemTM Germany.

2.2. TiO₂/BDD composite preparation and characterization

The way, in which the electrophoretic deposit was carried out to form the TiO_2/BDD composite, was based on an earlier report [19] with several improvements, as described below. The

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BDD surface was electrochemically cleaned, immersing the electrode in a 0.1 M of HClO₄ under 50 mA current intensity during 30 min, before its use in electrophoresis. The TiO₂/BDD composite electrode was then synthesized by electrophoretic deposition of the TiO₂ Degussa P25 nanoparticles onto the BDD surface.

The electrochemical characterization was developed in a 50 mL of 1 M H₂SO₄ solution by means of LSV experiments with different TiO₂/BDD composite working electrodes of 2 cm² area, using a three-electrode cell with an EpsilonTM potentiostat/galvanostat in an interval of 0.6 to 2.0 V at a sweep speed of 20 mV s⁻¹. The aqueous solution was thoroughly de-aerated with nitrogen (99.99% purity) prior to the experiments, and tests were made at 25 ± 2 °C. The counter electrode was a platinum wire, and the reference electrode was an Ag|AgCl (3 M KCl). Scanning electron microscope (SEM) images of the TiO₂/BDD composite, carried out electrophoretically, were evaluated using a Zeiss Sigma HD-VP Field Emission-Scanning Electron Microscope.

2.3. Detection of hydroxyl radicals during water discharge at TiO₂/BDD anode

Detection of hydroxyl radicals formed during electrolysis was confirmed using radical scavengers (spin traps), such as N,N-dimethyl-p-nitrosoaniline (RNO). RNO is an efficient spin trap, as it can be seen in the Eq. 5, where interaction of N,N-dimethyl-p-nitrosoaniline (RNO) plus •OH radical produces a much less reactive N-oxide radical.



The attractive characteristic of this reaction is the significant changes in the absorbance spectra of RNO during its reaction with hydroxyl radicals °OH, which can be followed by the bleaching of RNO. To carry out the absorbance decay of RNO, we take into account the methodology proposed by Aguilar et al. in Ref. [23], where the authors suggest performing the absorbance decay at $\lambda_{max} = 440$ nm. The solutions contained 4 mL of 2×10⁻⁵ M of RNO in phosphate buffer solution 1 M of pH 7.4, at 25 °C, and applying anodic potential of 1.3 V *vs* Ag/AgCl. Measurements were made under quiescent conditions over 0.25 cm² electrode area [24-26]. More details can be consulted elsewhere [23].

2.4 Electrochemical set-up

The degradation of 100 mL of 40 and 100 mg L⁻¹ methyl orange solutions in 0.05 mM Na₂SO₄ was made with a cylindrical tank reactor thermostated at 25 °C. The anode was either a bare BDD or a synthesized TiO₂/BDD composite electrode of 2 cm² area, and the cathode was a 3 cm² platinum. In all the analyses, the solution was dynamically disturbed with a magnetic bar at 400 rpm, in order to mix the organics and transport them toward/from the surface electrodes. Different current densities (*j*) of 25, 75 and 125 mA cm⁻² provided by a BK Precision 1688B power supply were continuously applied.

Photoelectro-oxidation assays were performed by directly irradiating the TiO₂/BDD composite electrode with a Steren UVA light of $\lambda_{max} = 365$ nm and a power density of 75 mW cm⁻² as shown in Figure 1. The solution pH was measured with a Pent pH-009(1) A pH-meter.



Figure 1. Electrochemical set up carrying out to MO degradation under photoelectrocatalysis TiO₂/BDD/UV process, a) power supply, b) UV lamp, c) magnetic stirred, d) cylindrical tank reactor, e) graphite cathode, f) TiO₂/BDD composite anode.

2.5. Analytical procedures

The decolorization of dye solutions followed from their absorbance (A) decay at the maximum wavelength in the visible region of $\lambda_{max} = 500$ nm for methyl orange, by using a GBC-Cintra 1010 UV–vis spectrophotometer. The percentage of color removal or decolorization efficiency was calculated by Eq. (6) [20]:

$$\% Color \quad removal = \frac{A_0 - A_t}{A_0} \times 100 \tag{6}$$

where A_0 and A_t are the initial and final absorbances at times 0 and t, respectively, at $\lambda_{max} = 500$ nm.

Generated carboxylic acids were quantified by ion-exclusion, using high resolution liquid chromatography (HPLC) with an Agilent Technologies 1200 Series coupled to a Bio-Rad HPLC Organic Acid Analysis Column, Aminex HPX-87H Ion Exclusion Column, 300 mm x 7.8 mm and UV detector at $\lambda = 210$ nm. The mobile phase was 4 mM of H₂SO₄, eluted at flow of 0.6 mL min⁻¹.

Stable aromatic products were identified under pre-concentration process, which consisted of the dilution of 2.5 mL of each sample in a carbonate buffer solution (20 mM) at pH of 7.5. Subsequently, a Supel-Select HLB 60 mg cartridge was activated and washed; first, passing 5 mL of HPLC grade methanol grade and then 5 mL of HPLC grade water. After that, 5 mL of the diluted sample was passed through the cartridge, and further, 3 mL of HPLC grade water was passed through it. The cartridge was dried, and the sample was eluted with 3 mL of methanol, which was collected for further analysis. The same procedure was used for MO samples withdrawn after every 20 min of treatment. Once, clean samples of salts were obtained, they were introduced by direct infusion at 3 μ L min⁻¹ to the electrospray ionization source of a quadrupole time-of-flight mass spectrometer (Bruker Daltonics ESI-QTOF-MS maXis impact), equipped with Data Analysis 4.1. ESI was operated in negative mode with ion spray voltage 4500 V, nitrogen dry gas 4 L min⁻¹, drying temperature 180 °C and nebulizing gas pressure 0.4 Bar. Mass calibration was accomplished based on sodium formate clusters.

3. RESULTS

3.1. Electrophoretic deposition and surface characterization

Composite TiO₂/BDD was obtained via electrophoretic technique, using the methodology proposed by Espinola-Portilla et al., reported recently [19]. It was carried out in the following way: a 4 cm² aluminum plate and a 2 cm² BDD electrode, separated at 0.5 cm, were immersed in a glass vessel containing 10 mL of a colloidal suspension of 2.5 % (m/v) of Degussa P25 TiO₂ powder in 5 % (v/v) isopropyl alcohol. Applying 4.8 V constant potential between the electrodes, provided by a BK Precision 1688B power supply during 15 s, a good uniform TiO₂ thin films coating was obtained. The coated surface was finally subjected to annealing at 350 °C for 30 min, in order to increase film crystallinity and sticking together. Figure 2a shows a photography of TiO₂/BDD deposit after electrophoretic process and annealing at 350 °C, where it is possible to observe a regular and uniform TiO₂ film over the BDD surface.



Figure 2. a) Photography of BDD plate covered TiO₂ film after electrophoretic deposition, b) SEM image of TiO₂/BDD at 1000X, c) cross section of TiO₂/BDD electrode.

In Figure 2b, we present the SEM analysis carrying out TiO_2/BDD electrophoretic deposition, as it can be observed, characterized by a uniform microcrystalline structure; obvious cracks are appreciated, but for our interest it does not represent any problem, as we will explain it later. It will be more useful to carry out the processes that are of great interest for us. Figure 2c represents the cross section of TiO_2/BDD electrode showing the thickness for the film, which is close to $10\mu m$.

3.2. Electrochemical characterization

Figure 3 shows the typical linear sweep voltammetry plot obtained in the potential region of supporting electrolyte decomposition, using 1 M H_2SO_4 solution and scan rate at 20 mV s⁻¹ in a potential interval from 0.6 to 2.0 V. This figure illustrated that the current density at a given potential in the region of supporting electrolyte decomposition improved for the presence of TiO₂. This shows that TiO₂ involves intermediates, which are formed during the oxidation of the H₂SO₄, supporting electrolyte (Eq. 7), and/or water discharge (Eq. 8).



Figure 3. Linear-sweep voltammetry plots of a) BDD, b) TiO₂/BDD and c) TiO₂/BDD/*hv* recorded in 1 M H₂SO₄ under scan rate 20 mV s⁻¹.

Indeed, it has been established that electrolysis in 1 MH₂SO₄ over BDD surfaces resulted in the production of peroxodisulfuric acid (Eq. 7), with high current efficiency in our case; the adding of TiO₂ film followed the next behavior: a) BDD < b) TiO₂/BDD < c) TiO₂/BDD/*hv* [21, 22].

$$2H_2SO_4 \to H_2S_2O_8 + 2H^+ + 2e^- \tag{7}$$

$$H_2 O \rightarrow OH + H^+ + e^-$$
 (8)

3.3. Production and detection of generated free hydroxyl radicals (•OH)

Figure 4 shows the different time course of the absorption spectra of RNO abatement with electrolysis time for the (a) BDD anode, where it is possible to observe a slow decay in the RNO discoloration, close to 39% after 120 min of electrolysis; a slight improvement is observed for the (b) TiO₂/BDD composite with a RNO color decrease of 53%. Definitely, the best color depletion of the RNO is achieved when the (c) TiO₂/BDD/*hv* composite is used, with which it reached an efficiency of 60% after 120 min treatment, thereby confirming its reaction with •OH, generated in all cases.

In the Figure 5a, it is possible to observe the decay of the RNO concentration as a function of time in the presence of different materials studied, (**•**) BDD, (**•**) TiO₂/BDD and (**•**) TiO₂/BDD/*hv*. Figure 5b shows the semilogarithmic plots of these curves and evidence of their good fit. Therefore, the concentration decay follows a pseudo-first-order reaction kinetics in three sets of experiments, which means that a constant concentration of **•**OH is formed during the (**•**) EO treatment under BDD k_1 -values of 0.0039 min⁻¹ ($R^2 = 0.9992$), (**•**) EO over composite TiO₂/BDD 0.0067 min⁻¹ ($R^2 = 0.9960$) and (**•**) photoelectron-oxidation using TiO₂/BDD/*hv* composite 0.0076 min⁻¹ ($R^2 = 0.9979$), with these types of composites, either in the absence or presence of light. It is an interesting finding, since it is proposed that the free radicals are produced from the oxidation of water that diffuses over the cracks of the composite and also improves with the action of the light, since it activates the superficial TiO₂.

3.4. Methyl orange degradation

The comparative oxidation power of EO and PEO for MO degradation was checked with three anodic materials, namely BDD, TiO₂/BDD and TiO₂/BDD/*hv*, and a platinum cathode. Solutions with 40 mg L⁻¹ in 0.05 M Na₂SO₄ at pH 3.0 and 25 °C were treated at different current densities (*j*) values between 25 mA cm⁻², 75 mA cm⁻² and 125 mA cm⁻² for 60 min. In all cases, its pH dropped slightly to a final value close to 2.9. On the other hand, the protons that are formed in the reaction (1) are compensated by the OH⁻ ions that are formed in the cathode, when water is reduced to H₂ gas; as expected if recalcitrant short-chain carboxylic acids are generated as final byproducts [27-31]. In fact, if the solution is electrolyzed without MO, no change in pH would be observed.

Figure 6a shows the normalized MO abatement for a 40 mg L⁻¹ MO solution at different *j* values by EO under BDD anode. Higher *j* increased the degradation rate due to the concomitant acceleration of reaction (1), generating greater quantities of oxidant BDD('OH). The exponential drop in concentration of these trials was examined as pseudo-order kinetics according to the expression, where k_1 is the apparent rate constant [32].

$$Ln(C_o / C_t) = k_1 t \tag{9}$$



Figure 4. Absorption spectra of RNO solutions obtained at 10 min intervals after 2 h electrolysis using a) BDD anode, b) TiO₂/BDD composite c) TiO₂/BDD/*hv* composite with immersed area of 0.25 cm². The solutions contained 4 mL of 2x10⁻⁵ M of RNO in phosphate buffer solution 1 M of pH=7.4, at 25 °C. Anodic potential: 1.3 V *vs* Ag/AgCl. Measurements were made under quiescent conditions.



Figure 5. Change of RNO concentration with electrolysis time using (■) BDD, (◆) TiO₂/BDD and (●) TiO₂/BDD/*hv*. (a) Curves obtained from absorbance data shown in Fig. 4. (b) Corresponding pseudo-first-order kinetic analysis.

The insertion highlights an excellent fit using Eq. (9), giving rise to increasing k_1 -values of 0.0444 min⁻¹ ($R^2 = 1$) for 25 A cm⁻², 0.0502 min⁻¹ ($R^2 = 1$) for 75 A cm⁻² and 0.0620 min⁻¹ ($R^2 = 1$) for 125 A cm⁻². This behavior suggests the formation of a low and steady concentration of BDD('OH) to attack the MO in each *j* tested.

As shown in the Figure 6b, it depicts an improvement over MO decay for the same solution, using the TiO_2/BDD composite upon comparable conditions, with gradual upgrading of the increasing *j*. This trend can be again accounted for the concomitant acceleration of reaction (1), thereby producing

more reactive BDD('OH) that destroys more rapidly the MO molecule. Insertion proves that the corresponding kinetics obeyed the pseudo-first-order reaction of Eq. (9). The increasing k₁-values of 0.0529 min⁻¹ ($R^2 = 1$), 0.0624 min⁻¹ ($R^2 = 1$) and 0.1060 min⁻¹ ($R^2 = 1$) were obtained for 25, 75 and 125 mA cm⁻², respectively.



Figure 6. Normalized MO concentration and insert is the kinetic analysis assuming a pseudo-first order reaction for MO under different electrodes tested: a) BDD, b)TiO₂/BDD and c) TiO₂/BDD/*hv* for the treatment of 100 mL of a 40 mg L⁻¹ MO and 0.05 M Na₂SO₄ solution of pH 3.0 and 25 °C using a stirred tank reactor equipped with a 2 cm² each composite electrode and 3 cm² graphite cathode at current density (*j*): (**•**) 25 mA cm⁻², (**•**) 75 mA cm⁻² and (**•**) 125 mA cm⁻².

This tendency corroborates the generation of a significant steady quantity of oxidant BDD/TiO₂ (OH); this is because the surface electroactive area of the composite was increased, accumulating the active sites for the discharge of water from reaction (1) in each trial.

In contrast, Figure 6c depicts the assays by TiO₂/BDD/*hv* composite, where it is possible to observe a much faster MO decay for the 40 mg L⁻¹ solution by photoelectro-oxidation process. These results can be again considered for the simultaneous acceleration of reactions 1 to 4, by this means generating more reactive 'OH that degraded more quickly the parent MO azo dye. The insertion demonstrates that the analogous kinetics followed the pseudo-first-order reaction of Eq. (9). It is possible to observe that the increasing k₁-values of 0.0687 min⁻¹ (R² = 1), 0.0951 min⁻¹ (R² = 1) and 0.1314 min⁻¹ (R² = 1) were obtained for 25, 75 and 125 mA cm⁻², respectively.

This result evidences an important rise in degradation efficiency of 99.98%, 99.99% and 100% for increasing *j* values of 25, 75 and 125 mA cm⁻². Compared to the data obtained for just BDD, higher k_1 -values were found using TiO₂/BDD/*hv* composite for much greater amounts of free radicals [•]OH.

The influence of azo dye MO concentration between 40 and 100 mg L⁻¹ on the PEO performance with the TiO₂/BDD/*hv* composite was assessed at 125 mA cm⁻². The changes of oxidation for these assays are shown in Figure 7, were is possible observe an increasing decolorization 95.22% (•) and 97.82% (•) with raising MO content of 40 and 100 mg L⁻¹, respectively. Since the same production of main •OH oxidants over TiO₂/BDD/*hv* is expected at the same current, because the above radicals can react more preferentially with the raising amounts of organics present in solution, thus enhancing the oxidation process. In the insert is possible to observe that the increasing k₁-values of 0.0646 min⁻¹ (R² = 1), and 0.08261 min⁻¹ (R² = 1) were obtained at 125 mA cm⁻², for 40 and 50 mg L⁻¹ MO oxidation, respectively.



Figure 7. Effect of azo dye concentration *vs* electrolysis time for the PEO treatment of 100 mL solutions in 0.05 mM Na₂SO₄ at pH 3.0 and 25 °C using a cylindrical tank reactor at 125 mA cm⁻² and with magnetic stirring. Initial MO content: (●) 40 mg L⁻¹ and (■) 100 mg L⁻¹.

The amount of oxidizable material via chemical oxygen demand (COD) tests were carried out for each material. COD was measured according to the method 5220D from Standard Methods. (APHA/AWWA/WEF., 2012), while nitrogen was estimated using HACH method 10071: TNT persulfate digestion method. Figure 8 shows the degradation of 100 mg L⁻¹ (140 mg L⁻¹ COD) methyl orange azo dye solution at 125 mA cm⁻² current density, where the level of COD removal is close to 61% (**•**) in the case of BDD anode, 70% (•) when BDD/TiO₂ composite is applied and 89% (•) for the best assay by means of TiO₂/BDD/*hv* composite. These results indicate that MO azo dye can be easily degraded by hydroxyl radicals formed on the surface TiO₂/BDD/*hv* composite and/or other oxidant species; they can easily attain an almost total oxidation in short electrolysis times [33].



Figure 8. Abatement of COD concentration with electrolysis time for the treatment of 100 mL of 40 mg L⁻¹ MO solution in 0.05M Na₂SO₄ using laboratory stirred tank reactor of 2 cm² electrode area. BDD (■), TiO₂/BDD (♦), TiO₂/BDD/hv (●). Applied current density with a power supply 125 mA cm².

The identification of carboxylic acids during the mineralization of Methyl Orange was carried out by liquid chromatography by exclusion of ions. Figure 9 shows the behavior of oxalic acid (\bullet) and malic acid (\bullet) during the degradation of the methyl orange azo dye, as it is possible to observe, after 90 min oxalic acid reaches its maximum concentration close to 3.25 mM, but at the end of assay it begins to decrease until 0.5 mM at 120 minutes. In the case of malic acid, the concentration accumulation starts in the first 20 min, and the end of the test is closely 0. The formation of carboxylic acids gives us information to verify that the dye is effectively being degraded into smaller molecules, which are not dangerous for the environment [34].



Figure 9. Time-course of the concentration of: (◆) oxalic and (•) malic acids detected during the photoelectrochemical oxidation with TiO₂/BDD/*hv* composite electrode of 100 mL of 40 mg L⁻¹ MO in 0.05 M Na₂SO₄ of pH 3.0.



Figure 10. Proposed route for the electrochemical oxidation of organic compound with simultaneous [•]OH in the TiO₂/BDD/*hv* composite system.

As a consequence, Figure 10 shows the possible mechanism for the photoelectrochemical production of free radicals 'OH with simultaneous $TiO_2/BDD/hv$ composite and the improvement of the oxidation of organic compounds in the coupled system: (1) water discharge to hydroxyl radicals over BDD surface, (2) under *hv* irradiation TiO_2/BDD is activated to produce 'OH, (3) corresponding water discharge and free hydroxyl radicals production, (4) renewed surface activation, steps (5 to 8) correspond to oxidation of organic compound by means of 'OH. Based on results presented in this study, the condition at which the synergetic effect can occur (steps 1 to 3) is under *hv* irradiation, as an accordance equations 1 to 4 [35].

3.6. Identification of aromatic intermediates

Several solutions with 40 mg L⁻¹ MO in 0.05 M Na₂SO₄ at pH 3.0 were degraded using the TiO₂/BDD/*hv* composite electrode at 125 mA cm⁻² for 30-60 min, and the resulting aromatic intermediates were further identified by MS. The results presented in the Table 1 indicate that the ion of the molecule MO (1) is attacked by the free hydroxyl radicals formed by the photoelectrocatalytic system (equations 1-4), to generate the species (4), (5), (6) and (8), where the MO molecule is directly oxidized; these new compounds continue be attacked by more free hydroxyl radicals, generating the oxidized species (3), (2) and (7) once the molecule has been oxidized, the free hydroxyl radicals again attack the molecule causing the rupture of the azo-type bond, and therefore, the fragmentation of the molecule in two parts generating the species (9), (10) and (11), afterwards these are still oxidized, causing the aromatic ring to break and generate the species (12), which subsequently breaks into molecules of very low m/z value that could not be detected [34].



| No. | Compound | Molecular structure | [M-H] ⁻ /Error |
|-----|---|-------------------------|---------------------------|
| | | | (ppm) |
| | | N====N | 304.076135 / |
| (1) | 4-((4 dimethylamino)phenyl)diazinyl)benzenesulfo | $H_3C-N_{CH_3}$ $O = 0$ | 1.2003 |
| | nate | | |

- (2) 1-(4-(dimethylamino)phenyl)-2-(4sulfophenyl)diazene 1,2.dioxide
- (3) 4-(2-(4-(dimethylamino)phenyl)-1,2dioxidodiazen-1-y1)benzenesulfonate
- (4) 4-(2-(4-nitrophenyl)-1-oxidodiazen-1y1)benzenesulfonate
- (5) 4-(2-(4-(dimethylamino)phenyl)-1oxidodiazen-1-y1)benzenesulfonate
- (6) 4-((4-nitrophenyl)diazenyl)benzenesulfonate

(7) 4-(1-(4-hydroxyphenyl)-1-oxidodiazen-2-

y1)benzenesulfonate



'n



4. CONCLUSIONS

In the present research, it has been demonstrated that it is possible to prepare uniform and compact TiO_2/BDD composites by the electrophoresis method. The electrochemical characterization of the composite shows real evidence of the formation of free hydroxyl radicals over the composite, which was corroborated with the RNO radical spin trap, observing the following behavior BDD<TiO_2/BDD<TiO_2/BDD/*hv*, what showed that the illumination of composite increases the production of free radicals. When the composition was applied in the degradation of the methyl orange azo dye, it was also observed that the electrode under *hv* lighting is the one that best degrades molecule, reducing 70% of the COD and 100% of color. Under the best conditions, it was possible to establish the carboxylic acids that evolve during the oxidative process and the hydroxylated derivatives

that are formed during the oxidation process, which shows that it is powerful when the coupled process is used.

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