Importance of Electrode Tailoring in the Coupling of Electrolysis with Renewable Energy


In this work, it has been evaluated how the performance of an electrolyzer, used to treat a clopyralid waste and directly powered without regulation by a battery, is influenced by the electrodes resistance. Electrolyzers were equipped with electrodes consisting of the same boron-doped diamond (BDD) coating deposited on different substrate (Si, Ta and Nb). The results expose great differences despite using the same coating. Faster removal rates were attained with Ta- and Nb-BDD electrodes. The amount of energy required to attain the same removal efficiency showed great differences. Up to 1.95 mg/Wh of pesticide were removed when using Si, compared to 2.14 mg/Wh removed with Ta. Furthermore, the quantity and strength of the generated oxidants were also quite different. 86.78 mmol of oxidants were needed to remove a gram of pesticide with Ta-BDD and 30.57 mmol with Si-BDD. Therefore, the electrode resistance is an important aspect that must be considered in order to get a suitable design of energy storage systems that allow the green photovoltaic powering of electrochemical technologies using conventional batteries as a booster to ensure a continuous operation.

1. Introduction

The United Nations Framework Convention on Climate Change has exposed the importance of the awareness about the climate change and has highlighted the efforts that should be done in order to stop it. In the Conference of the Parties celebrated at the end of 2019, 121 countries and 786 companies have committed to reach net zero emission in 2050 and to fight for the fulfilment of the Sustainable Development Goals focused on promoting prosperity while taking care of the environment. In this context, besides stopping the global warming, remediating environmental disasters caused by the improper and uncontrolled production and use of many hazardous chemicals must be a key issue to solve. Nowadays, high concentrations of persistent pollutants can be found in water bodies and soils. The high chemical stability and low biodegradability of many of these pollutants makes even possible their presence in the supply water, where they are known to affect the immune system of human beings.

Consequently, their removal from the natural environment is essential to reduce and get rid of their negative impact.

Electrochemical advanced oxidation processes (EAOPs) have been widely studied for the treatment of wastewater and polluted soils. Among them, the conductive diamond electro-chemical oxidation (CDEO) has been widely used for the oxidation of hazardous organic compounds. Diamond anodes are classified as "non-active" electrodes. This means that they exhibit a weak interaction with the hydroxyl radical (-OH) generated on their surface which, in turn, are responsible of the organic matter oxidation. Thus, the weaker is the electrode-(-OH) interaction, the higher is the oxidation efficiency. Because of the outstanding results, many researchers have focused their studies on the degradation of a huge variety of persistent organic pollutants (POPs) using boron-doped-diamond (BDD) anodes. In addition, BDD electrodes show a high chemical and electrochemical stability and a high electro-oxidation efficiency working in a wide range of current densities and initial concentrations. Furthermore, this EAOP does not need the addition of reactants, using the electric energy as unique reagent.

Looking for a further environmentally friendly treatment, the use of renewable energy to power these electrochemical technologies may become a key alternative. By contrast to the continuous working mode of treatment plants, the renewable power sources have an intermittent production, making necessary the development of novel powering strategies to achieve more sustainable electrochemical treatments. One of them consists of the use of energy storage systems. Thus, during the period in which the production of renewable energy is low, the energy storage system is expected to power the electrochemical treatment. One possibility to meet this goal is to directly couple the charged storage system with the electrolyzer, without fixing a cell potential with the assistance of...
electronics but simply letting the storage system to provide electricity until attaining its discharge down to a reasonable level. In this case, the applied current density to the electrochemical treatment will mainly depend on the resistance of the electrochemical cell which, in turn, is mainly influenced by the electrode material resistance. Thus, the lower is the cell resistance, the lower is the energy consumption of the treatment. In order to reduce the energy demand of these electrochemical technologies, novel electrode materials should be researched, aiming to reduce the ohmic losses while maintaining the oxidation efficiency.

The development of more conductive supports for the coating of BDD electrodes could be a key alternative to reduce operative costs. A previous work has reported the use of different support for the coating of BDD electrodes, evaluating their influence on the generation of oxidant species.[12] It was found that the substrate of BDD electrodes has low influence on the production of oxidants when the characteristics of the diamond coating are similar (even that, some differences were found). Nevertheless, the oxidation efficiency and the energy consumption of these systems were not assessed, as in that case it was considered not relevant, because the energy was supplied by a conventional power supply and the system was operated in galvanostatic mode. Nonetheless, important differences were found in the cell potential needed to reach the desired current densities, being these potentials lower when using metallic supports. These important differences in the cell resistance due to the diverse nature of the electrode substrates bring up the idea that, perhaps, this input can influence on a system in which the power comes from an energy storage device such as a conventional battery or a redox flow battery, because of the different use of the energy stored. These systems are typically used to accumulate the surplus of energy coming from wind turbines or photovoltaic (PV) panels and, hence, this has a direct application in the powering of electrolyzers with renewable energy.

In view the previous statements, the main aim of this work is to study the performance of electrolyzers equipped with electrodes consisting of the same coating on different supports (and hence with different electric resistances) when they are powered with the same charged battery. To do this, three BDD anodes with the same diamond coating and different substrate materials were tested (silicon, niobium and tantalum) to electrolyze a synthetic waste polluted with a model pollutant, comparing the degree of treatment achieved in each case and the way in which the battery was discharged. As far as the authors know, this is the first time that this type of study has been made and results can be very relevant for the design of novel treatment systems integrated with renewable energies, as these systems typically need for an energy storage stage which helps to fit the production and demand of energy.

2. Results and Discussion

As aforementioned, the main aim of this work is to evaluate the different behavior of electrolyzers equipped with the same diamond coating on different substrates when they are powered with the same fully charged battery.

In order to evaluate the performance of these electrodes, a first electrochemical characterization was developed using 1.0 g L⁻¹ of Na₂SO₄ as supporting electrolyte. Figure 1 shows the linear sweep voltammograms and the Nyquist plots of each BDD electrode. In addition, Table 1 collects the theoretical electric conductivity of the substrate materials and the ohmic resistance of the BDD electrolyzers.

Table 1. Theoretical electric conductivity of substrate materials and ohmic resistance of the BDD electrolyzers.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrical conductivity of the substrate material (S m⁻¹)</th>
<th>Ohmic resistance of the BDD electrolyzers (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>6.93 · 10⁶</td>
<td>0.78</td>
</tr>
<tr>
<td>Ta</td>
<td>7.61 · 10⁶</td>
<td>1.03</td>
</tr>
<tr>
<td>Si</td>
<td>4.35 · 10⁻⁸</td>
<td>4.27</td>
</tr>
</tbody>
</table>

Figure 1. Linear sweep voltammograms (a) and Nyquist plots (b) for different BDD electrooxidation cells. Nb-BDD (■), Ta-BDD (●) and Si-BDD (▲). [Na₂SO₄] = 1 g L⁻¹.
resistance of the different electrolysers. As seen in the voltammograms, there is a lower slope for the BDD electrode supported on Si, as compared to Nb- and Ta-BDD electrodes. Regarding oxygen evolution potentials (OEVs), the higher overpotential exposed by Si substrate could turn into a higher oxidation efficiency.\[4c,13\] Nb and Ta substrates show almost the same tendency at lower potentials. Nevertheless, the electrode supported on niobium exposes a higher slope at potential over 6 V, despite of the lower electric conductivity of this material as compared with Ta. Those results could be explained in terms of the coating film and its contact with the supporting material. The three electrodes were doped with the same concentration of boron (2500 ppm) which provides the electrode of a semi-metallic conductivity.\[14\] Despite the same amount of boron was deposited in the three cases, the coating films reached different thicknesses which can affect the conductivity of the electrodes. Results noticed that thinner coating films led to higher resistance. According to LSV data, over 38.2 mA cm\(^{-2}\), Ta-BDD electrode could attain higher removal efficiencies than Nb due to the higher overpotential reached by this electrode at higher current densities.

As the coating is the same, the slope of LSV analyses curves should be directly related to the ohmic resistance that the support materials offer. Thus, the higher is the slope, the lower is the ohmic resistance of the BDD electrode, as Figure 1b shows. The Si-BDD electrolyzer shows an ohmic resistance four times higher than that of Nb- and Ta-BDD electrolyzers. Considering that the lower is the ohmic resistance, the lower is the energy consumption, the energy cost of an electrooxidation treatment using Si-BDD electrodes would be much higher, taking into account the same removal efficiency for the three BDD electrodes, especially if there is not a significant influence on the oxidation progress attained.\[12\]

In view of the electrochemical characterization results exposed previously, the electrochemical oxidation treatment working under the same operational conditions (galvanostatic mode) and using Si-BDD electrodes should reach the best remediation efficiency. Nevertheless, keeping in mind the different ohmic resistances showed by each electrode, the powering of the electrochemical treatment under a constant power supply by an energy storage system, should supply different current and potential values to each electrode, which can turn into different removal efficiencies than expected under a traditional powering mode. Consequently, it is important to confirm this point and hence, to evaluate the electro-oxidation performance of each electrode in order to determine the best substrate for BDD electrodes in terms of pollutant removal and energy consumption.

Thus, with this objective, the electro-oxidation of 100 ppm of clopyralid using BDD electrodes supported on three different conductive materials and powered by a fully-charged lead-acid battery was carried out. The potential and current applied to the electrochemical treatment varied depending on the cell resistance and charge accumulated in the battery (fully charged in all cases). Figure 2 shows the potential recorded, the current applied to the cell and the total charge passed throughout the electrolyzer over 12 h of electro-oxidation treatment carried out with each cell. Furthermore, Table 2 shows a data review which collects the average potential and current and the total electric charge and energy applied to each electrolytic treatment.

As expected, huge differences were found in terms of potential and current supply when different electrolysers are powered by a lead-acid battery. Thus, the applied electric charge and the energy consumption of a particular electro-oxidation treatment highly depend on the electrolyzer resistances. As Figure 2a shows, the electrolyzers worked under a different range of potentials. At 120 minutes, the potential applied to the Si-BDD electrolyzer was almost the double than the potential supplied to Nb- and Ta-BDD electrodes. Those results are in line with the previous electrochemical characterization of each electrolyzer. As expected, the higher the ohmic

![Figure 2](image-url)
resistance of the electrodes, the lower the current applied to the electro-oxidation reactor. Regardless of the applied current, in the first few minutes, the current increased until reaching a maximum value around 14.34, 13.12 and 2.06 A for Nb, Ta and Si electrode substrates, respectively. After that, the current dropped slowly until the battery was discharged. Furthermore, it can be observed that the lower the applied current, the higher the discharge time. Thus, the electrolytic treatment using Si-BDD electrodes can work for a longer time until reaching the full discharge of the battery. Conversely, Nb- and Ta-BDD electrodes showed a closer tendency in terms of current values and treatment time, which could be explained by their similar ohmic resistances. If LSV analyses and discharge current values are compared for Nb and Ta electrodes, both results follow the same tendency. The higher slope exposed by Nb electrodes at higher potential values turn into higher currents as shown Figure 2b at the first time of the treatment. Conversely, its slightly lower slope at lower potential lead to lower current values after 1 h of treatment. In contrast to Si-BDD electrode, the higher current values supplied to those electrodes lead to a faster battery discharge. Regarding the current charge passed throughout the electrolyzers, again higher differences were obtained with the cell equipped with Si-BDD, which shows a more progressive passing of charge, reaching a lower value (13.1 Ah). Those results expose different battery states of charge (SOC) after twelve treatment hours. Once the electro-oxidation treatment performed with Si-BDD electrolyzer finished, the battery still had a 23% of its theoretical capacity (17 Ah), energy that could be used to attain a higher mineralization. By contrast, only a 6.53 and 10.23% of capacity remained in the battery after the electro-oxidation treatment developed with Nb and Ta electrolyzers, respectively.

Regarding the energy consumption, as expected, the huge resistances showed by the Si-BDD electrode lead to a higher power demand. Consequently, the use of a Si-BDD electrolyzer could be related with lower energy efficiency. Nevertheless, it is important to evaluate the behavior of these electrodes in terms of removal of organic compound to determine which is the best substrate material for BDD electrodes.

Figure 3 shows the changes in the clopyralid concentration over 12 h of electro-oxidation treatment for each electrolytic test (carried out with cells equipped with BDD electrodes supported on different substrate materials) as a function of reaction time and electric charge passed. The three tests attained almost the same removal of pesticide at the end of the treatment (12 h), achieving at least an 85% of removal in all cases. Nevertheless, a slightly better removal of clopyralid was attained with the Ta electrolyzer, 88.6%. Besides, it is important to note that the degradation of pesticide exposes a different tendency depending on the substrate material. Nb-BDD electrodes showed a faster removal at the first treatment hours. However, when almost a 50% of pollutant was removed, a slowly removal rate was observed. At a treatment time of 90 min, the higher removal of pesticide was attained by the BDD electrodes supported on Nb (51.8%). Conversely, 3.5 h later, the Ta-BDD electrolyzer had removed a 72.3% of pollutant in contrast to the 66.2% removed with Nb-BDD electrodes. As expected, the higher is the applied current density, the higher is the rate of pollutant degradation. In this case, the lower removal rate observed by the Si-BDD electrode can be directly related to the lower current densities applied to this electro-oxidation reactor during the first hours of electrolytic treatment. The higher removal achieved by the Ta-BDD electrolyzer regarding the Nb-BDD electrolyzer could be related to the higher current applied to this electrode after 80 min of treatment. On the other hand, if the removal of clopyralid is studied in terms of applied electric charge (Figure 3b), the results release information about the efficiency of the electrolysis treatment. In this case, the higher removal of pesticide per applied electric charge was attained for the Ta-BDD electrolyzer, followed by the BDD electrodes supported on Nb and Si substrates.

In order to determine the best available support for BDD electrodes, the ratio mg of removed pollutant/Wh was calcu-
lated. Si-BDD electrolyzer got the lowest removal of pesticide per energy unit, 1.95 mg removed clopyralid/Wh, while Ta-BDD electrodes showed the highest removal ratio, 2.14 mg removed clopyralid/Wh. Furthermore, it is important to evaluate the amount of total organic carbon that remained in the water effluent after 12 h of electro-oxidation treatment. In contrast to the pesticide removal results, the higher removal of TOC was achieved by the Nb-BDD electrolyzer, reaching a removal of 78.9% within the experimental time. As noted above, the electro-oxidation carried out using Si-BDD electrodes showed the lower removal of total organic carbon (67.3%).

Furthermore, the mineralization attained with Ta-BDD electrodes was slightly lower than that achieved by the electrolyzer equipped with Nb-BDD electrodes, 77.2%. The differences observed between the removal of pesticide and organic carbon are directly related to the generation of intermediate species as a result of secondary reactions between oxidants species and the pollutant in the bulk solution. Figure 4 shows the total chromatographic areas of intermediate species generated along the electro-oxidation treatment for the three studied electrolyzers.

As expected, the higher production of intermediate species corresponds to the electrolyzer that showed a lower removal of TOC, Si-BDD electrolyzer. Thereby, the total chromatographic areas of the intermediate species generated along the electro-oxidation treatment were 704.4, 1175.8 and 1940.1 a.u. (3-chloropilinic and chloropicolinic acids) for Nb-, Ta- and Si-BDD electrodes, respectively. Consequently, those results help to explain the differences observed between the removal of clopyralid and TOC for the Nb and Ta electrolyzers.

In order to clarify the difference between each substrate, the generation of oxidant species was measured throughout the electrooxidation treatments. Figure 5 shows the generation of total oxidants by each electrolyzer. Contrary to expectation according to changes observed in the organic pollutant concentration, huge differences were observed between the oxidant generation, despite attaining almost the same removal regardless of the used electrode substrate. Results are in line with previous studies that evaluated the generation of different oxidants using chloride and sulphate solutions as supporting electrolyte working at galvanostatic mode.[12] The higher oxidant generation was attained by the Ta-BDD electrode despite of the lower electric charge applied within a long treatment time regarding Nb electrolyzer. The high potential applied to the CDEO coupled with BDD-Ta after 1 h of treatment regarding the BDD-Nb could explain the higher generation of oxidants in those electrodes. Besides, those results are in line with the exposed by the LSV analyses for those electrodes. At higher current densities, Ta-BDD electrodes noticed huge overpotential values. It is worth to mention that a decomposition of oxidants could be carried out at very large cells potential values induced by the interactions of oxidants formed in the system, in particular by the action of hydroxyl radicals, which may promote the decomposition of stable...
oxidants to unstable radicals. These interactions have a low probability of being generated on Nb- and Ta-BDD electrodes surface because after one treatment hour the cell potential dropped below 6 V. Nevertheless, Si-BDD electrode worked along the 12 treatment hours over 8 V which could explain its low oxidant generation.

With the aim of quantifying the performance of each system in terms of total oxidant generated, the ratio energy consumption per unit of generated oxidant was calculated. Thus, Si-BDD electrode got the higher ratio, 14.34 Wh/mmol oxidant generated, that is, the highest energy cost to generate the same amount of oxidant. On the contrary, Ta-BDD electrolyzer showed the lowest energy cost per unit of generated oxidant, 3.36 Wh/mmol oxidant. Despite the higher generation of oxidants and the lower energy consumption exposed by Ta-BDD electrode, 86.78 mmol of oxidants must be generated in order to remove a gram of pesticide. Conversely, 30.57 mmol should be generated with the Si-BDD electrode to attain the same removal. This could be explained in terms of the oxidant’s strengths and the previously commented decomposition to radicals, which act immediately over the organics once formed. Some oxidants can be powerful for the oxidation of a specific pollutant, attaining higher and faster removal at lower concentrations. Among them, it is worth to mention sulphate radicals, which are one of the strongest oxidant species that can arise in the oxidation of sulphate solutions at an oxidation potential of 2.8 V, closer to the oxidation potential of hydroxyl radicals (2.7 V). These sulphate radicals can generate ·OH radicals at basic pH values. Conversely, persulfate ions could generate more sulphate radicals at acid pH values. Thus, the non-active persulfate ion can become in a strong oxidant agent. Besides, it is important to note that many other secondary reactions can take place in the bulk solution rising other oxidant species. ·OH radicals can be combined arising the production of H₂O₂. At same time, O₂ can be generated in the bulk solution due to secondary reaction between oxygen and hydroxyl radicals.

Regarding the relation of the electrochemical characterization of the different tested substrates and the oxidant species generation reached by each electrode, the higher oxygen evolution potential showed by the BDD electrode supported on Si substrate should be turned into a huge hydroxyl radical generation beside Nb and Ta substrates. Contrary to expectation, this electrolyzer showed the lower concentration of oxidants.

Keeping this in mind, pH and conductivity analyses were carried out over the treatment tests (Figure 6). Nb- and Ta-BDD electrodes show an increase of pH values the first hours of treatment, attaining almost constant and neutral pHs at the end of the study. Conversely, the use of Si-BDD electrodes showed low pH values along the complete treatment, leaving an effluent with acid properties. These differences could be related to the intermediate and oxidant species generation and their nature. In view of the previous arguments, those results could explain the higher removal attained by the Si-BDD electrolyzer in terms of oxidant’s strengths despite the lower number of oxidant species measured. Concerning conductivity, significant differences were not observed throughout the treatment regardless of the used BDD electrode.

Once all results have been exposed, it is worth to mention that metal substrates with higher conductivity (Ta and Nb) and lower ohmic resistance were supplied by higher current density that metal substrates with higher conductivity (Ta and Nb) and lower ohmic resistance were supplied by higher current density under a powering with a fully-charging battery. As a consequence, the huge current densities applied to both electrolysers turned into faster removal rates and a higher oxidant generation, attaining huge removal efficiencies with a lower energy consumption. Furthermore, in terms of mineralization, the electrode supported on Nb substrate exposed the higher TOC removal and a lower generation of intermediate species. Thus, the huge amount of oxidant species generated during the electro-oxidation treatment performed with this electrode should be directly related to oxidized organic matter to CO₂ and the remediation efficiency of the treatment. In view of the previous results, it can be claimed that Nb and Ta substrates exposed better remediation results than the electrooxidation developed using traditional Si-BDD electrodes. Furthermore,
these results expose an important and relevant breakthrough in terms of novel substrate materials for BDD electrodes and it helps to understand better how energy has to be dosed from renewable energy devices, when the powering of the treatment technology is carried out directly from an energy storage device.

3. Conclusions

From this work, the following conclusion can be drawn. BDD electrodes supported on Silicon substrate expose the highest ohmic resistance and consequently, the higher energy consumption for an electro-oxidation treatment powered by an energy storage system as power supply. Results suggested that BDD electrodes supported on Ta and Nb substrates showed a faster removal rate regarding the Si-BDD electrolyzer. After 12 h of treatment, the Ta-BDD electrolyzer attained the highest removal (88.56%). Nevertheless, the electrolyzer fitted with Nb-BDD electrodes exposed the highest TOC mineralization and the lowest generation of intermediate species. Regarding the use of energy, around 1.98 mg of pesticide/Wh were removed in the electrolyzers equipped with anodes supported on Nb and Si, while 2.14 mg were removed using Ta-BDD electrodes. Nevertheless, a lower energy consumption must be done in order to generate a mmol of oxidant using Si-BDD electrodes (14.34 Wh mmol⁻¹). In terms of strength of oxidants, almost 30 mmol of oxidant must be generated in order to remove a gram of pesticide using silicon as support of BDD electrodes. Conversely, a 35% of oxidant more must be generated by the Ta-BDD electrodes to remove the same amount of pesticide.

Experimental Section

Chemicals

Clopyralid supplied by Zymit Quimica (Spain) was selected as organochlorinated pesticide model. A synthetic effluent was prepared with 100 mg dm⁻³ of pesticide and 3.0 g L⁻¹ of Na₂SO₄, as supporting electrolyte (Panreac). Milli-Q water (Resistivity: 18.2 MΩ cm at 25 °C) was used to prepare the synthetic wastewater effluent.

Experimental Setup

The electro-oxidation of 4.0 L of a synthetic effluent polluted with clopyralid (an organochlorinated pesticide) was studied using a bench scale experimentation setup working in batch mode. BDD electrodes (78 cm²) were used as anodic and cathodic electrodes. The degradation was carried out in a commercial conductive diamond electrochemical oxidation (CDEO) reactor, DiaCell® 101, provided by Adamant Technologies (Switzerland) using BDD electrodes (WaterDiam, France) consisting on the same boron doped diamond coating film supported on different materials: Niobium (Nb), Tantalum (Ta) and Silicon (Si). The three electrodes were doped with 2500 ppm of boron leading to a coating film of 7.7, 7.3 and 5.9 μm of thickness for Nb, Ta and Si -BDD electrodes, respectively. The electrooxidation was powered using a lead-acid battery (DSK, India) of 12 V and 17 Ah of capacity.

Characterization Procedures and Analytical Techniques

Each electrolyzer was characterized using lineal sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements using an Autolab potentiostat/galvanostat (PGSTAT-302N) coupled with a FRA32M module. Clopyralid concentration, oxidants production, pH and conductivity were measured during the electrolysis. The concentration of clopyralid was measured by high performance liquid chromatography, HPLC (Agilent 1260 Infinity) as reported elsewhere.[16] Oxidants production were quantified by an iodometric titration with thiosulfate as reported elsewhere.[17] The pH and conductivity were measured using CRISON pH25+ and CRISON CM35+ instruments.

Acknowledgements

Financial support from the Spanish Agencia Estatal de Investigación through project CTM2016-76197-R (AEI/FEDER, UE) is gratefully acknowledged. M. Millán thanks the UCLM for the predoctoral contract within the framework of the Plan Propio I+ D.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: boron-doped diamond electrodes · electrooxidation · environmental chemistry · energy conversion · substrate

[9] a) C. A. Martinez-Huitle, M. A. Rodrigo, O. Scialdone, Electrochemical Water and Wastewater Treatment, Elsevier Science, 2018; b) W. T. Mook,


