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Evaluation of the toxicity reduction of an ionic liquid solution electrochemically treated using BDD films with different sp^3/sp^2 ratios

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ABSTRACT

It has previously been established that the sp^3/sp^2 ratio influences the type of degradation (direct or indirect) as well as the production of oxidants at boron-doped diamond (BDD) films. However, there are no published studies on the effects achieved (in terms of degradation performance) when an ionic liquid is treated nor any evaluations of effluent toxicity after treatment. For this reason, this study investigated the influence of the sp^3/sp^2 ratio of BDD anodes on the degradation of the ionic liquid 1-butyl-3-methylimidazolium chloride. The presence of a large fraction of C-sp^3 favored more efficient mineralization (significant at high current densities); however, phytotoxic analyses revealed a more toxic final effluent. Depending on the experimental conditions and the sp^3/sp^2 ratio, smaller amounts of undesirable chlorate and perchlorate anions as well as different oxidation by-products were detected, consequently affecting the toxicity level of the effluent. The results are discussed and compared with the existing literature.

1. Introduction

Ionic liquids (IL) have attracted attention for industrial applications due to their unusual intrinsic properties [1]. Some examples of their applications include electrodeposition, electrosynthesis, capacitors, lubricants, catalysis, plasticizers, solvents, batteries, fuel cells, solvents for preparing nanomaterials, extraction, and gas absorption, among others [2]. One family of ILs with wide application is the alkylimidazolium-based group. In particular, 1-butyl-3-methylimidazolium chloride (BMImCl) is utilized as a thermal fluid for solar thermal collectors [3], in the preparation of high performance fibers [4], for solvent extraction [5,6], as a reaction medium [7,8], as a co-catalyst for the degradation of lignin [9,10], as the supporting electrolyte in batteries and supercapacitors [11,12], as a hydrogen storage material [13,14], for azeotropic separations [15,16], as a support for electrocatalysts [17], and for electrodeposition [18], among other applications. However, care in handling and adequate disposal are essential as recent studies have demonstrated the high toxicity of IL wastes to aquatic ecosystems [19–21] and their limited biodegradation potential [22,23].

In this context, electrochemical technologies have emerged as a possible approach for treatment of IL pollution [24]. In particular, anodic oxidation with boron-doped diamond (BDD) electrodes has been shown to be efficient in treating various organic pollutants [24], including ionic liquids [25–29]. However, it has been reported that the sp^3/sp^2 ratio (ratio of diamond to graphitic carbon forms) on the BDD surface strongly influences the degradation processes. A high graphitic content favors direct oxidation of the pollutant on the surface, leading to the formation of many intermediates due to stronger adsorption on these types of sites, while a high diamond content promotes complete oxidation to CO_2 by the electro-generation of $OH^{\cdot}$ in the boundary region of the electrode [30]. Over recent years, the influence of this parameter has been demonstrated in studies of the electrochemical treatment of a variety of pollutants with BDD [31–34]. Moreover, the sp^3/sp^2 ratio also influences the generation of bulk oxidants [35,36]. There have been no studies of the effect of this parameter on the electrochemical treatment of BMImCl, which could help in understanding the efficacy of the process as well as the toxicity level of the effluent. Therefore, an evaluation of toxicity reduction was conducted through growth studies on *Lactuca Sativa* (lettuce) to determine the depollution level of a BMImCl solution electrochemically treated using BDD anodes with different sp^3/sp^2 ratios. The mechanism of the

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degradation of BMImCl was also investigated by monitoring its concentration and TOC abatement, as well as the evolution of oxidants and oxychloro-species. The intermediates remaining after the treatment process were also studied.

2. Materials and methods

The ionic liquid 1-butyl-3-methylimidazolium chloride, $KClO_3$ and $NaClO_4$ were purchased from Sigma-Aldrich. The chemicals Na_2SO_4, NaOH, H_2SO_4, H_2SO_4, $Na_2S_2O_3$, KI, KH_2PO_4, H_3PO_4, $CHCl_3$ and starch were acquired from Vetec. BDD anodes were provided by Adamant Technologies (Neuchatel, Switzerland). Two different anodes with different sp^3/sp^2 ratios were tested (BDD_1 = 175 and BDD_2 = 329). Both possess a similar diamond coating (2–3 μm) deposited with a similar boron content, approx. 500 ppm.

Electrochemical characterization of the BDD anodes was carried out by linear sweep voltammetry (LSV). For this, a three-electrode electrochemical cell was used, with the BDD anode as the working electrode (active area: 0.4 cm^2), a platinum wire as the counter-electrode and Ag/AgCl (3 mol L^{-1} KCl) as the reference electrode. The studies were carried out using 0.1 mol L^{-1} Na_2SO_4 as supporting electrolyte. The BMImCl degradation studies were carried out in a batch reactor. A volume of 0.3 L of a 0.25 g L^{-1} of BMImCl, in 0.1 mol L^{-1} Na_2SO_4 solution as supporting electrolyte, was electrolyzed by applying 25, 50 and 100 mA cm^{-2} for 5 h. The concentration of BMImCl (monitored by liquid chromatography, more details about the method elsewhere [28]), the chemical oxygen demand (COD), the total organic carbon (TOC, TOC-L Analyzer, Shimadzu), and chlorate and perchlorate concentrations [29] were monitored during the experiments. The degradation by-products were identified by gas chromatography coupled to a mass spectrometer (GC–MS 2010, Shimadzu – experimental conditions described elsewhere [28]). Bioassays of acute toxicity with lettuce seeds *Lactuca sativa* were performed by estimation of the germination index (GI) (Eq. (1)), where RLS is the radicle length of the sample, PGSS is the percentage of germinated seed in the sample, RLC is the radicle length of the control and PGSC is the percentage of germinated seed in the control. The methodology is described by Sobrero and Ronco [37]. Assays were performed in duplicate for each current density studied with the effluent before and after treatment.

$$GI = \frac{RLS \cdot PGSS \cdot 100}{RLC \cdot PGSC} \quad (1)$$

3. Results and discussion

Fig. 1 displays the linear sweep voltammograms (LSV) of the BDD electrodes with different sp^3/sp^2 ratios. As can be observed in the blank voltammograms, BDD_1 has a lower onset potential for the oxygen evolution reaction (OER). This is attributed to the presence of a higher proportion of sp^2-C in the BDD_1 electrode compared to BDD_2 [30]. sp^2-C is known to possess a higher adsorption strength and hydrophilicity, favoring the formation of strong OH_{ads} species, and a lower overpotential for OER [30,33]. In the presence of BMImCl, a decay in the current can be observed for the electrode with highest sp^2-C content (BDD_1). This behavior can be explained by a stronger interaction of BMImCl with the BDD_1 surface, blocking some of the active sites. Furthermore, a peak is detected for BDD_1 in the low potential region. This can be attributed to the direct oxidation of BMImCl on the BDD surface. Stronger adsorption can favor direct oxidation pathways, as reported for other organics [32,34,38].

Fig. 2 shows the BMImCl, COD and TOC values during the BMImCl electrolysis for both BDD anodes at different current densities. At 25 mA cm^{-2}, no significant differences between BDD_1 and BDD_2 were observed. However, BDD_2 outperforms BDD_1 at 50 and 100 mA cm^{-2}. The behavior at 25 mA cm^{-2} is rather unexpected since higher sp^3-loaded BDD is more effective for pollutant degradation due to more efficient generation of $OH^{\cdot}$ radicals compared with the indirect pathways of sp^2-heavy BDD electrodes [39]. One possible reason could be direct oxidation of BMImCl on BDD_1, shown in Fig. 1b, whose contribution at a low current density could be more significant. Furthermore, Barreto et al. [36], using the same pair of electrodes, showed that a larger proportion of sp^2 favors the formation of persulfate, which plays a key role in the mediated oxidation pathway. The combination of these two processes could explain the similar performance of the two BDDs. At higher current densities, the more intensive generation of $OH^{\cdot}$ radicals, favored on the non-active surface of the sp^3 diamond surface [33], explains the better performance of BDD_2. Indeed, the differences between the electrodes intensify as the current density rises. In the case of the COD, BDD_1 is less effective in removing the COD regardless of the current density. A decrease in the COD implies the effective oxidation of the organic compounds (BMImCl and intermediates), which is more efficient in sp^3-C enriched BDD due to the larger proportion of $OH^{\cdot}$ radicals [30]. This species is especially effective in completely oxidizing the organic compounds. The “final TOC remaining” ratio confirms the better capacity of the BDD with a higher sp^3 ratio for mineralization with an enhanced overall current efficiency (see inset in Fig. 2c). Moreover, the difference between the electrodes was intensified at higher current densities, where more parasitic reactions are expected to

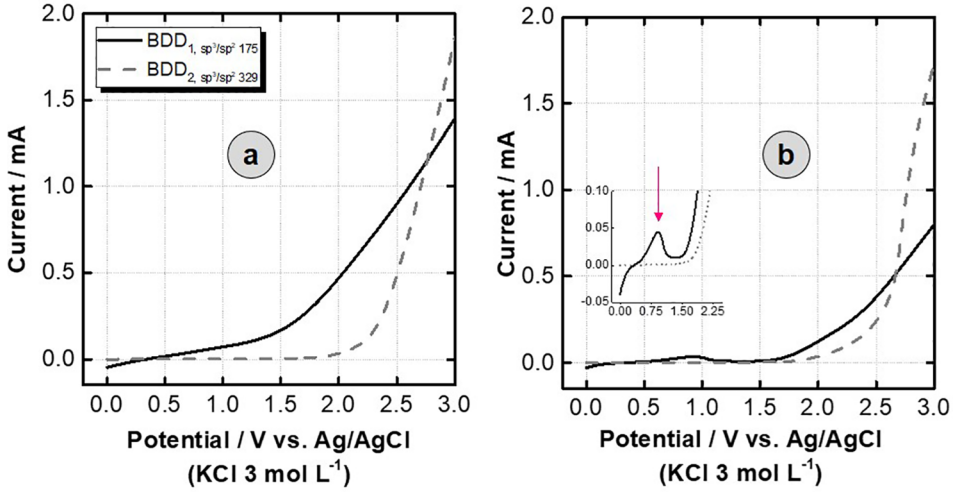

Fig. 1. LSV profiles of the different BDDs in (a) 0.1 mol L^{-1} Na_2SO_4, and (b) in 0.25 g L^{-1} BMImCl + 0.1 mol L^{-1} Na_2SO_4 (scan rate: 0.05 V s^{-1}).

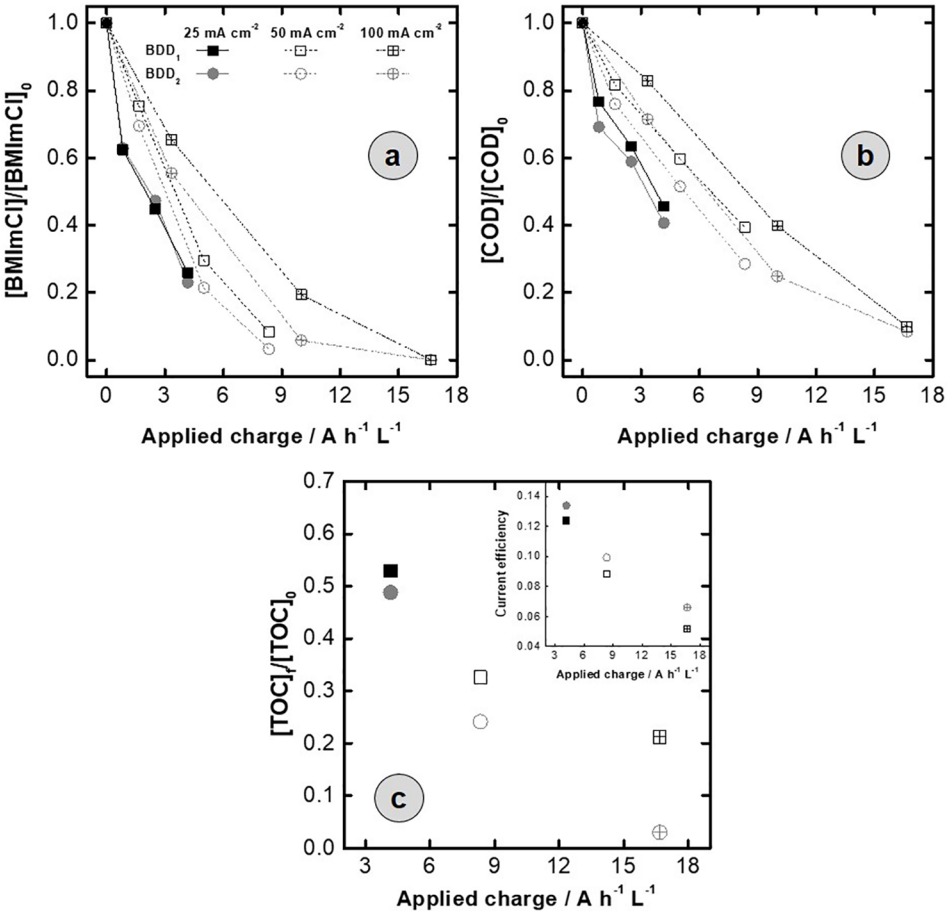

Fig. 2. Evolution of the (a) BMImCl and (b) COD decay rate for the different electrodes at different current densities, (c) remaining TOC and overall current efficiency after 5 h of electrolysis (subscript 0 indicates initial value, subscript f indicates final value).

occur on the sp^2-C enriched BDD.

Two secondary reactions on the BDD are the formation of toxic chlorates and perchlorates in the presence of chloride. Chloride can oxidatively aid the formation of ClO_3^- and ClO_4^- by reaction with the $OH^{\cdot}$ radicals on the surface of the BDD anode [35]. Fig. 3 shows the concentrations of ClO^{3-} and ClO^{4-} at the end of the treatment processes. BDD_1 tends to produce a larger fraction of both oxyanions. The stronger adsorption of the Cl species on the BDD_1 surface favors the consecutive reactions towards the formation of ClO_3^- from ClO^- or ClO_2^-, and the conversion of ClO_3^- to ClO_4^- [35]. In terms of current density, the higher the current, the smaller the concentration of both oxyanions. Chlorate behaves as an intermediate that more rapidly transforms to perchlorate. Unexpectedly, the perchlorate has a similar tendency. One possible explanation lies in the presence of two species: (i) ammonium, and (ii) hydrogen peroxide. Both can ameliorate the formation of more oxidized Cl-oxyanions by the formation of

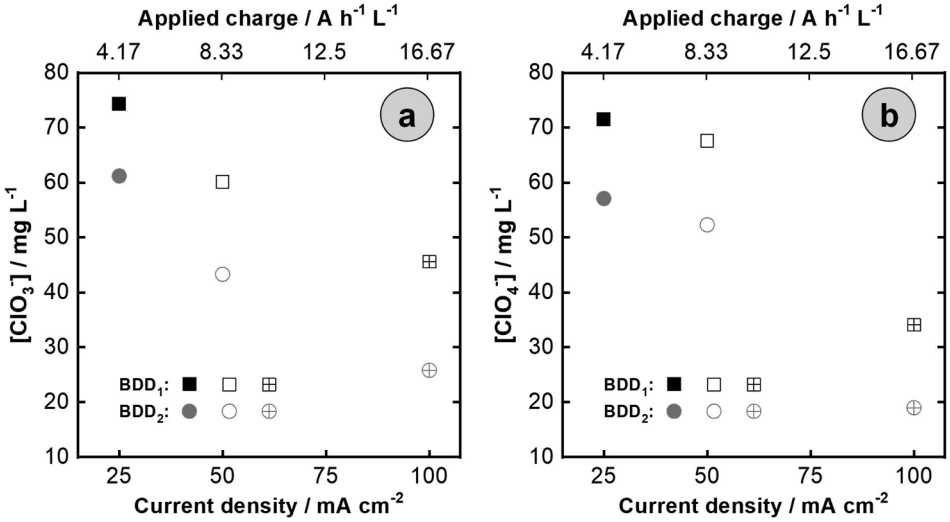

Fig. 3. Final (a) chlorate and (b) perchlorate concentrations after 5 h of BMImCl electrolysis.

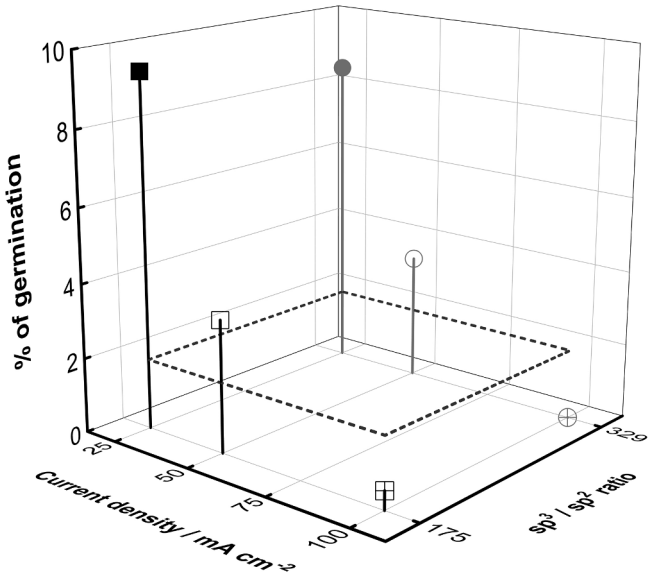

Fig. 4. Germination index with the treated effluents for the different BDD electrodes with various applied charges. The dashed line represents the GI of the initial effluent. [References: control (tap water): PGSC: 62.5%; RLC: 0.85 cm]

chloramines [35], $OH^{\cdot}$ scavenging and ClO^{-}/HClO quenching [40].

Fig. 4 presents the germination index of *Lactuca Sativa*, a parameter used to assess toxicity. Firstly, it is important to note the high toxicity of the initial effluent, which has a GI of approx. 1.2%. Despite the treatment, the effluent still has a high toxicity, although improvements are observed in relative terms. At 25 and 50 mA cm^{-2}, there are increases in the GI which approximate to 6% and 2%, respectively. However, treatment at a high current density produces a more phytotoxic effluent. This can be explained by the higher concentration of oxidants detrimental to *Lactuca Sativa* germination [41]. The slightly higher phytotoxicity observed for the higher sp^3/sp^2 ratio could also be attributed to the more oxidative conditions of the resulting medium after 5 h of electrolysis. An oxidant especially harmful for *Lactuca Sativa* germination is H_2O_2 [41]. Although H_2O_2 was not quantified, previous studies of BMImCl degradation in similar operating conditions have revealed its presence [28]. A higher concentration of H_2O_2 may be expected in BDD_2 from the recombination of $OH^{\cdot}$ radicals, which are produced in greater numbers on C-sp^3 enriched BDD [33].

Finally, the products detected at the end of the electrolysis were analysed. Table SM-1 (in the Supplementary Material) lists the species detected. No difference in the intermediates was observed between BDDs with different sp^3/sp^2 ratios. Thus, in overall terms, the degradation mechanism can be assumed to be similar. Nevertheless, the compounds detected at the end of the treatment processes differ. Operating with a C-sp^3 enriched BDD (BDD_2) leads to more oxidized and open-ring species compared with a C-sp^2 rich anode (BDD_1) at the same current densities, to the point that no compounds are detected at 100 mA cm^{-2} with BDD_2 at the end of the electrolysis.

4. Conclusions

BMImCl degradation is affected by the sp^3/sp^2 ratio of the BDD electrode. A higher sp^3/sp^2 ratio results in a more efficient process. The more intense non-active nature of the more C-sp^3 loaded BDD favors strong oxidative action instead of forming ineffective secondary compounds such as chlorate and perchlorate. Furthermore, operation at high current densities intensifies the enhanced performance of C-sp^3 rich BDD, allowing almost complete mineralization at 100 mA cm^{-2} and a reduced amount of chlorate and perchlorate. Detection of intermediates at the end of the treatment processes confirms this behavior. Nonetheless, care must be taken when analyzing the final toxicity of the treated effluents, since operation at higher current densities produces a final effluent more toxic than the initial sample. Other treatments might be required to further reduce the toxicity of the effluent. Special attention should be paid to the removal of the oxidants and the correction of the ionic strength, as both parameters can detrimentally influence the phytotoxicity. These insights into the nature of the BDD surface should make it possible to design efficient diamond-electrochemical devices for use in specific wastewater situations, whether domestic or industrial, to aid in the removal of polluting chemicals.

CRediT authorship contribution statement

Suzana M.L. de O.Marcionilio: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing - original draft. **Danyelle M. Araújo:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis. **Thaise de V. Nascimento:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis. **Carlos A. Martínez-Huitle:** Conceptualization, Formal analysis, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition. **José J. Linares:** Conceptualization, Formal analysis, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2020.106792.

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