Influence of the boron doping level on the electrochemical oxidation of raw landfill leachates: advanced pre-treatment prior to the biological nitrogen removal

S. Fudala-Ksiazek, M. Sobaszek, A. Luczkiewicz, A. Pieczynska, A. Ofiarska, A. Fiszka Borzyszkowska, M. Sawczak, M. Ficek, R. Bogdanowicz, E.M. Siedlecka

PII: S1385-8947(17)31703-5
DOI: https://doi.org/10.1016/j.cej.2017.09.196
Reference: CEJ 17781

To appear in: *Chemical Engineering Journal*

Received Date: 9 May 2017
Revised Date: 29 September 2017
Accepted Date: 30 September 2017

Please cite this article as: S. Fudala-Ksiazek, M. Sobaszek, A. Luczkiewicz, A. Pieczynska, A. Ofiarska, A. Fiszka Borzyszkowska, M. Sawczak, M. Ficek, R. Bogdanowicz, E.M. Siedlecka, Influence of the boron doping level on the electrochemical oxidation of raw landfill leachates: advanced pre-treatment prior to the biological nitrogen removal, *Chemical Engineering Journal* (2017), doi: https://doi.org/10.1016/j.cej.2017.09.196

Influence of the boron doping level on the electrochemical oxidation of raw landfill leachates: advanced pre-treatment prior to the biological nitrogen removal

S. Fudala-Ksiazek[1*], M. Sobaszek[2], A. Luczkiewicz[1], A. Pieczynska[3], A. Ofiarska[3], A. Fiszka Borzyszkowska[3], M. Sawczak[4], M. Ficek[2], R. Bogdanowicz[2] and E.M. Siedlecka[3*]

[1]Faculty of Civil and Environmental Engineering, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland

[2]Faculty of Electronics, Telecommunications and Informatics, Gdańsk University of Technology, 11/12 G. Narutowicza St., 80-233 Gdańsk, Poland

[3]Faculty of Chemistry, University of Gdansk, Wita Stwosza 63, 80-308 Gdansk, Poland

[4]Centre for Plasma and Laser Engineering, The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences, 14 Fiszera St., 80-231 Gdansk, Poland

*Corresponding authors: sksiazek@pg.gda.pl, ewa.siedlecka@ug.edu.pl

ABSTRACT

The electrochemical oxidative treatment of landfill leachates (LLs) containing high amounts of ammonia nitrogen and organic matter was used as a promising method, prior to biological processes, to achieve the final effluent quality that would be acceptable by current regulations. The deposited boron-doped diamond electrodes (BDDs) with different boron doping concentrations (10000, 5000 and 500 ppm of B) were applied as anodes. The results showed that the boron doping level influences the electrochemical activity and selectivity of electrode surface due to a decrease in the sp^3/sp^2 ratio of the BDD material. Special attention was paid to the oxidation efficiency of organic matter (COD = 4225 mg O_2/L, BOD = 366 mg O_2/L) and ammonia (2270 mg N-NH_4^+/dm^3) in the investigated LLs. Additionally, bisphenol A (BPA; 1539.6 μg/L), a suspected endocrine disruptor, was studied as a potential indicator of the removal efficiency of micropollutants.

It was found that the oxidation of BPA and BOD are correlated with the sp^3/sp^2 ratio, while a decrease in the sp^3/sp^2 ratio of the BDD material was associated with the elevated efficiency of N-NH_4^+ removal. Low pH and the addition of Fe(II) salts suppressed the oxygen evolution reaction, and overcame the mass transport limitation of organics in the case of •OH-mediated oxidation.

Regarding the elimination of ammonium nitrogen, lower effectiveness was generally achieved in comparison to the COD removal. The maximum removal of COD and ammonium nitrogen reached 79 and 41%, respectively. These values were much higher than those reported in the previous study involving a single-cell flow reactor. Thus, anaerobic ammonium oxidation (Anammox) processes seem to be a reasonable option as a final step of LL treatment.

Keywords: boron-doped diamonds, landfill leachates, advanced oxidation process, micropollutant removal, pre-treatment step

1. Introduction

Landfill leachates (LLs) are liquid byproducts generated during solid waste deposition as a result of combined physical, chemical and biological processes as well as precipitation. LLs are characterized by almost 400 parameters [1] as well as the compositional changes that occur under increased hydrophobicity conditions [2]. The aforementioned properties of LLs predestine them to cause major environmental problems in relation to water and soil pollution

[3–6] , including spatial heterogeneity in leachate strength [7] and its impact on biological life [8].

The common features of mature and old LLs are a strong colour, high concentrations of ammonia (N-NH_4^+; 1000 - 5000 mg N-NH_4^+/L) and the elevated contents of recalcitrant compounds, which is reflected, *inter alia*, by the ratio of biological oxygen demand to the chemical oxygen demand (BOD_5/COD) being much lower than 0.4 [9]. LLs were often treated together with municipal wastewater, but tightening the emission limits for wastewater treatment plants (WWTPs) has caused a significant threat to the sustainability of such co-treatment. For this reason, new approaches are widely researched in order to solve the overwhelming problems related to the LL treatment [10,11] .

In recent years, the electrochemical processes have been tested as a promising method, mainly due to their effectiveness in oxidizing the organic compounds and ammonia, although the removal rates were found to vary depending on the type of electrode materials (e.g., TiO_2/RuO_2, Ti/SnO_2, Ti/Pt, Ti/PbO_2 and boron-doped diamond (BDD)) [12–15] and the operating conditions [16–18]. Panizza and Martinez-Huitle [19] who studied the role of the electrode material in the anodic oxidation of LL focusing on $TiRuSnO_2$, Pb_2O and boron-doped diamond (BDD) electrodes, concluded that the BDD electrode is most efficient and cost-effective. Zhao *et al.* [20] investigated the combination of a biochemical treatment and electrochemical oxidation at a BBD electrode. The authors demonstrated the occurrence of a synergistic effect for such combined treatment. In addition, the value of BOD_5/COD increased from 0.016 to 0.51. Fernandes *et al.* [21] reported on the anodic oxidation of biologically pre-treated leachate at a BDD electrode. The influence of the LL dilution and applied current intensity on the electrochemical oxidation process was also described. Based on the available data, it has been presumed that the BDD electrodes could possibly degrade different micropollutants present in LLs. Moreover, due to the high Cl^- concentration in LLs, the effective oxidation of the ammonium ions to gaseous nitrogen and/or nitrates was also presumed [22].

To the best of our knowledge, commercial BDD anodes have been studied extensively in relation to their use for treating LLs. However, data on the influence of the boron doping concentration of the BDD electrodes on the treatment efficiency of raw LLs have not yet been reported. Moreover, in the case of LLs, the electrochemical oxidation via BDD anodes has been usually applied as a post-treatment method [20,22–26]. In this study, electrochemical oxidation at the BDD surface containing different boron doping concentrations was studied as a pre-treatment phase of old LLs prior to the biological step [27–30]. Due to the novelty of this approach, special attention was paid to the electrochemical removal efficiency of organic matter (expressed as COD) as well as to that of easily biodegradable and biodegradable organic matter (expressed as BOD_5 and BOD_{20}, respectively). Since old LLs are highly loaded with ammonia nitrogen, it was suspected that, due to the generation of nitrate, the total nitrogen will not be removed via electrochemical oxidation at a significant level. Thus, the TN/BOD_5 and TN/BOD_{20} ratios in raw and electrochemically pre-treated LLs were tested to check whether efficient denitrification or anaerobic ammonium oxidation (Anammox process) can be used for further nitrogen removal via a biological step [27–31].

Additionally, the presence of bisphenol A (BPA), a suspected endocrine disruptor, was investigated in electrochemically treated LL. In our previous study [31], very high concentrations of BPA (up to 8052 µg/L) were measured in leachates generated by old landfill prisms. In the present study, BPA was used as a potential indicator of micropollutant removal via electrochemical oxidation at the BDD electrode.

2. Experimental

2.1 *Characterization of landfill leachates*

Raw LLs were obtained from the municipal solid waste (MSW) plant ‘Eko Dolina Lezyce’ (northern Poland) from the so-called “old” landfill prisms, which have been in operation since 2003 serving approximately 440,000 inhabitants. The leachates are collected at the bottom of the landfill prisms by a drainage system, and their volume is estimated to be approximately 27000 m^3 per year. The collected leachates are treated by means of reverse osmosis (RO) and then the resulting effluent is discharged into the municipal sewage system, whereas the concentrate is pumped back into the landfill prism.

The collected samples of LL were transported to the laboratory, divided into several homogenized portions and stored at -20 °C until further analysis. The composition of leachate samples is listed in Table 1. As expected, the investigated raw LLs were characterized by a high concentration of ammonium nitrogen ($N\text{-}NH_4^+$), which constituted 90% of the total nitrogen, as well as an elevated COD value (4225 mg O_2/L). The average BOD_5/COD ratio equaled 0.087, indicating that the biodegradability of analyzed LLs was negligible and therefore the application of biological treatment would not be justified in this case. The concentration of total suspended solids (TSS) in the sampled LLs was lower than that observed in typical municipal wastewater, probably due to the leachate filtration during its passage through the landfill prism under gravity [9]. Additionally, the analyzed LLs contained relatively high concentrations of chloride and sulfate (respective mean values of 3191 mg Cl^-/L and 1860 mg SO_4^{2-}/L), which could be advantageous in relation to the application of electrolysis. Furthermore, the LLs were characterized by a high concentration of BPA (1539.6 µg/L), a very common, poorly biodegradable micropollutant that is considered an endocrine disruptor.

Data presented in this paper are in agreement with the outcome of our previous long-term study [31], which indicated that the quality of leachates originating from the old landfill prisms can vary. This is due to several factors but in general, the current values of COD and TN determined in LLs originating from the so-called old prisms are lower, possibly because these prisms were already managed in accordance with the new EU guidelines, limiting the landfilling of biodegradable substances (Council directive 1999/31/EC) [32].

The LLs tested in this study were characterized by the high amounts of organic matter and total nitrogen (see Table 1 to compare the values). Until 2011, the MSW plant ‘Eko Dolina Lezyce’ was operated without limiting the deposition of biodegradable waste (for details see [33]), and only later the changes have been introduced to fulfill the requirements of the EU Waste Framework Directive (2008/98/EC) [34]. In order to mimic the present quality of LLs, the original leachate samples were diluted (1:1) to obtain lower values of COD and nitrogen concentration.

Table 1. Characteristics of raw LLs from the old prisms at the Municipal Solid Waste Plant (Lezyce, Poland) sampled in this study contrasted with the corresponding values measured during the long-term study of leachates at the same site. Two modes of MSWP operation, i.e. with limited (in accordance with the Council directive (1999/31/EC of 26 April 1999) and unlimited deposition of biodegradable waste were considered [33].

Parameters	**Parameter values for raw leachates originating from old landfill prisms that were tested in this study**	**Parameter values for raw leachates sampled from old landfill prisms during the long-term study at Municipal Solid Waste Plant in Lezyce, Poland**	
		MSWP operated in accordance with Council directive 1999/31/EC, i.e. with limited deposition of biodegradable waste	**MSWP operating with no limit on the deposition of biodegradable waste**
pH	7.84±0.03	6.4 ÷ 8.1 (7.5)	7.3÷8.3 (7.8)
Color	brown	n.a.	n.a.
Cond [mS/cm]	27.6±0.4	5.4 ÷ 23.2 (12.9)	23.6 ÷ 31.1 (28.9)
ORP [mV/cm]	-420±6	n.a.	n.a.
TP [mg P/L]	19.0±0.2	5.1 ÷ 15.3 (6.3)	17.7 ÷ 26.4 (23.4)
$P-PO_4$ [mg $P-PO_4$/L]	16.6±0.3	14.0 ÷ 12.7 (4.1)	14 ÷ 43.6 (20.0)
TN [mg N/L]	2510±2	184 ÷ 864 (705)	1725 ÷ 2510 (2325)
$N-NH_4^+$ [mg $N-NH_4^+$/L]	2270±7	155 ÷ 820 (652)	1704 ÷ 2295 (2175)
$N-NO_3^-$ [mg $N-NO_3$/L]	19.45±1	3.3 ÷ 15.9 (5.4)	14.7 ÷ 24 (21)
$N-NO_2^-$ [mg $N-NO_2$/L]	0.375±0.124	0.2 ÷ 0.5 (0.4)	0.2 ÷ 0.6 (0.4)
COD [mg O_2/L]	4225±6	1011 ÷ 12620 (1925)	3260 ÷ 4715 (4270)
BOD_5 [mg O_2/L]	366±4	236 ÷ 7490 (439)	338 ÷ 677 (361)
BOD_{20} [mg O_2/L]	538±14	n.a.	n.a.

SO_4^{2-} [mg SO_4^{2-}/L]	1860±43	42 ÷ 475 (161)	1015 ÷ 2430 (1640)
Cl^- [mg Cl^-/L]	3191±110	851 ÷ 2595 (1489)	2836 ÷ 4786 (3545)
TSS [mg/L]	26±3	13 ÷ 596 (230)	13 ÷ 80 (31)
MSS [mg/L]	2±1	8 ÷ 174 (23)	2 ÷ 24 (9)
VSS [mg/L]	24±	1 ÷ 574 (97)	4 ÷ 60 (22)
BOD_5/COD	0.087±	0.17 ÷ 0.59 (0.28)	0.07 ÷ 0.16 (0.11)
TN/BOD_5	6.86±3	0.07 ÷ 2.88 (1.46)	3.28 ÷ 6.97 (4.86)
Bisphenol A [μg/L]	1539.6±0.01	<LOD÷8052	<LOD÷150

n.a. – not analyzed; LOD – limit of detection

2.2 Synthesis and characterization of boron-doped diamond electrode

In this study, the BDD electrodes with different boron doping levels were deposited on 2-inch silicon wafers by using a Microwave Plasma Assisted Chemical Vapor Deposition (MWPACVD) process. The three doping levels, expressed as the B/C ratios of 500 ppm (coded BDD-0.5k), 5000 ppm (BBD-5k) and 10000 ppm (BDD-10k), were applied to achieve various conductivity mechanisms, resulting in different concentrations of generated oxidants. Details of the synthesis process are described elsewhere [35]. The deposition duration was set to 12 hours.

The molecular structure of electrode surface was analyzed using the Raman technique. The Raman spectra were recorded at room temperature using the micro-Raman system (InVia, Renishaw, UK) and a 514 nm argon ion laser was used as an excitation source. Spectra were recorded in the range of 600 – 3500 cm^{-1}. The surface morphology was analyzed using a Scanning Electron Microscope (SEM) (EVO-40, Zeiss, Germany). In order to determine the sp^3/sp^2 ratio, the Raman spectra were deconvoluted using the Lorentzian function which allowed for the estimation of areal contribution of both carbon phases (OriginPro 8.0, OriginLab, Northampton, MA).

The electrochemical measurements were performed by using the potentionstat-galvanostat system (AutoLab PGStat 302N, Netherlands) in a standard three-electrode assembly at 295 K. A Si substrate overgrown with the BDD film served as a working electrode. The diameter of the round sample area wetted by electrolytes was 4 mm. All current densities in this manuscript were calculated on the basis of the geometric surface area. The counter electrode consisted of Pt gauze, while the reference electrode of Ag/AgCl/0.1 M KCl. The electrodes were tested by cyclic voltammetry in a solution of 0.5 M K_2SO_4.

2.3 Advanced Oxidation Processes

The electrochemical degradation experiments were conducted in a specially designed experimental set consisting of a 200-mL undivided electrolytic cell, thermostat and magnetic stirrer (Electrochemical Stirrer, ES24, Wigo, Poland). The cell contained three electrodes, i.e. the BDD electrode as an anode, a tantalum plate as a cathode and Ag/AgCl/ 0.1 M KCl as a reference electrode. The anode and cathode were flat and had the same surface area (10 cm^2), and the distance between them in all experiments was 1.0 cm. All electrochemical oxidation assays were performed under galvanostatic conditions provided by the power supply (Ami TTi PL303, UK). The effects of the operating parameters such as, the current density (12.5; 25; 50 mA cm^{-2}), pH (3.0; 5.0; 7.6) and the presence of Fe^{2+} ions (10 mg/L) on the efficiency of electrochemical oxidation of LLs were studied.

Each experiment was conducted for eight hours at the temperature maintained at 20-25 °C. Every hour the sample of V = 10 cm^3 was collected, and then subjected to degassing by mixing on a multipoint stirrer (Variomag, POLY 15 KOMED, Thermofisher Scientific, USA) at 50 rpm for 10 min. Next, the physical and chemical analyses of the samples were conducted.

The following parameters were analyzed according to the APHA standard [36]: pH, conductivity and temperature using a portable multi-parameter meter HL-HQ40d (multi, HACH, Germany); inorganic N compounds ($N\text{-}NH_4^+$, $N\text{-}NO_3^-$, $N\text{-}NO_2^-$), total phosphorus (TP), orthophosphate ($P\text{-}PO_4$), chemical oxygen demand (COD method for samples with Cl^- concentration of up to 1500 mg/L; 10 mg/L of iron present in the solution did not interfere in the COD determination), chloride (Cl^-), and sulfate (SO_4^{2-}) using a XION 500 spectrophotometer (Dr. Lange, GmbH, Germany), 5- and 20-day biochemical oxygen demand (BOD_5 and BOD_{20}) using the manometric respirometric BOD OxiTop® method; and total suspended solids (TSS), volatile suspended solids (VSSs) and mineral suspended solid (MSS) using the gravimetric method. In this study, the BOD_{20} values were determined because this parameter provides superior quantitative basis for the estimation of biodegradable fractions in industrial wastewater, especially in the case of wastewater rich in micropollutants [37]. The UV-Vis absorbance spectra of LLs were recorded using a spectrophotometer (Evolution 220 Thermo Scientific, German). The variation of UV-VIS absorbance spectra during electrolysis had been previously analyzed for the 200-500 nm range. The 400 nm wavelength was chosen as appropriate for assessing the color disappearance. The TN_8 values were determined after an 8h electrolysis of wastewater with a TN/TOC analyzer (Shimadzu). The TN_8 value was similar to the sum of ($N\text{-}NH_4^+$ + $N\text{-}NO_3^-$). Therefore, N_2 generated in the process was presented in discussion section as a difference between TN_0 and other forms of nitrogen in the equation (1) below:

$$\mathbf{N_2 = TN_0 - TN_8 = TN_0 - (N\text{-}NH_4^+ + N\text{-}NO_3^-)} \qquad \mathbf{(1)}$$

where: $\mathbf{N_2}$ is a nitrogen in its gaseous form (in mg N/L), $\mathbf{TN_0}$ is the initial value of total nitrogen (in mg N/L), $\mathbf{TN_8}$ is the value of total nitrogen after 8h of electrolysis, approximately equal to the sum of ammonia ($N\text{-}NH_4^+$) and nitrate nitrogen ($N\text{-}NO_3^-$) (in mg N/L).

Additionally, the efficiency of the electrochemical oxidation of LLs, expressed as the chemical oxygen demand (COD) and $N\text{-}NH_4^+$ removal, was determined.

2.4 Bisphenol A analysis

In terms of the BPA analysis, a 5-ml aliquot of analyzed water was added to a round-bottom test tube with a nut and gasket, which contained the following reagents: 1 ml of Tetrahydrofuran/Acetonitrile (THF/ACN) 20/80 (v/v), 1 ml of 1% formic acid solution, 3 g of sodium chloride, and 2 g of magnesium sulfate. The test tube and its contents were shaken by hand for approximately 2 min. Then, the test tube was centrifuged (3000 rpm for 2 min). The upper organic layer was collected and analyzed by GC/MS.

GC/MS analysis was performed on a Shimadzu QP2010 SE gas chromatograph-mass spectrometer. Chromatographic separations were conducted by using a ZB-5MS capillary column (30 m length, 0.25 mm internal diameter, and 0.50 µm film thickness) from Phenomenex. The carrier gas was helium, with a flow rate of 1 mL/min. The injection was performed in split mode (5:1) at a temperature of 325°C. The oven temperature was programmed as follows: 100°C for 2 min with a 40°C/min increase to 325°C, where it was held for 4 min. The injection volume was 2 µl. The interface temperature was 325°C, and the ion source temperature was 200°C. The ion energy for electron impact (EI) was 70 eV. The solvent cut time was 4 min. Mass detection was performed in the single-ion monitoring (SIM) mode; the selected ions (m/z) used for qualitative and quantitative purposes are shown in Table 2.

Table 2. Details of GC/MS analysis aimed at determining BPA in LLs.

Analyte	**Quantifier [m/z]**	**Qualifier [m/z]**	**Retention time [min]**	**Limit of detection (LOD) [µg/L]**	**Limit of quantification (LOQ) [µg/L]**
BPA	213	228	7.797	124.9	37.3

2.5 The energy consumption

The specific energy consumption (EC) for the electrochemical cell operation per unit COD mass was estimated from Eq. (2) [38]

$$\mathbf{EC = (1000 \times Ecell \times I \times \Delta t) / (Vs\ (\Delta COD)) \quad (2)}$$

where: **1000** is a conversion factor (in mg/g), **Ecell** is the average cell voltage (in V), **I** is the applied current (in A), **Δt** is the electrolysis time (in h), **Vs** is the solution volume (in L) and (**ΔCOD**) is the experimental COD concentration decay (in mg/L).

3. Results and discussion

3.1 Structure and morphology of BDD electrodes

Figure 1 shows the Raman spectra of electrodes used in this study for the oxidization of LLs. All samples, namely, BDD-0.5k, BDD-5k and BDD-10k exhibited an intense band attributable to the sp^3 diamond at 1332, 1321 and 1311 cm^{-1}, respectively [35,39]. For samples BDD-5k and BDD-10k, the diamond bands were shifted due to boron doping. The boron doping has been confirmed by the presence of bands at 1218 and 1204 cm^{-1} [40,41]. The Raman “G” band at 1492-1508 cm^{-1} was attributed to the C-H bending bonds; this finding is connected to a hydrogen-rich plasma used in the deposition process. The calculated sp^3/sp^2 ratio decreased from 78 for BDD-0.5k to 53 for BDD-10k sample. This can be explained by the influence of boron on the surface morphology, resulting in a smaller grain size and thus richer sp^2 grain boundaries [41,42].

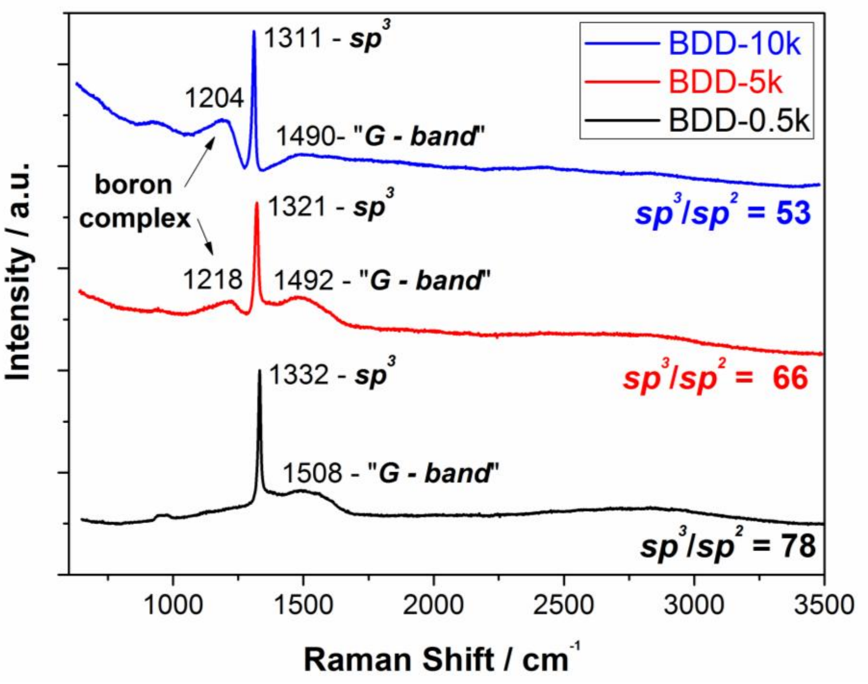


Figure *1***.** Raman spectra of BDD samples in relation to various [B]/[C] ratios in plasma.

The size of crystallites on the deposited BDD electrodes with different [B]/[C] ratios was investigated by means of scanning electron microscopy (SEM) (see Fig. 2). For all electrodes, the films were continuous and no impurities were observed. The average grain size for the BDD-0.5k and BDD-5k electrodes was 1 µm. In the case of highly boron-doped BDD-10k electrode, the observed crystallites were smaller, with a mean grain size of approximately 0.5 µm [41].

Many parameters, *inter alia*, boron concentration can influence the charge transport and, subsequently, conductivity and oxidation properties such as grain size distribution, specific structures of B defects or the amount of conductive carbon [43–45]. Boron provides higher conductivity, modifying it directly or indirectly [46,47]. At higher boron concentrations, the BDD films display many different conducting regions, and possibly different conducting pathways and electrochemical properties, as revealed in our prior studies [35,48,49].

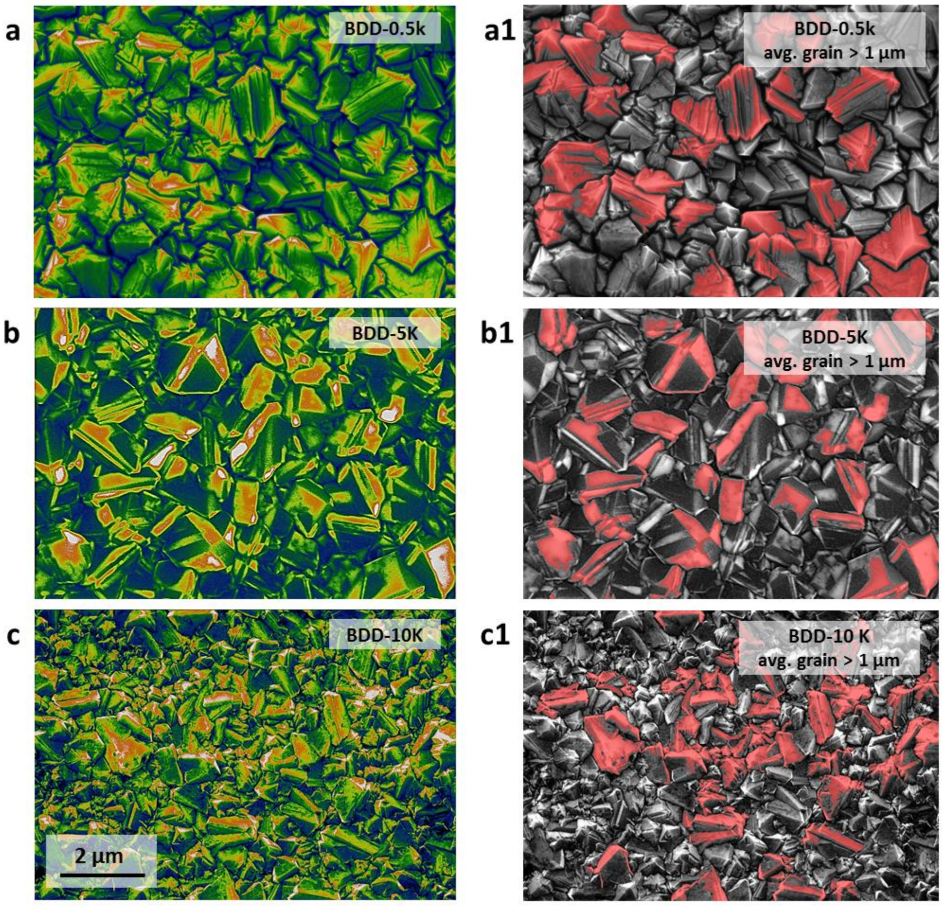


Figure 2**.** SEM images of BDD films deposited at different [B]/[C] ratios in plasma, namely, BDD-0.5k, 5k and 10k ppm. Magnification of 10000×. The (111) and (110) facets of crystal grains larger than 1 micron are color marked (see right panel of the figure).

3.2 Advanced Oxidation Processes of LLs

Effect of electrode material on the organic matter removal

A boron-doped diamond electrode is a very good candidate for performing the degradation of organic compounds because of its high O_2 evolution overpotential leading to an enhanced oxidation of organic matter [50,51]. Three boron-doped diamond electrodes with different boron levels, i.e. BDD-0.5k (500 ppm of B), BDD-5K (5000 ppm of B) and BDD-10k (10000 ppm of B), were used to remove the organic matter and ammonium nitrogen from diluted (1:1) raw LLs. The measured anodic potentials reached up to 1.5 V vs. Ag/AgCl/ 3M KCl for all electrodes in the region of O_2 evolution [52]. Figs. 3 and 4 summarize the results obtained for the LLs oxidized at a current density of 25 mA/cm^2 by using the aforementioned BDD electrodes. As illustrated in Fig. 3, the spectra of LLs displayed a wide but weak absorbance peak positioned at a wavelength of 285 nm, suggesting the presence of aromatic compounds. Regardless of the electrode used, the absorbance values decreased over time for the wavelength values below 220 nm, while an increase in absorbance was observed for the wavelength range from 220 to 500 nm. This finding indicates that the organic pollutants were successfully mineralized to CO_2 or oxidized to small-molecule intermediates which adsorbed the UV light below 220 nm. Moreover, an increase in the absorbance profile within the short wavelength range (below 220 nm) can indicate continuous oxygen evolution via Eq. (3) simultaneously with the generation of •OH radicals at the BDD anodes [53]:

$$\bullet\mathbf{OH} + \bullet\mathbf{OH} \rightarrow \tfrac{1}{2}\,\mathbf{O_2} + \mathbf{H_2O} \qquad (3).$$

This situation occurred for the values above the standard potential of oxygen evolution (for the studied BDD, E=1.9 -2.0 V vs. SHE). The observed increase in the redox potential (from – 420 mV to 330 mV) in the electrolyzed LLs confirmed the presence of elevated concentrations of oxygen and other oxidants in the solution.

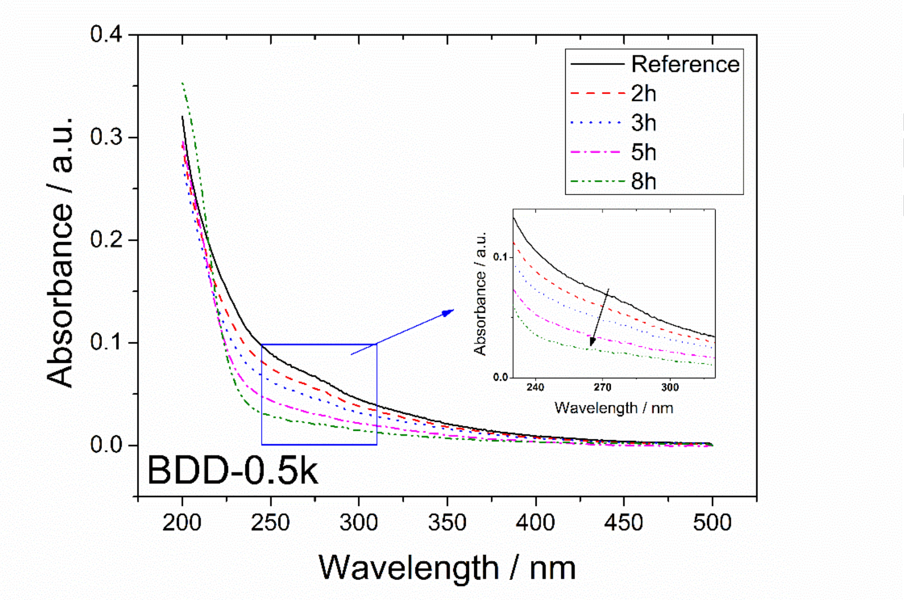


Figure. 3. Temporal changes in UV-VIS spectra of LLs that were electrolyzed by means of the BDD-0.5k electrode at a current density of 25 mA/cm^2 and pH 7.6.

The values of process efficiency for the removal of organic matter during the electrodegradation assays at a specific charge Q =12.5 Ah/L, expressed as the solution color, COD, BOD$_{20}$, and BPA, are shown in Fig 4. It is noticeable that in the case of tested BDD anodes, there were no significant differences in the color intensity and COD removal, whereas the efficiency of BPA removal decreased in the following order: BDD-0.5k > BDD-10k > BDD-5k. Despite the high COD values in raw LLs, the measured BOD$_{20}$ level was low (183 mgO$_2$/L), which had been expected due to the fact that the mature LLs were used in the experiment. Respectively, 78, 55 and 48% of BOD$_{20}$ were removed from the analyzed solutions by using the BDD-0.5k, BDD-10k and BDD-5k electrodes.

Regardless of the type of electrode film, under the same operating conditions (current density of 25 mA/cm^2 and specific electric charge Q of 12.5 Ah/L) the color removal was higher than the COD and BOD$_{20}$ removal, suggesting the presence of organic chemicals resistant to oxidation. In addition, the efficiency of BOD$_{20}$ removal and BPA decomposition varied among the studied BDD electrodes. Similar removal values should be expected because the systems are under mass transfer limitation. In such a system, every organic molecule that arrives at the electrode surface will be immediately oxidized by the •OH radicals. Based on the previous reports, the •OH radical concentration generated at the BDD electrode is independent of the boron doping level. Fierro *et al.* [54] showed that the boron doping level of diamond electrodes under mass transfer limitation has no influence on both the amount of hydroxyl radicals produced at the electrode surface and the removal of COD from formic acid solutions. However, not only the nonselective •OH radicals can be generated under the experimental conditions applied in the present study. The presence of less effective $SO_4^{-\bullet}$ and selective HOCl ions are also expected, and their generation at the BDD surface can vary in dependence on the morphology and chemical properties of the electrodes with different doping levels. The formation efficiency of these oxidizing species can affect the level of organic matter removal.

The research group led by de Araújo [55] observed that a BDD anode with a higher diamond-carbon content (high sp^3/sp^2 carbon ratio) provides higher organic matter elimination compared to the anode with a higher graphite-carbon content (low sp^3/sp^2 carbon ratio). In our work, such a trend was also observed as assessed by the BPA decomposition and BOD_{20} removal. Panizza and Martinez-Huitle [19] studied the role of the electrode material in the anodic oxidation of LL, indicating that the BDD electrodes are more efficient and cost-effective compared to $TiRuSnO_2$ and PbO_2 electrodes. The reported COD removal rate was comparable with the results achieved in the present study.

Currently, a vast variety of electrodes is available. However, BDD and titanium coated with RuO_2, IrO_2, or PtO are regarded as leading electrodes for the electrochemical oxidation of industrial wastewater contaminated with dyes, pesticides, pharmaceuticals, etc. [56]. This is due to their excellent catalytic properties and resistance to both corrosion and dissolution.

Moreover, Pirsaheb *et al.*[57] demonstrated that the highest efficiencies of COD removal by means of Al and Fe electrodes were not exceeding 70% even under optimal conditions.

Effect of electrode material on nitrogen removal

The mass balance of all nitrogen forms determined via assays performed with the use of tested electrode materials is shown in Fig. 4. In the case of BDD-10k, the level of ammonium nitrogen removal reached 41%. Slight differences in the nitrogen elimination values were observed between the BDD-0.5k and BDD-10k electrodes. The removal efficiency of ammonium nitrogen for BDD-5k was clearly lower.

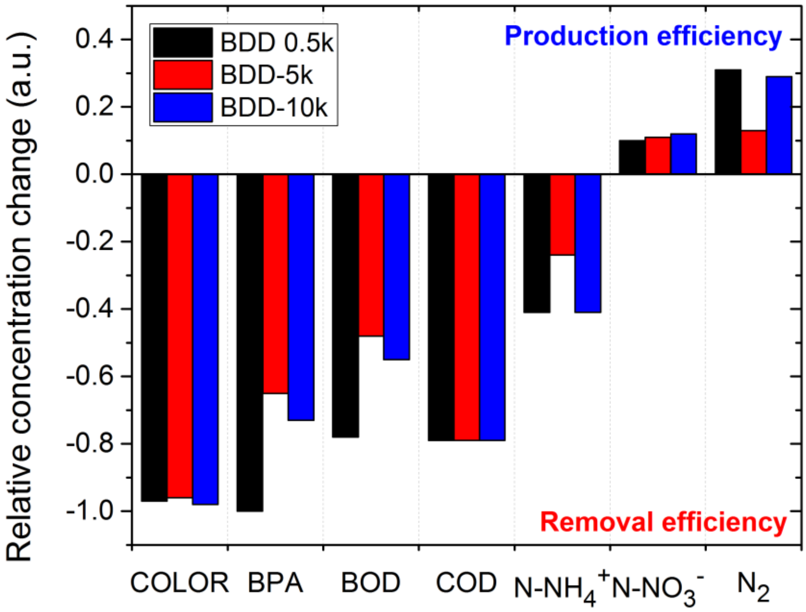


Figure 4. Removal efficiency of organic matter and ammonium nitrogen, and the generation of inorganic nitrogen forms in the LLs subjected to an 8-h electrolysis by means of various BDD electrodes at a current density of 25 mA/cm^2 and initial pH 7.8.

The main benefit of the application of the aforementioned BDD anodes to the electrolysis of LLs is the oxidation of N-NH$_4^+$, mainly to nitrogen gas. The amount of nitrate ions produced during such electrolysis was lower than the amount of nitrogen gas. Pérez *et al.* [58] identified nitrogen gas and pointed to nitrate ions as the main products of ammonium oxidation obtained during the electrochemical oxidation of a LL with a BDD anode. In this study, the volume ratio of the nitrogen gas to N-NO_3^- was 7:3, a value similar to that obtained in our study for the BDD-0.5k and BDD-10k electrodes. In contrast, the application of BDD-5k electrode resulted in a rather different ratio of N_2 to N-NO_3^- ,i.e. approximately 1:1.

Ammonium nitrogen can be electrochemically oxidized in direct (less effective) and indirect ways (more effective). The main species resulting from the indirect oxidation of ammonium nitrogen in saline wastewater are Cl_2/HOCl, which will be discussed in detail in the next section of this paper, although the •OH radicals also play some role in this process. Here it should be noted that graphite has low chlorine over potential, but no correlation between the nitrogen removal efficiency and the sp^3/sp^2 ratio in the BDD anode was observed.

Regarding the elimination of ammonium nitrogen, lower effectiveness was generally achieved in comparison to that of COD removal. Nevertheless, the maximum removal values for COD and ammonium nitrogen reached 79 and 41%, respectively. These values were much higher than those observed during preliminary studies employing a single-cell flow reactor. The physico-chemical properties of LLs used in both aforementioned studies were similar. In comparison, after an 8-h electrolysis, Anglada *et al.* [26] achieved the removal of COD and N-NH_4^+ at the level of 51 and 34%, respectively.

3.3 Effect of the operating conditions

Influence of the current density

The direct electron transfer from organic matter to the anode and highly effective oxidant generation at the BDD surface can be responsible for the enhanced degradation of organic matter and nitrogen compounds in an aqueous solution. The capability to generate the hydroxyl radicals and other oxidants ($SO_4^{-\bullet}$, HOCl) depends on the applied current density and the properties of anode material [59]. Therefore, the effect of the applied current on the degradation rates of organic matter, expressed as COD and ammonium elimination, was investigated using current densities of 12.5, 25.0 and 50.0 mA cm^{-2} (see Figs. 5 and 6). The electrochemical treatment was carried out for 8 h at an initial pH of 7.8 using three BDD electrodes with different boron levels.

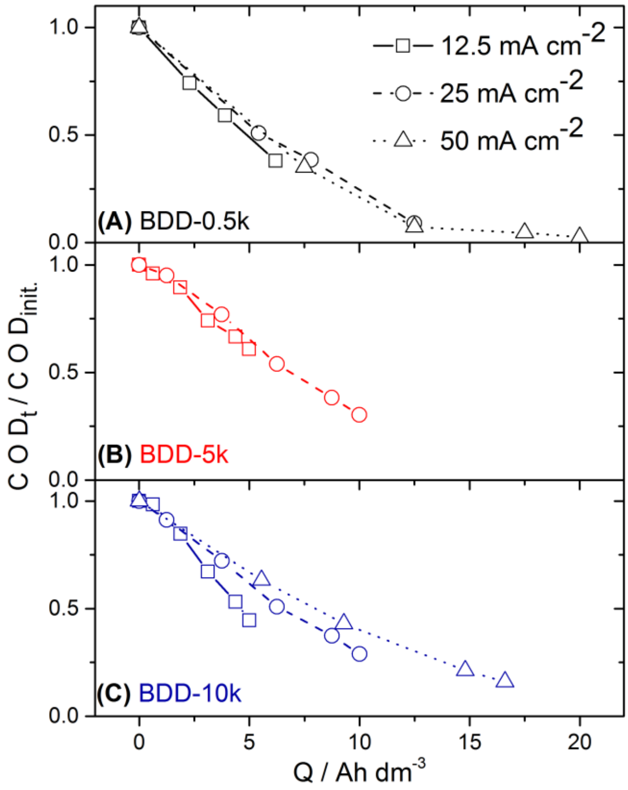


Figure 5. Variation of COD (pH 7.8) as a function of the specific charge Q plotted for all studied BDD materials at different current densities.

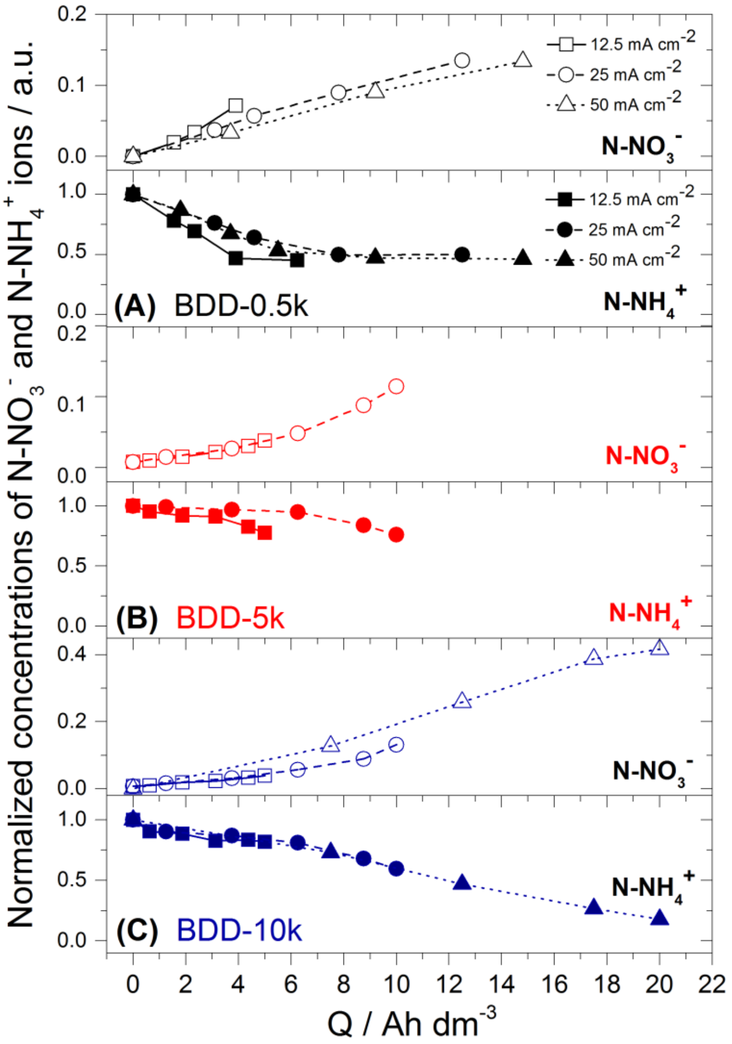


Figure 6. Concentration variation of inorganic forms of nitrogen in LLs (pH 7.8) as a function of specific charge Q for all studied BDD materials at different current densities.

From among the tested BDD electrodes, the performance of BDD-10k electrode differed because an increase in the current density resulted in a decreased rate of COD elimination. For the Q value of 6.2 Ah/L, 62, 49 and 39% of COD were removed from LLs at current densities of 12.5, 25 and 50 mA cm^{-2}, respectively. The results indicate the enhanced oxidation rate at the BDD-10k surface compared to that achieved at 12.5 mA cm^{-2}, owing to the increase of energy consumption in O_2 and/or Cl_2 evolution at a higher current density. This finding is correlated with the electrochemical working potential, which is slightly narrower for BDD-10k than for other electrodes in the range of positive potential values; thus, O_2 and/or Cl_2 evolution can begin at a lower potential.

It is worth noting that an increase in Cl_2 concentration at the anode surface can be beneficial because Cl_2 is hydrolyzed in aqueous solutions to the relatively strong oxidant HOCl, which mainly participates in the indirect elimination of nitrogen from water [22]. However, HOCl can also remove some organic matter and participate in the supression of COD removal.

When analyzing the profiles of ammonium nitrogen removal (see Fig. 6) from the anodic oxidation experiments with different BDD electrodes, clear differences with regard to their shape were found. At the BDD-0.5k electrode, ammonium nitrogen removal occurred in two steps: a relatively rapid oxidation followed by the second step after stopping the process. Different behavior was observed for the BDD-5k electrode, namely, the initial step was very slow but afterwards, the rapid oxidation of ammonium nitrogen was observed. When the BDD-10k electrode was applied, the concentration of ammonium nitrogen continuously decreased with increasing duration of electrolysis. Moreover, the rate of N-NH_4^+ oxidation at the BDD-0.5k and BDD10k electrodes was independent of the current density.

The lower removal rate of ammonium ions at the initial step of electro-oxidation has also been reported by Cossu *et al.* [16]. This research group reported that at the Ti/Pt anode, ammonium nitrogen was substantially removed in the subsequent electrochemical oxidation step when indirect oxidation became prevalent. The increase in the indirect oxidation rate of N-NH_4^+ may be attributed to the formation of reactive chloride oxidants, such as Cl_2/HOCl [22,58]. According to Pérez et al., ammonium reacts with hypochlorite in agreement with reactions (4) and (5), regenerating chloride ions [58]:

$$\mathbf{2/3NH_4^+ + HOCl \rightarrow 1/3\ N_2 + H_2O + 5/3H^+ + Cl^-} \qquad \mathbf{(4)},$$

$$\mathbf{NH_4^+ + 4HOCl \rightarrow NO_3^{\ -} + H_2O + 6H^+ + 4Cl^-} \qquad \mathbf{(5)}.$$

Considering previous reports, our results suggest that the BDD-10k electrode with the highest boron doping level shows the strongest tendency to oxidize chloride ions, leading to the highest current efficiency and rate of ammonium nitrogen removal. In such complex matrices as LLs where chlorides are present in significant concentrations, most of the applied current is involved in the oxidation of Cl^-. This behavior has also been considered in the investigations of Lee *et al.* [60], Katayose *et al.* [61], and Vijayaraghavan *et al.* [62]. For BDD-10k, the lowest COD removal rate was found at the highest current density (50 mA/cm^2) due to the highest energy consumption, including side reactions (e.g., O_2 and/or Cl_2 increase). However, the oxidation of ammonium was still effective, probably due to the enhancing effect of the current density in relation to Cl_2/HOCl production [63]. A decrease in Cl^- ion concentration in LLs at BDD-10k from 1595 mg/L to 780, 1134 and 1525 mg/L at current densities of 50, 25 and 12.5 mA/cm^2, respectively (data obtained after 8 h of electrolysis) suggests the effective Cl_2 generation, but the production of perchlorates is also possible. Thus, our assumption that the lowest value of the sp^3/sp^2 ratio displayed by BDD-10k can lead to higher chloride generation should be confirmed by further investigations.

Based on the obtained results, we can conclude that the removal of ammonium nitrogen by means of the BDD electrode is a complex process, which is connected to the competition between the generation of the •OH and SO_4-• radicals and the evolution of O_2 and Cl_2 at the electrode surface. Further investigations of this phenomenon should be conducted. At the highly doped BDD electrode, the oxidation process is partially carried out on the sp^2 phase [64], which significantly increases the adsorption of organic material [65] and reduces the efficiency of oxidation in an indirect way [66,67]. The BDD enhances the ability of diamond film to undergo anodic oxidation of chlorides to chlorine/hypochlorides due to the decreased sp^3/sp^2 ratio [55]. However, the drawback of the highly doped BDD electrode is that the high sp^2 phase content can produce poor mechanical, structural and aging parameters compared to the less doped electrode [68].

Influence of the initial pH and the addition of a small amount of Fe^{2+}

The electro-generation of certain oxidizing agents [69] and the chemical forms of organic and inorganic pollutants present in wastewater are pH dependent. The pH of wastewater is an essential parameter in indirect electrochemical oxidation. Moreover, the hypochlorous acid (HOCl) generated during the electrolysis of LL is able to react with Fe^{2+} ions in a Fenton-like reaction and produce more powerful •OH radicals [70].

Therefore, a number of experiments was performed to check the effect of the initial pH of LLs and the addition of a small amount of Fe^{2+} ions on the rate and efficiency of COD removal and ammonium nitrogen elimination.

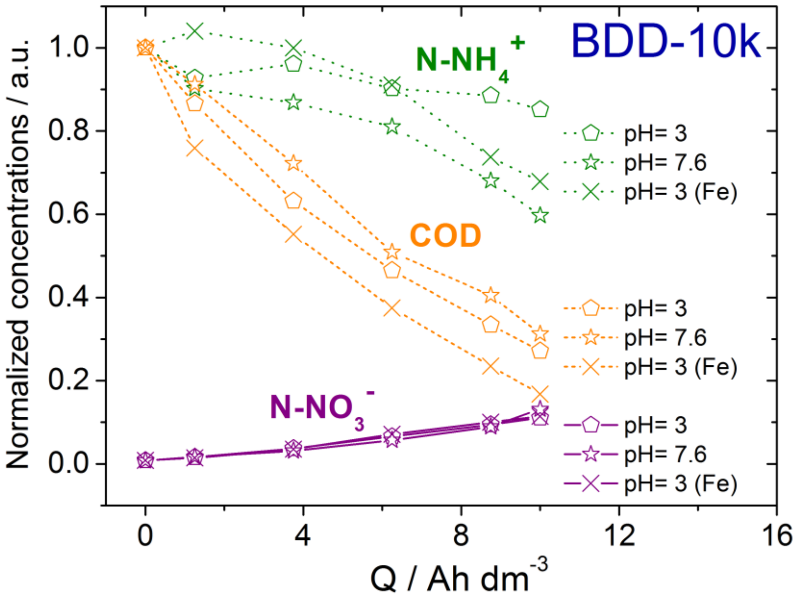


Figure 7. Variation of COD and the concentrations of inorganic forms of nitrogen as a function of specific charge Q at the BDD-10k electrode for different pH values, with the addition of 10 mg/L Fe^{2+} (current density 25 mA/cm^2).

Fig. 7 presents the results of the COD removal, ammonium nitrogen elimination and nitrate ion formation as a function of specific charge Q in the LL samples. The various initial pH values and the addition of 10 mg/L of Fe^{2+} ions were specifically illustrated here. The applied current density was 25 mA/cm^2, and BDD-10k was used as an anode due to the likely effective Cl_2 generation. In the case of LLs with a pH of 3.0, the COD removal rate was higher than that for the samples with a natural pH of 7.8. This fact can be explained by the high concentration of carbonate/bicarbonate ions in raw LLs, which are effective •OH radicals scavengers [16] and thus may decrease the oxidation rate of COD elimination. The acidification of LLs to a pH of 3.0 caused a shift in the carbonate/bicarbonate ion balance to CO_2 evolution, and the concentration of scavengers decreased. The difference between the COD removal rates under acidic and neutral conditions was not as significant as we expected. Under natural conditions, the carbonate ions can be electrochemically oxidized to carbonate radicals, which, simultaneously with scavenging •OH and $SO_4^{-\bullet}$ radicals, can selectively participate in the oxidation of organic matter [71].

In contrast to COD removal, the oxidation of ammonium nitrogen was inhibited under acidic conditions. At pH ≤ 7, where the dominant species is NH_4^+, the main removal process of these ions from LL proceeded via indirect electrochemical decomposition by HOCl, as shown in Eq. (4) and (5) [72].

In the pH range of 3–8 the predominant species are HOCl, whereas in the acidic solution (pH < 3.0) the main forms are $Cl_2(aq)/Cl_2^{\bullet}$. Therefore, a decrease in the rate of ammonium nitrogen removal at pH 3.0 can be connected to the fact that the concentration of HOCl was low and the free chlorine was not reacting with N-NH_4^+.

In the published literature, the effective remediation of LL by the conventional photo-Fenton process via applying the wide range of iron concentrations (10–2000 mg L^{-1}, with a preferable range of 60–80 mg L^{-1}) has been reported [73–76]. Because of the cathodic Fe^{2+}

regeneration in Eq. (6), the photoelectro-Fenton process may allow us to work at minor iron doses compared to the analogous chemical process. However, the theoretical challenge of the competing cathodic reductions of O_2 to H_2O_2 and Fe^{3+} to Fe^{2+} could be observed here. To avoid the competition between these cathodic reactions, a new electrochemical Fenton-type process using Fe^{2+} and electro-generated Cl_2/hypochlorous acid (reaction 7 and 8) as Fenton-like reagents (reaction 9) has been proposed [77]. We used a small amount of Fe^{2+} (10 mg/L) to enhance the electrochemical oxidation of organic matter in LLs in accordance with the following processes:

$$\mathbf{Fe^{3+} + e^{-} \rightarrow Fe^{2+}\ (cathode\ reaction)} \qquad \mathbf{(6)},$$

$$\mathbf{2Cl^{-} \rightarrow Cl_2 + 2e^{-}\ (anode\ reaction)} \qquad \mathbf{(7)},$$

$$\mathbf{Cl_2 + H_2O \rightarrow HOCl + H^{+} + Cl^{-}} \qquad \mathbf{(8)},$$

$$\mathbf{HOCl + Fe^{2+} \rightarrow Fe^{3+} + \bullet OH + Cl^{-}\ (bulk\ solution)} \qquad \mathbf{(9)}.$$

In agreement with the above assumptions, the addition of Fe^{2+} to acidic LLs accelerated the COD removal rate but completely inhibited the ammonium ion oxidation. However, when the COD removal reached 60%, the ammonium nitrogen oxidation process began.

The enhancement of COD removal suggested that at the highly doped BDD electrode, powerful •OH radicals were obtained in reaction (9). The inhibition of ammonium nitrogen elimination confirmed that HOCl is the predominant form of oxidants participating in N-NH_4^+ oxidation at BDD-10k.

The energy consumption

Regarding the influence of parameter j, as shown in Table 3, an increase in j_{app} results in the higher EC value, from 26.5 kWh/kgCOD for a current density of 12 mA/cm^2 to 71.22 kWh/kgCOD for 50 mA/cm^2. This demonstrates that the excess of energy was spent in side reactions at higher current density. Low pH and the addition of Fe(II) salt suppressed the oxygen evolution reaction and overcame the mass transport limitation of organics in the case of •OH-mediated oxidation. Furthermore, HClO in the presence of Fe(II) acted as an additional source of •OH radicals, which resulted in the faster oxidation kinetics and lower EC values.

Table 3. Energy consumption of BDD electrodes.

j_{app} **BDD-0.5k [mA/cm^2]**	**EC [kWh/kgCOD]**
	COD
50	71.22
25	53.8
12.5	26.5

j_{app} **BDD-10k [mA/cm^2]**	**EC [kWh/kgCOD]**
25	55.8
25 (acid conditions)	49.1
25 (acid conditions + 10mg Fe(II)	45.0

Due to significant differences in experimental conditions, it is difficult to compare the results of COD removal and the corresponding energy consumption obtained in this study with the pertinent values reported by other authors. Nevertheless, the values listed in Table 3 are of the same order of magnitude as the values of energy consumption in the published literature. Wang et al. [78] reported the energy consumption of 55 kWh/kgCOD, which is a higher value than 26 kWh/kgCOD obtained in our study during the electrochemical oxidation of LLs for j_{app} = 12.5mA/cm^2. At higher values of current density ($j_{app} > j_{lim.}$), the mass transport limitation of the reagents causes a dramatic increase in the voltage loss, and a subsequent increase in EC, as presented in Table 3.

According to the published reports, the lifespan of BDD electrodes is over 850 hours as established during the accelerated life test at 100,000 A/m^2 in 0.5 M H_2SO_4 solution. Moreover, after several weeks of oxidation, the properties of those electrodes were not affected and the poisoning of the surface was not detectable [79].

At present, the issues such as the electrode lifetime and the efficiency of chemical oxidation of low/nonbiodegradable organic matter, the latter commonly occurring in leachates from the old landfill prisms, are being further investigated.

4. Conclusions

The electrochemical oxidative treatment of LLs containing N-NH_4^+ and COD at the respective concentrations of 1135 mg N/L and 2112 mgO_2/L, and a low BOD_5/COD ratio was investigated by using a boron-doped diamond electrode (BDD). The BDD electrodes were doped with boron at the levels of 500, 5000 and 10000 ppm, which changed their structure and electrochemical performance. Under different current densities, the evolution trends of COD, N-NH_4^+ and N-NO_3^- were monitored in relation to the consumption of specific charge (Q). The type of electrode did not affect the color intensity of the solution or COD removal, whereas the elimination of BPA and BOD_{20} were found to be correlated with the sp^3/sp^2 ratio at the BDD surface. However, a decrease in the sp^3/sp^2 ratio of the applied BDD material resulted in the elevated removal efficiency of N-NH_4^+. The effect of the sp^3/sp^2 ratio of the BDD electrode on the Cl_2/HOCl generation should be further investigated. The generation of oxidants other than •OH radicals in electrodes with a lower sp^3/sp^2 ratio could be the reason for the observed differences in the efficiency of bisphenol A and BOD_{20} removal. The sp^2 presence on the BDD surface could also be responsible for the higher adsorption of aromatic compounds at the BDD electrode. The electrochemical treatment of LLs under acidic conditions in the presence of Fe^{2+} ions increased the COD oxidation, but inhibited the removal of N-NH_4^+. The applied BDD anodes were effective in case of organic matter removal as the electrolyzed organic matter decomposed to mineral forms rather than to more oxidized intermediates. In summary, the obtained results indicate that electrochemically pre-treated LLs are largely devoid of organic matter, including micropollutants (e.g., BPA), but they still contain relatively high concentrations of ammonia nitrogen. Because the ratio of total nitrogen to BOD_{20} increased during the experiments (from 4.7 in raw LLs to 213 in pre-treated LLs), anaerobic ammonium oxidation (Anammox) processes seem to be a reasonable option as a final step of LL treatment.

Acknowledgments

This work was supported by the Polish National Science Centre (NCN) under Grants No. 2014/14/M/ST5/00715 and 2014/14/E/ST7/00104. The DS funds of the Faculty of Chemistry at the University of Gdansk 530-8626-D596-17 BMN 538-8626-B402-16 BMN 538-8375-B409-16 and BMN 538-8626-B392-16, and the DS funds of the Faculty of Electronics, Telecommunications and Informatics at the Gdansk University of Technology are also acknowledged. The authors acknowledge Alexander Tools (Gdynia, Poland) for their technical support.

References

[1] C.B. Öman, C. Junestedt, Chemical characterization of landfill leachates – 400 parameters and compounds, Waste Management. 28 (2008) 1876–1891. doi:10.1016/j.wasman.2007.06.018.

[2] X.-S. He, B.-D. Xi, R.-T. Gao, H. Zhang, Q.-L. Dang, D. Li, C.-H. Huang, Insight into the composition and degradation potential of dissolved organic matter with different hydrophobicity in landfill leachates, Chemosphere. 144 (2016) 75–80. doi:10.1016/j.chemosphere.2015.08.071.

[3] T. Eggen, M. Moeder, A. Arukwe, Municipal landfill leachates: A significant source for new and emerging pollutants, Science of The Total Environment. 408 (2010) 5147–5157. doi:10.1016/j.scitotenv.2010.07.049.

[4] D. Fatta, A. Papadopoulos, M. Loizidou, A study on the landfill leachate and its impact on the groundwater quality of the greater area, Environmental Geochemistry and Health. 21 (1999) 175–190. doi:10.1023/A:1006613530137.

[5] S. Mor, K. Ravindra, R.P. Dahiya, A. Chandra, Leachate Characterization and Assessment of Groundwater Pollution Near Municipal Solid Waste Landfill Site, Environ Monit Assess. 118 (2006) 435–456. doi:10.1007/s10661-006-1505-7.

[6] N. Calace, A. Liberatori, B.M. Petronio, M. Pietroletti, Characteristics of different molecular weight fractions of organic matter in landfill leachate and their role in soil

sorption of heavy metals, Environmental Pollution. 113 (2001) 331–339. doi:10.1016/S0269-7491(00)00186-X.

[7] R.B. Brennan, M.G. Healy, L. Morrison, S. Hynes, D. Norton, E. Clifford, Management of landfill leachate: The legacy of European Union Directives, Waste Management. 55 (2016) 355–363. doi:10.1016/j.wasman.2015.10.010.

[8] M. Morozesk, M.M. Bonomo, I. da C. Souza, L.D. Rocha, I.D. Duarte, I.O. Martins, L.B. Dobbss, M.T.W.D. Carneiro, M.N. Fernandes, S.T. Matsumoto, Effects of humic acids from landfill leachate on plants: An integrated approach using chemical, biochemical and cytogenetic analysis, Chemosphere. 184 (2017) 309–317. doi:10.1016/j.chemosphere.2017.06.007.

[9] S. Fudala-Ksiazek, M. Pierpaoli, E. Kulbat, A. Luczkiewicz, A modern solid waste management strategy – the generation of new by-products, Waste Management. 49 (2016) 516–529. doi:10.1016/j.wasman.2016.01.022.

[10] E. Kattel, A. Kivi, K. Klein, T. Tenno, N. Dulova, M. Trapido, Hazardous waste landfill leachate treatment by combined chemical and biological techniques, Desalination and Water Treatment. 57 (2016) 13236–13245. doi:10.1080/19443994.2015.1057539.

[11] S.M. Iskander, B. Brazil, J.T. Novak, Z. He, Resource recovery from landfill leachate using bioelectrochemical systems: Opportunities, challenges, and perspectives, Bioresource Technology. 201 (2016) 347–354. doi:10.1016/j.biortech.2015.11.051.

[12] H. Yoo, K. Oh, G. Lee, J. Choi, RuO2-Doped Anodic TiO2 Nanotubes for Water Oxidation: Single-Step Anodization vs Potential Shock Method, J. Electrochem. Soc. 164 (2017) H104–H111. doi:10.1149/2.1201702jes.

[13] L. Labiadh, A. Barbucci, M.P. Carpanese, A. Gadri, S. Ammar, M. Panizza, Direct and indirect electrochemical oxidation of Indigo Carmine using PbO2 and TiRuSnO2, J Solid State Electrochem. 21 (2017) 2167–2175. doi:10.1007/s10008-017-3559-6.

[14] D. Clematis, G. Cerisola, M. Panizza, Electrochemical oxidation of a synthetic dye using a BDD anode with a solid polymer electrolyte, Electrochemistry Communications. 75 (2017) 21–24. doi:10.1016/j.elecom.2016.12.008.

[15] F.L. Souza, C. Saéz, M.R.V. Lanza, P. Cañizares, M.A. Rodrigo, The effect of the sp3/sp2 carbon ratio on the electrochemical oxidation of 2,4-D with p-Si BDD anodes, Electrochimica Acta. 187 (2016) 119–124. doi:10.1016/j.electacta.2015.11.031.

[16] R. Cossu, A.M. Polcaro, M.C. Lavagnolo, M. Mascia, S. Palmas, F. Renoldi, Electrochemical Treatment of Landfill Leachate: Oxidation at Ti/PbO2 and Ti/SnO2 Anodes, Environ. Sci. Technol. 32 (1998) 3570–3573. doi:10.1021/es971094o.

[17] P.B. Moraes, R. Bertazzoli, Electrodegradation of landfill leachate in a flow electrochemical reactor, Chemosphere. 58 (2005) 41–46. doi:10.1016/j.chemosphere.2004.09.026.

[18] Y. Deng, J.D. Englehardt, Treatment of landfill leachate by the Fenton process, Water Research. 40 (2006) 3683–3694. doi:10.1016/j.watres.2006.08.009.

[19] M. Panizza, C.A. Martinez-Huitle, Role of electrode materials for the anodic oxidation of a real landfill leachate – Comparison between Ti–Ru–Sn ternary oxide, PbO2 and boron-doped diamond anode, Chemosphere. 90 (2013) 1455–1460. doi:10.1016/j.chemosphere.2012.09.006.

[20] G. Zhao, Y. Pang, L. Liu, J. Gao, B. Lv, Highly efficient and energy-saving sectional treatment of landfill leachate with a synergistic system of biochemical treatment and electrochemical oxidation on a boron-doped diamond electrode, Journal of Hazardous Materials. 179 (2010) 1078–1083. doi:10.1016/j.jhazmat.2010.03.115.

[21] A. Fernandes, M.J. Pacheco, L. Ciríaco, A. Lopes, Anodic oxidation of a biologically treated leachate on a boron-doped diamond anode, Journal of Hazardous Materials. 199–200 (2012) 82–87. doi:10.1016/j.jhazmat.2011.10.074.

[22] A. Cabeza, A. Urtiaga, M.-J. Rivero, I. Ortiz, Ammonium removal from landfill leachate by anodic oxidation, Journal of Hazardous Materials. 144 (2007) 715–719. doi:10.1016/j.jhazmat.2007.01.106.

[23] B. Zhou, Z. Yu, Q. Wei, H. Long, Y. Xie, Y. Wang, Electrochemical oxidation of biological pretreated and membrane separated landfill leachate concentrates on boron doped diamond anode, Applied Surface Science. 377 (2016) 406–415. doi:10.1016/j.apsusc.2016.03.045.

[24] A. Urtiaga, A. Rueda, Á. Anglada, I. Ortiz, Integrated treatment of landfill leachates including electrooxidation at pilot plant scale, Journal of Hazardous Materials. 166 (2009) 1530–1534. doi:10.1016/j.jhazmat.2008.11.037.

[25] Á. Anglada, A. Urtiaga, I. Ortiz, D. Mantzavinos, E. Diamadopoulos, Boron-doped diamond anodic treatment of landfill leachate: Evaluation of operating variables and formation of oxidation by-products, Water Research. 45 (2011) 828–838. doi:10.1016/j.watres.2010.09.017.

[26] Á. Anglada, A. Urtiaga, I. Ortiz, Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications, J. Chem. Technol. Biotechnol. 84 (2009) 1747–1755. doi:10.1002/jctb.2214.

[27] T. Zhu, Y. Zhang, G. Bu, X. Quan, Y. Liu, Producing nitrite from anodic ammonia oxidation to accelerate anammox in a bioelectrochemical system with a given anode potential, Chemical Engineering Journal. 291 (2016) 184–191. doi:10.1016/j.cej.2016.01.099.

[28] T. Li, X. Li, J. Chen, G. Zhang, H. Wang, Treatment of Landfill Leachate by Electrochemical Oxidation and Anaerobic Process, Water Environment Research. 79 (2007) 514–520. doi:10.2175/106143006X115435.

[29] S. Qiao, X. Yin, J. Zhou, Application of cathode modified by reduced graphene oxide/polypyrrole to enhance anammox activity, RSC Adv. 6 (2016) 97208–97215. doi:10.1039/C6RA18941E.

[30] Z. Liang, J. Liu, Landfill leachate treatment with a novel process: Anaerobic ammonium oxidation (Anammox) combined with soil infiltration system, Journal of Hazardous Materials. 151 (2008) 202–212. doi:10.1016/j.jhazmat.2007.05.068.

[31] S. Fudala-Ksiazek, E. Kulbat, A. Luczkiewicz, Nitrification, denitrification, and dephosphatation capability of activated sludge during co-treatment of intermediate-age landfill leachates with municipal wastewater, Environmental Technology. 0 (2017) 1–11. doi:10.1080/09593330.2017.1317842.

[32] EUR-Lex - 31999L0031 - EN - EUR-Lex, (n.d.). http://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX%3A31999L0031 (accessed August 22, 2017).

[33] S. Fudala-Ksiazek, M. Pierpaoli, A. Luczkiewicz, Fate and significance of phthalates and bisphenol A in liquid by-products generated during municipal solid waste mechanical-biological pre-treatment and disposal, Waste Management. 64 (2017) 28–38. doi:10.1016/j.wasman.2017.03.040.

[34] Directive 2008/98/EC on waste (Waste Framework Directive) - Environment - European Commission, (n.d.). http://ec.europa.eu/environment/waste/framework/ (accessed August 22, 2017).

[35] R. Bogdanowicz, A. Fabiańska, L. Golunski, M. Sobaszek, M. Gnyba, J. Ryl, K. Darowicki, T. Ossowski, S.D. Janssens, K. Haenen, E.M. Siedlecka, Influence of the boron doping level on the electrochemical oxidation of the azo dyes at Si/BDD thin film electrodes, Diamond and Related Materials. 39 (2013) 82–88. doi:10.1016/j.diamond.2013.08.004.

[36] American Public Health Association, American Water Works Association, Water Environment Federation, Standard methods for the examination of water and wastewater, APHA-AWWA-WEF, Washington, D.C., 2005.

[37] S.R. Weijers, On BOD tests for the determination of biodegradable COD for calibrating Activated Sludge Model No. 1, Water Science and Technology. 39 (1999) 177–184. doi:10.1016/S0273-1223(99)00077-3.

[38] C. Flox, P.-L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, C. Arias, E. Brillas, Solar photoelectro-Fenton degradation of cresols using a flow reactor with a boron-doped diamond anode, Applied Catalysis B: Environmental. 75 (2007) 17–28. doi:10.1016/j.apcatb.2007.03.010.

[39] A.C. Ferrari, J. Robertson, Raman spectroscopy of amorphous, nanostructured, diamond–like carbon, and nanodiamond, Phil. Trans. R. Soc. Lond. A. 362 (2004) 2477–2512. doi:10.1098/rsta.2004.1452.

[40] P.W. May, W.J. Ludlow, M. Hannaway, P.J. Heard, J.A. Smith, K.N. Rosser, Raman and conductivity studies of boron-doped microcrystalline diamond, facetted nanocrystalline diamond and cauliflower diamond films, Diamond and Related Materials. 17 (2008) 105–117. doi:10.1016/j.diamond.2007.11.005.

[41] X.Z. Liao, R.J. Zhang, C.S. Lee, S.T. Lee, Y.W. Lam, The influence of boron doping on the structure and characteristics of diamond thin films, Diamond and Related Materials. 6 (1997) 521–525. doi:10.1016/S0925-9635(96)00640-1.

[42] W.L. Wang, M.C. Polo, G. Sánchez, J. Cifre, J. Esteve, Internal stress and strain in heavily boron- doped diamond films grown by microwave plasma and hot filament chemical vapor deposition, Journal of Applied Physics. 80 (1996) 1846–1850. doi:10.1063/1.362996.

[43] B.L. Willems, G. Zhang, J. Vanacken, V.V. Moshchalkov, S.D. Janssens, K. Haenen, P. Wagner, Granular superconductivity in metallic and insulating nanocrystalline boron-doped diamond thin films, J. Phys. D: Appl. Phys. 43 (2010) 374019. doi:10.1088/0022-3727/43/37/374019.

[44] Z.V. Živcová, O. Frank, V. Petrák, H. Tarábková, J. Vacík, M. Nesládek, L. Kavan, Electrochemistry and in situ Raman spectroelectrochemistry of low and high quality boron doped diamond layers in aqueous electrolyte solution, Electrochimica Acta. 87 (2013) 518–525. doi:10.1016/j.electacta.2012.09.031.

[45] Y.-G. Lu, S. Turner, J. Verbeeck, S.D. Janssens, P. Wagner, K. Haenen, G. Van Tendeloo, Direct visualization of boron dopant distribution and coordination in individual chemical vapor deposition nanocrystalline B-doped diamond grains, Appl. Phys. Lett. 101 (2012) 041907. doi:10.1063/1.4738885.

[46] K.E. Bennet, K.H. Lee, J.N. Kruchowski, S.-Y. Chang, M.P. Marsh, A.A. Van Orsow, A. Paez, F.S. Manciu, Development of Conductive Boron-Doped Diamond Electrode: A microscopic, Spectroscopic, and Voltammetric Study, Materials (Basel). 6 (2013) 5726–5741. doi:10.3390/ma6125726.

[47] P. Ashcheulov, J. Šebera, A. Kovalenko, V. Petrák, F. Fendrych, M. Nesládek, A. Taylor, Z. Vlčková Živcová, O. Frank, L. Kavan, M. Dračínský, P. Hubík, J. Vacík, I. Kraus, I. Kratochvílová, Conductivity of boron-doped polycrystalline diamond films: influence of specific boron defects, The European Physical Journal B. 86 (2013). doi:10.1140/epjb/e2013-40528-x.

[48] A. Zieliński, R. Bogdanowicz, J. Ryl, L. Burczyk, K. Darowicki, Local impedance imaging of boron-doped polycrystalline diamond thin films, Appl. Phys. Lett. 105 (2014) 131908. doi:10.1063/1.4897346.

[49] J. Ryl, R. Bogdanowicz, P. Slepski, M. Sobaszek, K. Darowicki, Dynamic Electrochemical Impedance Spectroscopy (DEIS) as a Tool for Analyzing Surface

Oxidation Processes on Boron-Doped Diamond Electrodes, J. Electrochem. Soc. 161 (2014) H359–H364. doi:10.1149/2.016406jes.

[50] G.R. Salazar-Banda, L.S. Andrade, P.A.P. Nascente, P.S. Pizani, R.C. Rocha-Filho, L.A. Avaca, On the changing electrochemical behaviour of boron-doped diamond surfaces with time after cathodic pre-treatments, Electrochimica Acta. 51 (2006) 4612–4619. doi:10.1016/j.electacta.2005.12.039.

[51] A.I. del Río, J. Molina, J. Bonastre, F. Cases, Study of the electrochemical oxidation and reduction of C.I. Reactive Orange 4 in sodium sulphate alkaline solutions, Journal of Hazardous Materials. 172 (2009) 187–195. doi:10.1016/j.jhazmat.2009.06.147.

[52] S.A. Alves, T.C.R. Ferreira, N.S. Sabatini, A.C.A. Trientini, F.L. Migliorini, M.R. Baldan, N.G. Ferreira, M.R.V. Lanza, A comparative study of the electrochemical oxidation of the herbicide tebuthiuron using boron-doped diamond electrodes, Chemosphere. 88 (2012) 155–160. doi:10.1016/j.chemosphere.2012.02.042.

[53] M. Panizza, G. Cerisola, Application of diamond electrodes to electrochemical processes, Electrochimica Acta. 51 (2005) 191–199. doi:10.1016/j.electacta.2005.04.023.

[54] S. Fierro, K. Abe, C. Christos, Y. Einaga, Influence of Doping Level on the Electrochemical Oxidation of Formic Acid on Boron Doped Diamond Electrodes, J. Electrochem. Soc. 158 (2011) F183–F189. doi:10.1149/2.050112jes.

[55] D. Medeiros de Araújo, P. Cañizares, C.A. Martínez-Huitle, M.A. Rodrigo, Electrochemical conversion/combustion of a model organic pollutant on BDD anode: Role of sp3/sp2 ratio, Electrochemistry Communications. 47 (2014) 37–40. doi:10.1016/j.elecom.2014.07.017.

[56] M. Shestakova, M. Sillanpää, Electrode materials used for electrochemical oxidation of organic compounds in wastewater, Rev Environ Sci Biotechnol. 16 (2017) 223–238. doi:10.1007/s11157-017-9426-1.

[57] M. Pirsaheb, E. Azizi, A. Almasi, M. Soltanian, T. Khosravi, M. Ghayebzadeh, K. Sharafi, Evaluating the efficiency of electrochemical process in removing COD and NH4-N from landfill leachate, Desalination and Water Treatment. 57 (2016) 6644–6651. doi:10.1080/19443994.2015.1012560.

[58] G. Pérez, J. Saiz, R. Ibañez, A.M. Urtiaga, I. Ortiz, Assessment of the formation of inorganic oxidation by-products during the electrocatalytic treatment of ammonium from landfill leachates, Water Research. 46 (2012) 2579–2590. doi:10.1016/j.watres.2012.02.015.

[59] A. Fernandes, M.J. Pacheco, L. Ciríaco, A. Lopes, Anodic oxidation of a biologically treated leachate on a boron-doped diamond anode, Journal of Hazardous Materials. 199–200 (2012) 82–87. doi:10.1016/j.jhazmat.2011.10.074.

[60] J.-K. Lee, K.-R. Lee, S.-H. Hong, K.-H. Kim, B.-H. Lee, J.-H. Lim, Residual Chlorine Distribution and Disinfection during Electrochemical Removal of Dilute Ammonia from an Aqueous Solution, Journal of Chemical Engineering of Japan. 35 (2002) 285–289. doi:10.1252/jcej.35.285.

[61] M. Katayose, K. Yoshida, N. Achiwa, M. Eguchi, Safety of electrolyzed seawater for use in aquaculture, Aquaculture. 264 (2007) 119–129. doi:10.1016/j.aquaculture.2006.08.050.

[62] K. Vijayaraghavan, D. Ahmad, T.S. Bin Fadzin, In situ hypochlorous acid generation for the treatment of brackish shrimp aquaculture wastewater, Aquaculture Research. 39 (2008) 449–456. doi:10.1111/j.1365-2109.2007.01895.x.

[63] E. Lacasa, J. Llanos, P. Cañizares, M.A. Rodrigo, Electrochemical denitrificacion with chlorides using DSA and BDD anodes, Chemical Engineering Journal. 184 (2012) 66–71. doi:10.1016/j.cej.2011.12.090.

[64] M.C. Granger, G.M. Swain, The Influence of Surface Interactions on the Reversibility of Ferri/Ferrocyanide at Boron- Doped Diamond Thin- Film Electrodes, J. Electrochem. Soc. 146 (1999) 4551–4558. doi:10.1149/1.1392673.

[65] A. Pop, F. Manea, C. Radovan, D. Dascalu, N. Vaszilcsin, J. Schoonman, Non-enzymatic electrochemical detection of glycerol on boron-doped diamond electrode, Analyst. 137 (2012) 641–647. doi:10.1039/C2AN15645H.

[66] M.C. Granger, M. Witek, J. Xu, J. Wang, M. Hupert, A. Hanks, M.D. Koppang, J.E. Butler, G. Lucazeau, M. Mermoux, J.W. Strojek, G.M. Swain, Standard Electrochemical Behavior of High-Quality, Boron-Doped Polycrystalline Diamond Thin-Film Electrodes, Anal. Chem. 72 (2000) 3793–3804. doi:10.1021/ac0000675.

[67] E. Guinea, F. Centellas, E. Brillas, P. Cañizares, C. Sáez, M.A. Rodrigo, Electrocatalytic properties of diamond in the oxidation of a persistant pollutant, Applied Catalysis B: Environmental. 89 (2009) 645–650. doi:10.1016/j.apcatb.2009.01.028.

[68] K. Ushizawa, K. Watanabe, T. Ando, I. Sakaguchi, M. Nishitani-Gamo, Y. Sato, H. Kanda, Boron concentration dependence of Raman spectra on {100} and {111} facets of B-doped CVD diamond, Diamond and Related Materials. 7 (1998) 1719–1722. doi:10.1016/S0925-9635(98)00296-9.

[69] E. Brillas, M.Á. Baños, M. Skoumal, P.L. Cabot, J.A. Garrido, R.M. Rodríguez, Degradation of the herbicide 2,4-DP by anodic oxidation, electro-Fenton and photoelectro-Fenton using platinum and boron-doped diamond anodes, Chemosphere. 68 (2007) 199–209. doi:10.1016/j.chemosphere.2007.01.038.

[70] F.C. Moreira, J. Soler, A. Fonseca, I. Saraiva, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Electrochemical advanced oxidation processes for sanitary landfill leachate remediation: Evaluation of operational variables, Applied Catalysis B: Environmental. 182 (2016) 161–171. doi:10.1016/j.apcatb.2015.09.014.

[71] G.V. Buxton, A.J. Elliot, Rate constant for reaction of hydroxyl radicals with bicarbonate ions, International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry. 27 (1986) 241–243. doi:10.1016/1359-0197(86)90059-7.

[72] A.J. Bard, R. Parsons, J. Jordan, Standard Potentials in Aqueous Solution, 1st edition, CRC Press, New York, 1985.

[73] J.L. de Morais, P.P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, Journal of Hazardous Materials. 123 (2005) 181–186. doi:10.1016/j.jhazmat.2005.03.041.

[74] O. Primo, M.J. Rivero, I. Ortiz, Photo-Fenton process as an efficient alternative to the treatment of landfill leachates, Journal of Hazardous Materials. 153 (2008) 834–842. doi:10.1016/j.jhazmat.2007.09.053.

[75] T.F.C.V. Silva, A. Fonseca, I. Saraiva, V.J.P. Vilar, R.A.R. Boaventura, Biodegradability enhancement of a leachate after biological lagooning using a solar driven photo-Fenton reaction, and further combination with an activated sludge biological process, at pre-industrial scale, Water Research. 47 (2013) 3543–3557. doi:10.1016/j.watres.2013.04.008.

[76] T.F.C.V. Silva, M.E.F. Silva, A.C. Cunha-Queda, A. Fonseca, I. Saraiva, M.A. Sousa, C. Gonçalves, M.F. Alpendurada, R.A.R. Boaventura, V.J.P. Vilar, Multistage treatment system for raw leachate from sanitary landfill combining biological nitrification–denitrification/solar photo-Fenton/biological processes, at a scale close to industrial – Biodegradability enhancement and evolution profile of trace pollutants, Water Research. 47 (2013) 6167–6186. doi:10.1016/j.watres.2013.07.036.

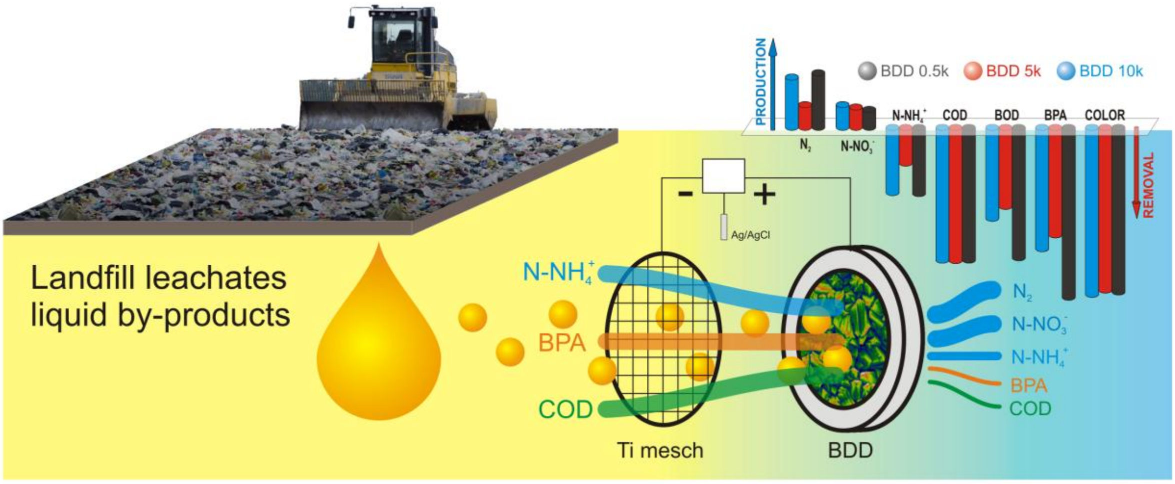
[77] N. Kishimoto, E. Sugimura, Feasibility of an electrochemically assisted Fenton method using Fe2 +/HOCl system as an advanced oxidation process, Water Science and Technology. 62 (2010) 2321–2329. doi:10.2166/wst.2010.203.

[78] W. P, L. Iw, F. Hh, [Landfill leachate treatment by anaerobic process and electrochemical oxidation]., Huan Jing Ke Xue. 22 (2001) 70–73.

[79] G. Chen, Electrochemical technologies in wastewater treatment, Separation and Purification Technology. 38 (2004) 11–41. doi:10.1016/j.seppur.2003.10.006.

Highlights

- Diamond anodes were revealed as an efficient electrodes in the landfill leachates oxidation
- A decrease in the sp^3/sp^2 ratio increased the Cl_2/HOCl evolution at diamond anodes
- Electrochemical oxidation degraded micropollutants, such as bisphenol A
- Acidic conditions and the addition of 10 mg/L of Fe^{2+} inhibited N-NH_4 elimination
- Electrochemically pre-treaded landfill leachates were appropriate for further biological nitrogen removal


PRODUCTION
BDD 0.5k
BDD 5k
BDD 10k
N_2
$N\text{-}NO_3^-$
$N\text{-}NH_4^+$
COD
BOD
BPA
COLOR
REMOVAL
Ag/AgCl
-
+
Landfill leachates
liquid by-products
$N\text{-}NH_4^+$
BPA
COD
Ti mesch
BDD
N_2
$N\text{-}NO_3^-$
$N\text{-}NH_4^+$
BPA
COD