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# 1           **Electrochemical oxidation of landfill leachate using boron-doped diamond** 2           **anodes: pollution degradation rate, energy efficiency and toxicity assessment**

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22                 leachate sampling.

## 23          **Abstract:**

24                 Electrochemical oxidation (EO), due to high efficiency and small carbon footprint, is regarded as an attractive option  
25                 for on-site treatment of highly contaminated wastewater. This work shows the effectiveness of EO using three boron-  
26                 doped diamond electrodes (BDDs) in sustainable management of landfill leachate (LL). The effect of the applied  
27                 current density (25–100 mA cm<sup>-2</sup>) and boron doping concentration (B/C ratio: 500 ppm, 10,000 ppm and 15,000 ppm)  
28                 on the performance of EO was investigated. It was found that, of the electrodes used, the one most effective at COD,  
29                 BOD<sub>20</sub> and ammonia removal (97.1%, 98.8% and 62%, respectively) was the electrode with the lowest boron doping.  
30                 Then, to better elucidate the ecological role of LLs, before and after EO, cultivation of faecal bacteria and microscopic  
31                 analysis of total (prokaryotic) cell number, together with eco-toxicity assay (*Daphnia magna*, *Thamnocephalus*  
32                 *platyurus* and *Artemia salina*) were combined for the two better-performing electrodes. The EO process was very  
33                 effective at bacterial cell inactivation using each of the two anodes, even within 2 h of contact time. In a complex

34 matrix of LLs, this is probably a combined effect of electrogenerated oxidants (hydroxyl radicals, active chlorine and  
35 sulphate radicals), which may penetrate into the bacterial cells and/or react with cellular components. The toxicity of  
36 EO-treated LLs proved to be lower than that of raw ones. Since toxicity drops with increased boron doping, it is  
37 believed that appropriate electrolysis parameters can diminish the toxicity effect without compromising the nutrient-  
38 removal and disinfection capability, although salinity of LLs and related multistep-oxidation pathways needs to be  
39 further elucidated.

40 **Keywords:** landfill leachates; boron-doped diamond electrode (BDD); advanced oxidation process; multistep-  
41 oxidation pathways; ecotoxicology; biodegradability; degradation efficacy.

42 **Abbreviations:**

43 **0.5k BDD** – Boron-doped diamond electrode with B/C ratio of 500 ppm

44 **10k BDD** – Boron-doped diamond electrode with B/C ratio of 10,000 ppm

45 **15k BDD** – Boron-doped diamond electrode with B/C ratio of 15,000 ppm

46 ***A. salina*** – *Artemia salina*

47 **AOPs** – Advanced oxidation processes

48 **B/C** – Boron-to-carbon ratio

49 **BDD** – Boron-doped diamond electrode

50 **BOD** – Biochemical oxygen demand

51 **COD** – Chemical oxygen demand

52 ***D. magna*** – *Daphnia magna*

53 **EO** – electrochemical oxidation

54 **LL** – Landfill leachate

55 **MSS** – Mineral suspended solids

56 **MSWP** – Municipal solid-waste plant

57 **TN** – Total nitrogen

58 ***T. platyurus*** – *Thamnocephalus platyurus*

59 **TSS** – Total suspended solids

60 **VSS** – Volatile suspended solids

61 **WWTP** – Wastewater treatment plant

62

63

## 64 1. Introduction

65 Landfill leachate (LL), a by-product of waste landfilling, poses a significant environmental problem  
66 worldwide (Fudala-Ksiazek et al. 2017; De Brito et al. 2019; Farsani et al. 2021). It contains such a large and complex  
67 load of pollutants that it has been included, among others, on the hazardous material list by the US EPA (items: 19 07  
68 02 and 19 07 03) (EPA 2015). Retention and recirculation are often used as an inexpensive LL treatment process;  
69 especially in low-income countries (Mendoza et al. 2010; Oktiawan et al. 2020; Zhang et al. 2021). Another often-  
70 considered option is an end-of-pipe approach, whereby LLs are discharged into the sewage system and directed to  
71 wastewater treatment plant (WWTP). But ammonia-rich LLs, which also contain high loads of non- or slowly  
72 biodegradable organic compounds, may lead to a reduction in performance of municipal WWTPs (especially, if by  
73 volume LLs constitute more than 10% of the inflow) (Fudala-Ksiazek et al. 2014; Kamaruddin et al. 2015; Mojiri  
74 et al. 2021). Moreover, in recent years, the legal requirements for treated wastewater quality standards have become  
75 more demanding (Bogacki et al. 2019; Srivastava and Singh 2021). This change has limited the direct discharge of  
76 LLs to wastewater system and forced municipal solid-waste plant (MSWP) managers to consider effective LL  
77 treatment on site (Luo et al. 2020).

78 LLs are generated by landfill cells for more than 30 years, therefore their quantity and quality result from many  
79 factors – mainly the age of the landfill cell and the decomposition stage (initial aerobic, acid anaerobic, initial and  
80 stable methanogenic), climatic conditions and operating procedures (waste stream dedicated to disposal, aeration  
81 procedures, LLs recirculation, etc.) (Abiriga et al. 2021; Farsani et al. 2021; Wilk et al. 2021). In terms of LL treatment,  
82 it is suggested that young and intermediate cells generate LLs that are more susceptible to biological treatment as  
83 compared to old ones (Aziz et al. 2010; Khoo et al. 2020; Siracusa et al. 2020; Tałałaj et al. 2021), which contain an  
84 essential amount of refractory organic matter (expressed, e.g. by  $BOD_5/COD < 0.5$ ) as well as an inadequate C/N ratio  
85 (Fudala-Ksiazek et al., 2018a, b; Tałałaj et al., 2019). But the effective treatment of LLs has also to consider their  
86 potential toxicity, due to the possible presence of xenobiotic compounds and heavy metals (Aziz et al. 2010; Bandala  
87 et al. 2021). Thus, it is generally suggested that high efficacy of LL treatment cannot be achieved via the activated  
88 sludge process (Ren et al. 2017; Grosser et al. 2018; Bandala et al. 2021), making it imperative to develop and  
89 implement more suitable treatment technologies to replace or support conventional ones.

90 Although many technologies have been tested, developed and implemented (Ying et al. 2013; Song et al. 2020;  
91 Wai et al. 2020), proper LL treatment is still an open issue, mainly in the former Eastern Bloc and developing countries,  
92 and is a very urgent topic in environmental policy (Žgajnar Gotvajn and Pavko 2015; Ahmad et al. 2020; Deng et al.  
93 2020; Pisharody et al. 2022). Nowadays, chemical and physical methods (adsorption, air stripping, chemical oxidation  
94 and precipitation, sedimentation/flotation, coagulation/flocculation, membrane technologies and biological methods  
95 (aerobic, anaerobic, or mixed) are used for LL treatment (Pereira et al. 2016; Amor et al. 2019). Unfortunately, these  
96 technologies have many disadvantages. In case of biological treatment, the changes of LLs quality and quantity cause  
97 serious operational problems (e.g. foaming or difficulties in biomass acclimation) (Payandeh et al. 2017; Cossu 2018;  
98 Ehrig et al. 2018; Teng et al. 2021). Biological methods are also not effective for the removal of toxic and recalcitrant  
99 compounds (polyaromatic hydrocarbons, polychlorinated biphenyls, etc.) and produces a remarkable amount of excess  
100 sludge (Torretta et al. 2017; Teng et al. 2021). Other, commonly used technology is membrane treatment, which

101 besides being very expensive, also causes the formation of retentate (a highly concentrated by-product that needs to  
102 be further treated by some means) (Huang et al. 2018; Suo and Ren 2021). Moreover, membranes are prone to fouling,  
103 have a generally short lifetime (Saleh and Gupta 2016; Rahmawati et al. 2021; Zhang and Hao 2021). Thus, usually  
104 the combination of different techniques (e.g., activated sludge system combined with membrane filtration) tends to be  
105 implemented as the most effective (Fudala-Ksiazek et al. 2016; Dubey 2019; Wilk et al. 2021), however, it  
106 significantly increases the investment and exploitation costs (Costa et al. 2019; Bandala et al. 2021; Mojiri et al. 2021).

107 Additional implementation possibilities are noted for AOP technologies, whose treatment effectiveness for  
108 highly contaminated wastewater has been studied with promising results (Didier et al. 2006; Tejera et al. 2019;  
109 Pierpaoli et al. 2020). AOPs have been reported as effective in removing organic matter, including recalcitrant  
110 pollutants, and in eliminating microorganisms and pathogens (Ike et al. 2019; Sánchez-Montes et al. 2020). Among  
111 AOP processes, electrochemical oxidation (EO) was found to be a promising technology for treating highly  
112 concentrated wastewater (Cheng et al. 2020; Solomon et al. 2020). Another important aspect of EO is disinfecting  
113 capability, already tested in wastewater, ballast and surface water (Kraft 2008; Lacasa et al. 2012; Cho et al. 2014;  
114 Ghernaout 2019). Operated without the addition of any chemical, EO seems to be a promising environmentally  
115 friendly technology, as compared to other disinfection methods (e.g., chlorination, photo-catalytic oxidation,  
116 ozonation) (Ferreira et al. 2020; Qiao and Xiong 2021). But strongly oxidising conditions, which allow disinfection  
117 and nutrient removal to be combined, may also result in the formation of toxic by-products, especially in a complex  
118 matrix of LLs (Jasper et al. 2017; Ambauen et al. 2020; Liu and He 2020). Moreover, a crucial point (though often  
119 overlooked) is hazard assessment of by-products generated during LL treatment. In the work of Silva et al. (2004),  
120 acute LL toxicity was assessed by *Vibrio fisheri*, *Daphnia similis*, *Artemia salina* and *Brachydanio rerio* before and  
121 after ozonation, coagulation/flocculation, and membrane fractionation treatments. It was found that acute toxicity was  
122 almost the same in all the fractionated samples, and significant toxicity removal was only achieved when high ozone  
123 doses were used (Silva et al. 2004). No significant changes in toxicity were noted during the photo-Fenton, solar TiO<sub>2</sub>-  
124 heterogeneous photocatalysis, and ozonation of LLs (Martinen et al. 2002; Prieto-Rodríguez et al. 2013; Yang et al.  
125 2022). In this term, the implementation of EO technology for treatment of a LL complex matrix has not been fully  
126 investigated.

127 So far a significant number of EO-dedicated electrode materials have been tested, such as granular activated  
128 carbon, glassy carbon, polypyrrole, graphite, massive Pt, pure and doped PbO<sub>2</sub> (Dbira et al. 2019; Wai et al. 2020;  
129 Barrios et al. 2021; Jiang et al. 2021). Among them BDD is known as a non-active electrode with a high oxygen  
130 overpotential, which produces numerous hydroxyl radicals and other powerful oxidants effective for LL oxidation (El  
131 Ouaer et al. 2017; Dec et al. 2018; Amor et al. 2019). Furthermore, it has a wide electro-chemical window (from -1.25  
132 to +2.3 V) as compared to a standard hydrogen electrode (Cornejo et al. 2020; Bogdanowicz and Ryl 2022). Thus, in  
133 this study, EO was evaluated using various boron-doped diamond anodes prepared on Nb substrate. Long-term studies  
134 on the effects of the boron doping level of diamond electrode and current densities (25–100 mA cm<sup>-2</sup>) on the efficiency  
135 of LL treatment were conducted. The sanitary condition of LLs, as well as inactivation effectiveness of  
136 microorganisms by BDD electrodes, were investigated using conventional cultivation and microscopic analysis.

137 Moreover, the eco-toxicity of raw LLs and those treated by EO was tested on model species, i.e.: *Thamnocephalus*  
138 *platyurus*, *Daphnia magna* and *Artemia salina*.

## 139 **2. Materials and methods**

### 140 **2.1. MSWP description and sampling of raw LLs**

141 The LLs originated from MSWP “Eko Dolina Lezyce” located in the Pomerania region (northern Poland),  
142 from cell operated from 2003 to 2011, which was receiving mainly municipal waste mixed with food services. The  
143 samples of raw LLs were collected to polyethylene bottles in 2018 and 2019 and transported to the laboratory (at  $4 \pm$   
144  $1$  °C), where their physicochemical properties were immediately evaluated. In total, three 24-h composite samples (10  
145 L each) as mix of discrete samples were collected.

### 146 **2.2. Analytical methods**

147 The characterization of LLs considered the measurement of the following parameters (according to the  
148 APHA 2005 standard): chemical oxygen demand (COD), total nitrogen (TN), inorganic N compounds ( $\text{N-NH}_4^+$ ,  $\text{N-NO}_3^-$ ,  $\text{N-NO}_2^-$ ), total phosphorus (TP) and orthophosphate ( $\text{P-PO}_4^{3-}$ ), which were all measured using a XION 500  
149 spectrophotometer (Dr Lange, GmbH, Germany)(APHA 2005). Conductivity, pH and oxidation-reduction potential  
150 (ORP) were determined by a portable multi-parameter meter, the HL-HQ40d multi (HACH, Germany), and 20-day  
151 biochemical oxygen demand ( $\text{BOD}_{20}$ ) by manometric respirometric BOD OxiTop® method (Fudala-Ksiazek et al.  
152 2018b). Chloride ( $\text{Cl}^-$ ) and sulphate ( $\text{SO}_4^{2-}$ ) concentrations were measured by ion chromatography using: a DIONEX  
153 3000 chromatograph (DIONEX, USA) (column: Ion Pac®AS2 [ $2 \times 250$  mm]; suppressor: ASRS-300, 2 mm; mobile  
154 phase: 4.5 mM  $\text{CO}_3^{2-}$ , 1.4 mM  $\text{HCO}_3^-$ ; flow rate: 0.38 mL  $\text{min}^{-1}$ ; detection: conductivity) (Szopińska et al. 2016), and  
155 total suspended solids (TSS), volatile suspended solids (VSSs) and mineral suspended solid (MSS) using the  
156 gravimetric method according to Polish Standards (PKN 2007).

### 158 **2.3. Preparation of BDD electrodes**

159 The BDD electrodes were deposited on two-inch Niobium substrates (Spinex, Poland) using a Microwave  
160 Plasma Assisted Chemical Vapour Deposition (MWPACVD) process. The optimized process parameters were 1%  
161  $\text{CH}_4$  of total flow equal to 300 sccm, microwave power was set to 1,300 W, the induction heating stage temperature  
162 was set to 700 °C, and process pressure was 50 Torr (Fudala-Ksiazek et al. 2018b). Three BDD electrodes  
163 characterized by different doping levels were investigated. During the BDD growth, the  $\text{B}_2\text{H}_6/\text{CH}_4$  gas ratio was kept  
164 at 500 ppm, 10,000 ppm and 15,000 ppm, in order to obtain three BDD electrodes named 0.5k BDD, 10k BDD and  
165 15k BDD, respectively. The time of the deposition was set to 12 hours. The molecular structure of the electrode surface  
166 was analysed using the Raman technique. The Raman spectra were recorded at room temperature using the micro-  
167 Raman system (InVia, Renishaw, UK) and a 514-nm argon ion laser was used for excitation. Spectra were recorded  
168 in the range of 600–3,500  $\text{cm}^{-1}$ . The surface morphology was analysed using a Scanning Electron Microscope (SEM)  
169 (EVO-40, Zeiss, Germany). To determine  $\text{sp}^3/\text{sp}^2$  ratio, the Raman spectra were deconvoluted using the Lorentzian  
170 function that allows the estimation of a real contribution of both carbon phases (OriginPro 8.0, OriginLab,  
171 Northampton, MA).



172

#### 173 2.4. Electrochemical oxidation assay

174 Samples of raw LLs were diluted using deionized water (1:1 (v:v)) prior to EO. Then, 400 mL of diluted  
175 LL sample was treated by different current densities of between 25 and 100 mA cm<sup>-2</sup> using a 500-mL single-  
176 chambered reactor (Fig S1, Supplementary Material). A magnetic stirrer (Electrochemical Stirrer, ES34, Wigo,  
177 Poland) with stirring speed of 300 rpm was used to maintain the homogeneity of sample. The electrochemical system  
178 for LL treatment was operated under the galvanostatic condition provided by the power supply (GW Instek GPD-  
179 23035, Taiwan). Both BDD anode and stainless-steel plates of cathode were flat and had an active area of 10.5 cm<sup>2</sup>,  
180 and the distance between them was 1.0 cm. The assessment of the process was performed on samples collected every  
181 two hours (15 mL volume each) for the eight hours of the experiment. All samples were degassed by mixing on a  
182 multipoint stirrer (Variomag, POLY 15 KOMED, Thermofisher Scientific, USA) at 50 rpm for 15 min, then physico-  
183 chemical analyses were performed (determination of chemical oxygen demand [COD], total nitrogen [TN], inorganic  
184 N compounds [N-NH<sub>4</sub><sup>+</sup>, N-NO<sub>3</sub><sup>-</sup>, N-NO<sub>2</sub><sup>-</sup>], 20-day biochemical oxygen demand [BOD<sub>20</sub>] concentrations, pH, and ORP  
185 according to procedures described in point 2.2). Each experiment was performed in triplicate. To reduce the effect of  
186 temperature on EO process (current density above 50 mA cm<sup>-2</sup> caused an increase of electrolytes' temperature) the  
187 experimental set-up was subjected to cooling, and the temperature was maintained at 25 ± 2 °C.

188 The energy consumption [W, kWh] was calculated by multiplying the applied current [A], electrolysis time  
189 [8 h] and the average cell voltage (E<sub>cell</sub>) [V]. Next, this value (W, kWh) was recalculated and expressed in kWh m<sup>-3</sup>,  
190 or specific energy consumption was calculated in units of COD mass [kWh kg<sup>-1</sup> COD] and per unit N-NH<sub>4</sub><sup>+</sup> mass  
191 [kWh kg<sup>-1</sup> N-NH<sub>4</sub><sup>+</sup>]. The specific energy consumption (EC) for the electrochemical cell operation was estimated from  
192 Eq. 1 per unit COD mass, or by Eq. 2 per unit N-NH<sub>4</sub><sup>+</sup> mass (Flox et al. 2007)

193 **Eq. (1)**  $EC_{COD} = (1000 \times E_{cell} \times I \times \Delta t) / (V_s [\Delta COD])$

194 **Eq. (2)**  $EC_{N-NH_4^+} = (1000 \times E_{cell} \times I \times \Delta t) / (V_s [\Delta N-NH_4^+])$

195 where: 1000 is a conversion factor (in mg/g), E<sub>cell</sub> is the average cell voltage (in V), I is the applied current (in A), Δt  
196 is the electrolysis time (in h), V<sub>s</sub> is the solution volume (in L), and (ΔCOD) is the experimental COD concentration  
197 decay (in mg L<sup>-1</sup>).

#### 198 2.5. Microbiological and toxicological assays

199 Conventional plate count was used to evaluate the sanitary condition of raw LLs. Disinfection capability of  
200 EO was also tested by calculating the inactivation rate (R) as the ratio between bacterial occurrence in raw (N<sub>0</sub>) and  
201 electrochemically treated (N<sub>t</sub>) LLs at the respective time of EO experiment (samples were taken after t = 2 h, 4 h, 6 h,  
202 8 h) according to the formula below:

203 **Eq. (3)**  $R = 1 - N_t \times N_0^{-1}$

204 The presence of faecal indicators (*E. coli* and *Enterococcus* spp.) were tested using membrane filtration  
205 according to EN ISO 9308-1:2014/A1:2017 and EN ISO 7899-2:2000, respectively (ISO 2000; PKN 2014). The  
206 number of mesophilic and psychophilic bacteria was evaluated using agar plates incubated in 37 °C and 22 °C,  
207 respectively, for seven days. All results were expressed as colony-forming units (CFU) per mL.

208 Total prokaryotic cell number (TCN), average cell volume (ACV) and prokaryote biomass (PB) in raw and  
209 treated LLs were determined by DAPI staining and direct counting using standard epifluorescence microscopy  
210 technique (Porter and Feig 1980). Samples were stained in  $1 \mu\text{g mL}^{-1}$  final DAPI concentration for 10 minutes in  
211 darkness, filtered through 0.2- $\mu\text{m}$  polycarbonate Whatman filters (Merck, Germany) and then rinsed twice with:  
212 bacterium-free distilled 1 mL of water and 1 mL of particle-free 80% ethanol. Filters were examined under UV light  
213 (BO-103W high-pressure mercury burner, 330–380-nm excitation filter, 420-nm barrier filter and 400-nm dichroic  
214 mirror) with an epifluorescence microscope (Nikon Eclipse 80i) under  $1000\times$  magnification. Bacteria were counted  
215 in two repeats of 10 separate fields. The image analysis system of Świątecki (Świątecki 1997) was applied. Bacterial  
216 biomass was estimated using the conversion factors of Norland (Norland 1993).

217 The toxicity of raw and treated LLs was determined using acute toxicity microbioassays: Thamnotoxkit F (24-  
218 hour test based on *Thamnocephalus platyurus* crustaceans), Rapidtoxkit F (a 30–60-minute test for inhibition of food  
219 intake based on *Thamnocephalus platyurus* crustaceans.), Daphtoxkit F. magna (24–48-hour test based on *Daphnia*  
220 magna crustaceans) and Artoxkit M. (4–48-hour test based on *Artemia franciscana* crustaceans). The tests were  
221 performed according to the procedures described by the manufacturer MicroBioTests Inc. (Nazareth, Belgium).

222 The following concentrations of LLs were used: 0.4, 0.8, 1.6, 3.1, 6.2, 12.5, 25, 50, and 100%. Tests were  
223 performed in triplicate. The test organisms were prepared for the experiment by incubating their cryptobiotic forms in  
224 Standard Freshwater (SF) (for *T. platyurus*), in Standard Medium (SM) (for *D. magna*) and in Standard Marine Water  
225 (SMW) (for *A. franciscana*). The assay plates containing larvae were incubated at  $20^\circ\text{C}$  in the dark. Mortality  
226 percentage was calculated after 24 hours. Additionally, *T. platyurus* and *D. magna* organisms were monitored at  
227 different times of exposure (1, 5, 20 min and 1.5, 3, 12 h). The individuals were presumed dead if they did not show  
228 any movement for 15 seconds of observation. The test was valid when the mortality of individuals in the control  
229 sample did not exceed 10%.

230 In this work, microbioassay for rapid detection of water contamination was performed using *Thamnocephalus*  
231 *platyurus* (MicroBioTests Inc., Nazareth, Belgium). This test measures a sub-lethal toxic stress after 30 minutes or  
232 1 hour exposure of the crustaceans to water samples suspected to contain toxicants.

### 233 3. Results and discussion

#### 234 3.1. Characteristics of the Raw LL

235 The LLs were collected from the cell (operated in years 2003-2011), which was receiving mainly municipal  
236 waste mixed with food services. The observed chemical profile of tested LLs matrix (Table 1), together with the stable  
237 methane production (according to personal communication), confirmed the metagenomic phase of the landfill cell  
238 (Fudala-Ksiazek et al. 2018b; Gomes et al. 2019; Tejera et al. 2019). The raw LLs were characterized by dark brown  
239 colour, high COD ( $3608 \pm 123 \text{ mg O}_2 \text{ L}^{-1}$ ) and TN ( $2148 \pm 108 \text{ mg TN L}^{-1}$ ) but relatively low BOD<sub>20</sub> value ( $403 \pm$   
240  $54 \text{ mg O}_2 \text{ L}^{-1}$ ). Such characteristic, together with LLs low biodegradability (BOD<sub>20</sub>/COD ratio  $<0.15$ ), high ammonia  
241 concentration (N-NH<sub>4</sub><sup>+</sup>/TN ratio from 0.95 to 0.98) and low TSS ( $<90 \text{ mg L}^{-1}$ ) are typical for LLs generated by mature  
242 sites (Ying et al. 2013; Peng et al. 2020). In addition to the age of the landfill cell, its exploitation also had an impact  
243 on LL quality, here especially the fact that (1) the deposition of biodegradable substances had gradually been limited

244 (Wilk et al. 2019) and that (2) the concentrate generated during on-site, reverse-osmosis treatment of LLs was  
 245 recycling back the landfill cell. The latter one can explain high concentrations of chloride ( $2690 \pm 70 \text{ mg Cl}^- \text{ L}^{-1}$ ),  
 246 sulphate ( $1353 \pm 70 \text{ mg SO}_4^{2-} \text{ L}^{-1}$ ) and electrolytic conductivity of raw LLs ranging from 21.2 to 26.8  $\text{mS cm}^{-1}$ .

247 Table 1. Characteristic of raw landfill leachates [mean<sup>1</sup>  $\pm$  SD]

	Parameter	Value
<b>Organic and inorganic matter characteristics [mg L<sup>-1</sup>]</b>	COD	3608 $\pm$ 123
	BOD <sub>20</sub>	403 $\pm$ 54
	BOD <sub>20</sub> /COD	0.12 $\pm$ 0.01
	TSS	71 $\pm$ 10
	MSS	38 $\pm$ 12
	VSS	33 $\pm$ 10
<b>Nitrogen forms [mg L<sup>-1</sup>]</b>	N-NH <sub>4</sub> <sup>+</sup>	2069 $\pm$ 93
	N-NO <sub>3</sub> <sup>-</sup>	9.4 $\pm$ 7.1
	N-NO <sub>2</sub> <sup>-</sup>	0.40 $\pm$ 0.10
	TN	2148 $\pm$ 108
	N-NH <sub>4</sub> <sup>+</sup> /TN	0.97 $\pm$ 0.02
<b>Phosphate forms [mg L<sup>-1</sup>]</b>	P-PO <sub>4</sub> <sup>3-</sup>	10.7 $\pm$ 1.2
	TP	15.3 $\pm$ 1.0
	P-PO <sub>4</sub> <sup>3-</sup> /TP	0.70 $\pm$ 0.10
<b>Other ions [mg L<sup>-1</sup>]</b>	Cl <sup>-</sup>	2690 $\pm$ 70
	SO <sub>4</sub> <sup>2-</sup>	1353 $\pm$ 70
	S <sup>2-</sup>	8.70 $\pm$ 0.80
<b>Physicochemical parameters</b>	pH	7.80 $\pm$ 0.10
	redox [mV]	-414.0 $\pm$ 7.6
	Conductivity [ $\text{mS cm}^{-1}$ ]	24.0 $\pm$ 2.8

<sup>1)</sup> number of samples n = 3

248

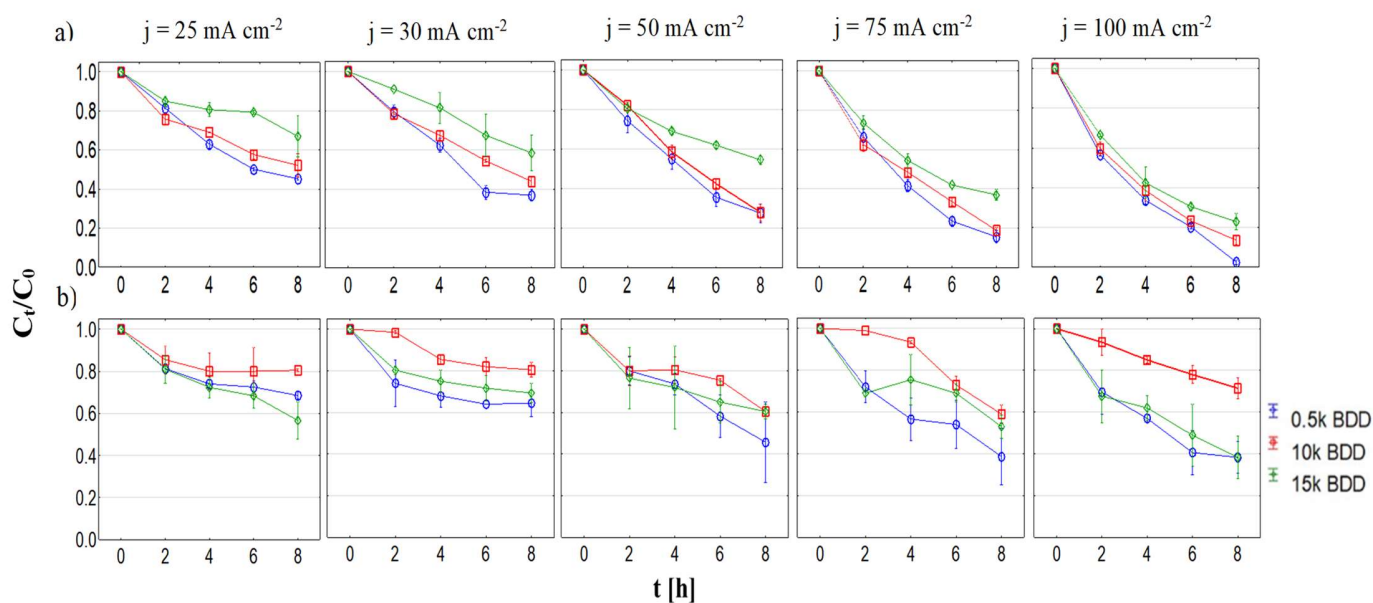
### 249 3.2. Results of the electrochemical oxidation of LL

250 According to the Comminellis group model (Panizza et al. 2008, 2010; Urtiaga et al. 2012), oxidation of  
 251 organic matter is mainly caused by hydroxyl radicals ( $\cdot\text{OH}$ ) through direct and/or indirect oxidation. Although, in  
 252 complex matrix as LLs, a BDD anode is suspected to generate strong oxidants from salts such as: sulfates, carbonates  
 253 and chlorides (Serrano 2014; Patra et al. 2020; Du et al. 2021). Taking into consideration the high concentration of  
 254 chloride ions ( $2620\text{--}2760 \text{ mg L}^{-1}$ ) in the tested LLs, active chlorine ( $\text{HOCl}$ ,  $\text{OCl}^-$ ,  $\text{Cl}_2$ ) may also play a significant role  
 255 during EO-treatment, applied in this study. Ding et al. (2017) and Lacasa et al. (2012) have described that active  
 256 chlorine has a significant impact on N-NH<sub>4</sub><sup>+</sup> removal from wastewater (Lacasa et al. 2012; Ding et al. 2017). Detailed  
 257 EO mechanisms of ammonium species in the presence of Cl<sup>-</sup> ions is presented in Fig. S2 (see in Supplementary



258 Material). Furthermore, recent studies (Ukundimana et al. 2018; Ding et al. 2020) have shown that if wastewater has  
 259 an excess of active chlorine needed for oxidation of ammonium compounds, an improvement in the oxidation of  
 260 organic compounds is also achieved at high current densities. Nevertheless, above a threshold NaCl concentration, the  
 261 indirect oxidation process near the anode and in the bulk solution can hinder the oxygen evolution reaction on the  
 262 BDD surface by the interaction between hydroxyl radicals (physisorbed) and  $\text{Cl}^-$  to form active chlorine species (de  
 263 Moura et al. 2015). Strong oxidants such as sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) can be electrogenerated using a BDD anode, by  
 264 reaction of  $\text{HSO}_4^-$  and undissociated  $\text{H}_2\text{SO}_4$  present in LLs with  $(\cdot\text{OH})$  (Serrano et al. 2002). Available scientific  
 265 publications report that the removal of organic pollutants can be 10–15-fold higher when sulfate ions are present in  
 266 electrolyte compared to  $\cdot\text{OH}$ -based anodic oxidation via indirect oxidation (Agustina et al. 2019; Cheng et al. 2020).  
 267 Nevertheless, it should be emphasized that sulfate radicals do not have such a significant effect on the removal of  
 268 ammonia as chloride ions. Moreover, the role of sulfate radicals in mineralization of organic matter and ammonia  
 269 oxidation in LLs matrix still remains little known (Lan et al. 2017; Wang et al. 2021). Hence, salinity of LLs and the  
 270 related multistep oxidation pathway process need to be further elucidated in terms of organic matter mineralization  
 271 and nitrogen removal (Chen et al. 2019).

272 In this study, the COD removal using three BDD electrodes with different boron doping levels is shown in  
 273 Fig. 1a as a function of normalized concentration ( $C_t/C_0$ ) and EO-treatment time.

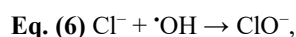
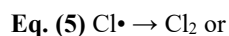
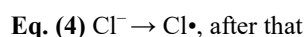


274  
 275 **Fig. 1** (a) COD and (b)  $\text{N-NH}_4^+$  changes in LLs with different BDD anodes and current densities (25–100  $\text{mA cm}^{-2}$ )  
 276 during 8 h electrolysis time

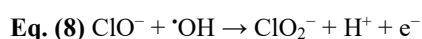
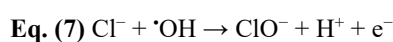
277 It can be ascertained that the rate of COD reduction increased with increasing current densities. In general,  
 278 all experiments showed that the most effective electrode in COD and  $\text{BOD}_{20}$  removal was 0.5k BDD (Fig. 1a and  
 279 Supplementary Material, Table S1). After eight hours of treatment with an applied current density of 100  $\text{mA cm}^{-2}$ ,  
 280 the  $C_t/C_0$  for COD and  $\text{BOD}_{20}$  was equal to 0.03 and 0.1, respectively. In comparison, under the same conditions,  $C_t/C_0$   
 281 for COD was 0.23 using 15k BDD and 0.14 using 10k BDD. Moreover, after 8 h  $C_t/C_0$  for  $\text{BOD}_{20}$  was 0.03 and 0.37

282 for 15k and 10k, respectively. Efficient organic matter removal can therefore be achieved by using BDD electrodes  
 283 with a higher  $sp^3/sp^2$  ratio (the lower-doped), which increases production of hydroxyl radical (Espinoza et al. 2018).  
 284 The largest amount of COD was removed during the first four hours of the process (Fig. 1a and Supplementary  
 285 Material, Table S2). With applied current density of  $100 \text{ mA cm}^{-2}$  an increasing biodegradability index ( $BOD_{20}/COD$   
 286 ratio) was observed in the EO-treated wastewater (e.g. from 0.11 in non-treated LLs to 0.26 using 0.5k BDD, and  
 287 from 0.11 LLs to 0.29 using 10k BDD). However, using the 15k BDD electrode, an inverse relationship was noted  
 288 (from 0.11 to 0.06). Changes in the biodegradability index were not high, though, which may have been influenced  
 289 by the formation of non-biodegradable intermediates during the EO-treatment process.

290 In turn, nitrogen compounds were not removed as effectively as was COD. The reasons for this could be  
 291 insufficient  $Cl^-$  concentration in the tested samples and excessive organic matter content. According to the literature,  
 292  $N-NH_4^+$  is commonly oxidized via a chlorine-mediated pathway ( $Cl_2/HOCl$ ) and production of chlorinated compounds  
 293 increased by using BDD electrodes with a lower  $sp^3/sp^2$  ratio (Medeiros De Araújo et al. 2014; Espinoza et al. 2018).  
 294 BDD anodes promote the generation of hydroxyl radicals, and the high content of chloride ions induces the  
 295 simultaneous formation of free chlorine, which is responsible for the indirect oxidation of ammonium (Supplementary  
 296 Material, Fig. S2). However, chlorine evolution may be enhanced at lower COD concentrations (Fernandes et al.  
 297 2014). A higher active chlorine concentration may be found at lower COD concentration because of the limited  
 298 reaction with organic compounds. Since the production of chlorinated compounds, possibly follows the reaction  
 299 pathway (Laheäär et al. 2015)



303 the presence of organic matter hinders the production those stable oxidants, by reacting directly with the hydroxyl  
 304 radical, thus limiting also the further production of oxochlorinated compounds:



305 Hence, higher COD concentration could result in limited ammonium oxidation rates. The effective removal  
 306 of high ammonium concentrations by EO can be achieved using very high chlorine concentrations (*ca* 5,000 to  
 307 20,000  $\text{mg L}^{-1}$ ). However, this may lead to the formation of hazardous organic compounds as final products, e.g.  
 308 trihalomethane. In research conducted by Perez et al. (2012) it was found that during 2 h of LLs electrolysis 64, 82  
 309 and 98% of  $N-NH_4^+$  was removed from samples containing 5,000, 10,000 and 20,000  $\text{mg L}^{-1}$  of  $Cl^-$ , respectively (Pérez  
 310 et al. 2012). This phenomenon was also confirmed by Ding et al. (2017) and Lacasa et al. (2012).

311 In our study, increasing specific current densities achieve higher  $N-NH_4^+$  and TN removal rates (Fig. 1b;  
 312 Supplementary Material, Fig. S3c). After eight hours of treatment with an applied current density of  $100 \text{ mA cm}^{-2}$ , the



313  $C_i/C_0$  for TN was 0.61, 0.69 and 0.51 using 0.5k BDD, 10k BDD and 15k BDD, respectively. In turn,  $C_i/C_0$  after 8 h  
314 for  $N-NH_4^+$  ( $j = 100 \text{ mA cm}^{-2}$ ) was 0.38 (0.5k BDD), 0.59 (10k BDD) and 0.38 (15k BDD).  $N-NH_4^+/TN$  for raw LLs  
315 was in the range 0.88–0.99, and after 8 h of treatment ( $j = 100 \text{ mA cm}^{-2}$ ) it was in the range 0.62–0.82. This difference  
316 shows that after EO-treatment ammonia ions are either transformed to nitrate or nitrite forms, and only partly to  
317 gaseous nitrogen. For the current density range of 25–75  $\text{mA cm}^{-2}$  both TN and  $N-NH_4^+$  were most effectively removed  
318 in the first four hours of the process. For  $j = 100 \text{ mA cm}^{-2}$  TN and  $N-NH_4^+$ , removal rates are more stable over the  
319 whole electrolysis time (8 h) (Fig. 1b; Supplementary Material, Fig. S3c). A similar dependence was observed by  
320 Ghazouani et al. (2017) and Zhou et al. (2016) using BDD silicon-based electrodes (with a set-up of three electrodes  
321 with  $70 \text{ cm}^2$  surface area each) for municipal wastewater treatment. During the process, ammonium nitrogen was  
322 removed mainly in the first hour of EO, after which its concentration stabilized.

323 Nevertheless, as already mentioned in previous studies (Fudala-Ksiazek et al. 2018b) it was expected that,  
324 due to the high concentration of ammonia nitrogen in the tested non-treated LLs, nitrate is generated during EO and,  
325 in fact, the total nitrogen will not be removed at a significant level. Nitrate concentrations show a notable increase for  
326 all tested current densities during the application of 0.5k BDD (Supplementary Material, Fig. S3a). With the  
327 application of 0.5k BDD, due to the lower boron doping level, direct oxidation of ammonium is predominant reaction  
328 (in comparison to other tested BDD electrodes) with the reaction expressed in Eq. 11 (Wilk et al. 2021).



330 No increase in nitrate is observed during the EO process with the application of 10k BDD, and in the case of 15k BDD  
331 the increase in this species varied irregularly according to the current applied (Supplementary Material, Fig. S3a).  
332 Hence, it is observed that the current density affects the process of nitrate formation, while the boron doping affects  
333 the efficiency, resulting in the better performance of this reaction (Eq. 11) at the lower doping level. At the same time,  
334 an increase in nitrite ions (from  $0.22 \text{ mg L}^{-1}$  up to  $28.3 \text{ mg L}^{-1}$  for 15k BDD,  $j = 100 \text{ mA cm}^{-2}$ ) was detected during  
335 eight hours of process (Supplementary Material, Fig. S3b). The nitrite increase during electrolysis is directly related  
336 to the increase in nitrates and the reaction given in Eq. 12 (Ghazouani et al., 2017). This reaction is reversible; hence,  
337 it is hard to observe any tendency in nitrite concentration during the EO process.



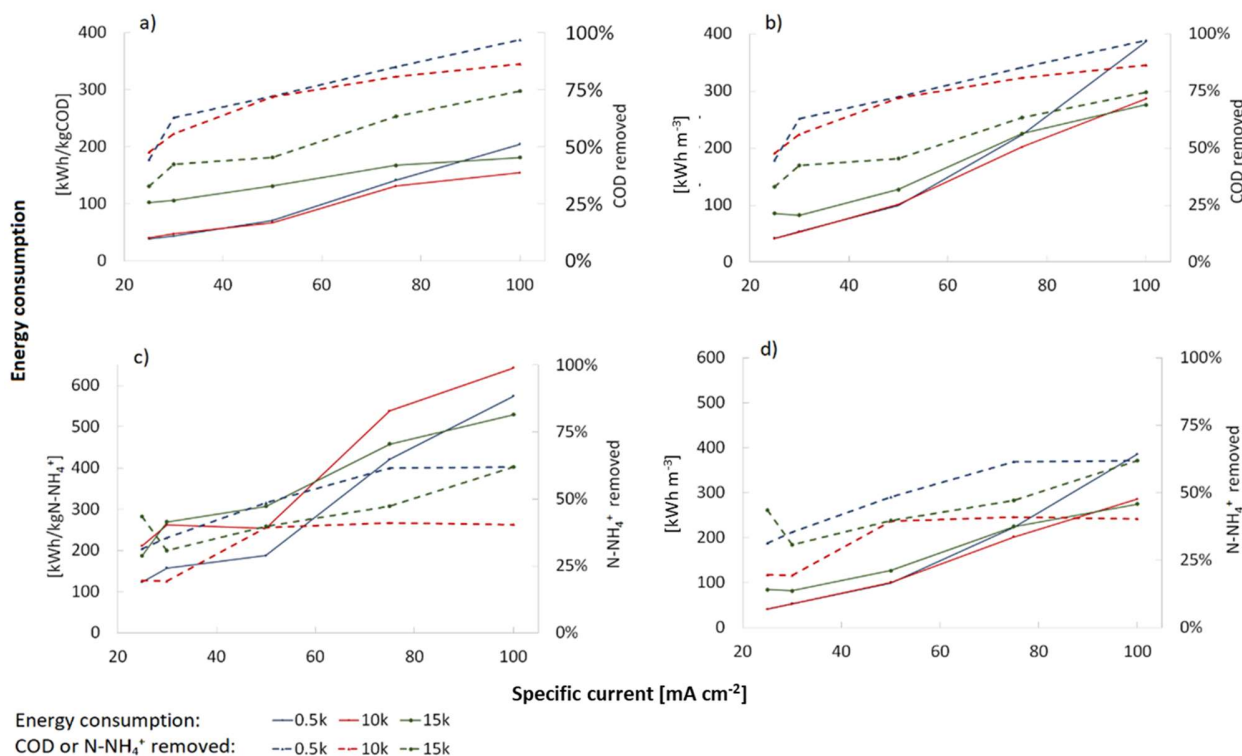
339 The pH of treated LLs basically increased over the process duration (Supplementary Material, Fig. S4),  
340 reaching the maximum value after eight hours of EO. An increase was observed from 7.81 up to 9.58 (0.5k BDD,  $j =$   
341  $100 \text{ mA cm}^{-2}$ ). Together with the pH increase, the current efficiency for hydroxyl radical formation may decrease and  
342 at the same time the oxygen evolution reaction may occur more intensively (Zhang et al. 2013). Hence, having more  
343 alkaline conditions, oxygen is generated at a greater rate, which consequently slows down the rate of  $\cdot OH$  generation  
344 (McBeath et al. 2019). Moreover, competitive reactions of  $\cdot OH$  with the organic matter (Fig. 1a) may also influence  
345  $NH_4^+$  degradation rate, which was also confirmed by our previous studies (Wilk et al. 2021). Then, a decrease in  
346 pollutant degradation rate is observed. As already mentioned, this phenomenon is observed after approximately four  
347 hours of process (see Fig. 1).

348 Another important aspect of EO control is energy consumption analysis. Detailed evaluation of energy consumption  
349 during eight hours of processes is presented in Fig. 2. An increase in applied specific current results in a higher  $EC_{COD}$   
350 and  $EC_{N-NH_4^+}$  value (Fig. 2a, c). The highest COD removal rate, which was 97.1%, required energy equal to 205 kWh  
351  $kg^{-1}$  COD and 386 kWh  $m^{-3}$  (0.5k BDD,  $j = 100 \text{ mA cm}^{-2}$ ). The highest N- $NH_4^+$  removal rate, equal to 62% was  
352 achieved by 0.5k BDD and 15k BDD after 8 h of process with an applied current density of  $100 \text{ mA cm}^{-2}$ . Under these  
353 conditions  $EC_{N-NH_4^+}$  was 575 and 530 kWh  $kg^{-1}$  N- $NH_4^+$ , for 0.5k BDD and 15k BDD, respectively. We see the  
354 difference between maximum achieved removal for COD – 97.1% and N- $NH_4^+$ – 62%. This also influence specific  
355 energy consumption. That is why higher EC values are we observed for N- $NH_4^+$ , than for COD. A result obtained by  
356 Ghazouani et al. (2017) with the application of BDD electrode ( $j = 37.7 \text{ mA cm}^{-2}$ ) shows that for 91% of COD removal  
357 from municipal wastewater 230 kWh  $kg^{-1}$  COD is required. However, the initial concentration of the studied  
358 wastewater was  $920 \text{ mg L}^{-1}$ . At the same time, the authors pointed out that an increase in COD content involved a  
359 significant decrease in  $EC_{COD}$ , which was also highlighted by Fernandes et al. (2013). Hence, this tendency promotes  
360 the BDD EO technique for the treatment of high COD-load LLs and also condensed by-products generated during the  
361 application of reverse osmosis.

362 Moreover, as was also mentioned by Ghazouani et al. (2017), the EO process is regarded as relatively  
363 expensive in comparison to the conventional treatment and, from an economical point of view, should be considered  
364 more as a combined process or as an auxiliary unit. Despite its relatively high energy consumption, the big advantage  
365 of applying EO in LLs (and other industrial wastewater) treatment is that it generates no by-products, such as highly  
366 contaminated condensate, which always occurs with reverse osmosis and any other filtration method (Pressman et al.  
367 2012; Chen et al. 2021). EO-treatment of LLs can be also regarded as a competitive method for activated carbon (Jin  
368 et al. 2013; Bourgin et al. 2018) and coagulation (Zhao et al. 2013) technologies.

369 On the other hand, interesting results presented by Fernandes et al. (2013) show that energy consumption  
370 decreases in experiments, which were performed in a semi-pilot plant operating in batch mode with recirculation.  
371 With the initial COD of  $8,900 \pm 800 \text{ mg L}^{-1}$ , 69% COD removal was achieved during following experimental  
372 condition:  $j = 200 \text{ mA cm}^{-2}$ , flow =  $360 \text{ L h}^{-1}$ , reactor volume 5 L, where specific energy consumption was estimated  
373 at  $91.1 \text{ kWh kg}^{-1}$  COD, which is far less than in the case of batch experiments without LL recirculation.





374  
 375 **Fig. 2** (a and b) Specific energy consumption after 8 h of EO process expressed in [kWh kg<sup>-1</sup> COD], [kWh kg<sup>-1</sup> N-  
 376 NH<sub>4</sub><sup>+</sup>] and [kWh m<sup>-3</sup>], at the different current densities plotted against COD removed [%] and (c and d) N-NH<sub>4</sub><sup>+</sup>  
 377 removed [%]  
 378

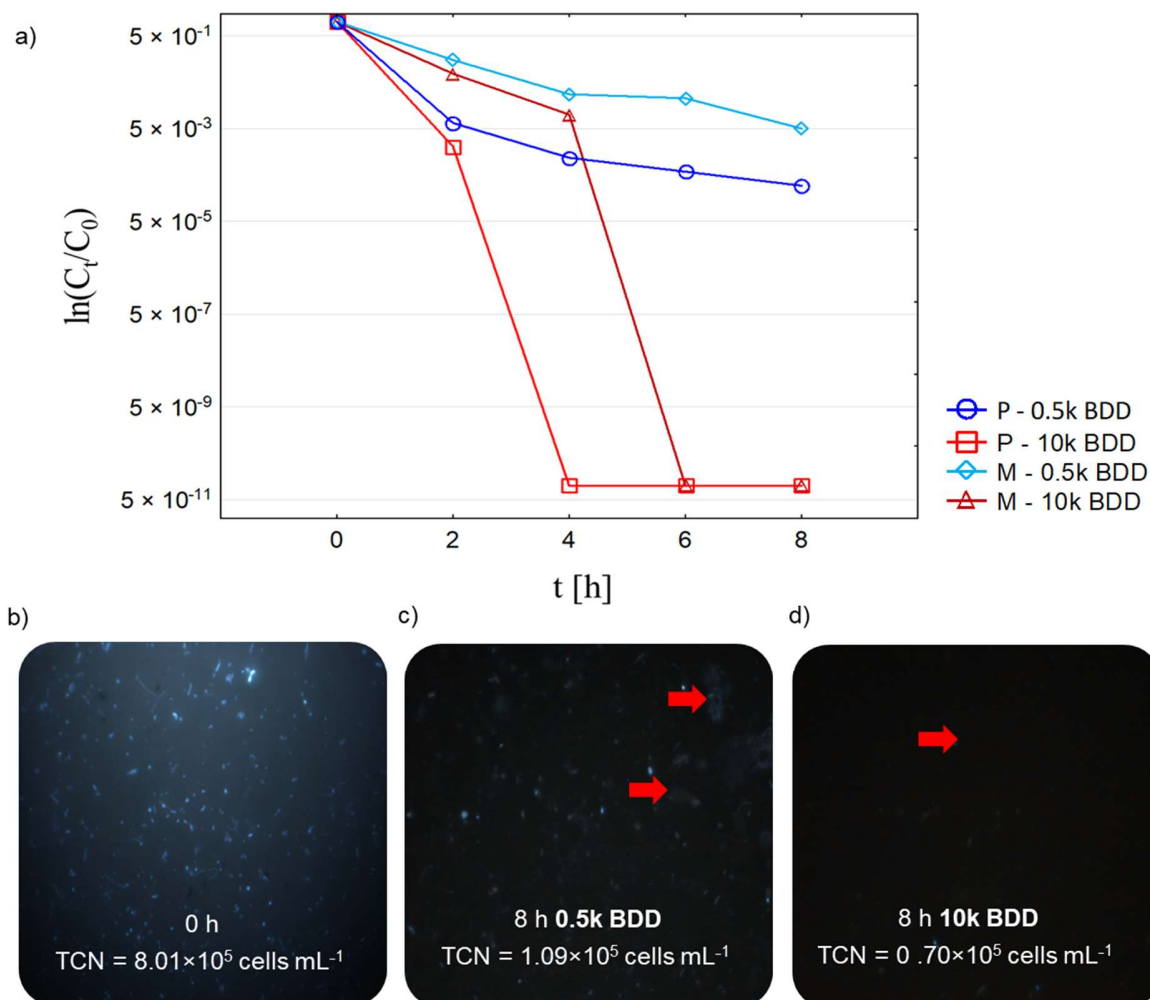
### 3.3. Evaluation of the raw and treated LLs microbiological quality

380 Based on the presented results (Fig.1), the most effective electrode in terms of COD, BOD<sub>20</sub> and N-NH<sub>4</sub><sup>+</sup>  
 381 removal was 0.5k BDD. 10k BDD also removed COD and BOD<sub>20</sub> highly effectively, but in the case of N-NH<sub>4</sub><sup>+</sup>, the  
 382 removal results were less satisfactory. Taking into account all the results obtained, 0.5k BDD and 10k BDD electrodes  
 383 were selected for toxicological and microbiological assay.

384 As suspected, faecal indicators were not detected in tested, raw LLs (which in this study were collected  
 385 from mature prism) because both enterococci and *E. coli* are considered to be good markers of rather recent faecal  
 386 contamination. Besides faecal indicators also presence of mesophilic and psychrophilic bacteria were analysed in  
 387 raw LLs, and were calculated at levels of  $0.4 \times 10^3$  CFU mL<sup>-1</sup> and  $3.4 \times 10^3$  CFU mL<sup>-1</sup>, respectively. Obtained values  
 388 were much lower as compared with raw municipal wastewater, where they reach up to  $10^7$ – $10^8$  CFU mL<sup>-1</sup>  
 389 (Michałkiewicz et al. 2018). In the case of DAPI staining, small prokaryote cells were detected in raw LLs (Fig. 3b),  
 390 in total numbered  $8.01 \times 10^5$  cells mL<sup>-1</sup>, with the highest amount of rods, constituting 80%.

391 The disinfection capabilities were tested for two electrodes: 0.5k BDD and 10k BDD, which were the most  
 392 effective at COD and N-NH<sub>4</sub><sup>+</sup> removal. During the EO 8-h tests, samples were collected every two hours for

393 bacteriological assay. According to the results, the inactivation of bacterial cells was readily achieved for 10 k BDD  
 394 electrode, after 2 h (the  $C_t/C_0$  was 0.002 for psychrophilic bacteria and 0.076 for mesophilic) (Fig. 3a).



395 **Fig. 3** Change of bacterial concentration during the 0.5k BDD and 10k BDD experiments, presented as (a)  $\ln(C_t/C_0)$   
 396 of colony forming units of psychrophilic (P) and mesophilic (M) bacteria as well as (b) microscopic observation of  
 397 DAPI stained prokaryotic cell in LLs prior to experiment, and (c) after 8h of treatment by 0.5k BDD electrode and  
 398 (d) 10k BDD electrode; presence of some “bacterial ghosts” representing inactivated cells, which have lost  
 399 cytoplasmic content (including DNA) via perforated membranes are marked with red arrow  
 400  
 401

402 It is suggested that inactivation of bacterial cells by both electrodes in the studied LLs was mainly the synergic  
 403 effect of hydroxyl radicals ( $\cdot\text{OH}$ ) and active chlorine ( $\text{HOCl}$ ,  $\text{OCl}^-$ ,  $\text{Cl}_2$ ). In contrast to hydroxyl radicals, whose  
 404 instability causes them to react mostly non-selectively with cellular components (causing damage to the outer  
 405 membrane), active chlorine compounds can penetrate the bacterial cell and cause decarboxylation of amino acids, and  
 406 can react with nucleic acids and key enzymes (Long et al. 2015). According to scientific studies (Jeong et al. 2009; Li  
 407 and Ni 2012; Martínez-Huitle and Brillas 2021), bacterial inactivation occurs faster in electrolytes with a lower

408 concentration of organic substances and ammonia. In our study, the greatest decrease in bacterial concentration was  
409 observed during the first 4 h, which corresponds to the greatest COD and N-NH<sub>4</sub><sup>+</sup> removal in 1st phase of the process.  
410 At high concentrations of COD and N-NH<sub>4</sub><sup>+</sup> in LLs, the rate of inactivation of bacterial cells reached the maximum.  
411 In this study, however, taking into consideration the presence of sulphate ions (1353 ± 275 mg L<sup>-1</sup>) in the tested LLs,  
412 also other electroactive ions and their oxidation products needs to be considered. Long et al. (2015) reported that  
413 electrogenerated oxidants of sulphate radicals (SO<sub>4</sub><sup>•-</sup>) and peroxydisulphate (Shin et al. 2019) attacked the cell  
414 membrane proteins, causing damage to the K<sup>+</sup> ion transport systems, inhibiting cell division and ATP synthesis, while  
415 reactions with the intracellular enzymes was mostly negligible. The changes in bacterial community structure during  
416 the EO assay were indirectly confirmed by imaging DAPI staining and the presence of so called “bacterial ghosts”  
417 (Fig. 3c-d) – inactivated cells that have lost cytoplasmic content (including DNA) via perforated membranes (Taddese  
418 et al. 2018). Cultivation method also confirmed that dissemination of LLs microorganism is mitigated, since a high  
419 inactivation rate of mesophilic and psychrophilic bacteria was achieved (Fig. 3). According to the obtained data, the  
420 electrosynthesis of oxidants BDD system may have effectively inactivated bacterial cells, and thus the toxicity of EO-  
421 treated LLs needs to be tested against other species.

#### 422 3.4. Toxicity assessment of electrochemical oxidation process using in vivo microassays

423 The current work examined the toxic effects of raw and EO-treated LLs on aquatic crustaceans  
424 *Thamnocephalus platyurus*, *Daphnia magna* and *Artemia franciscana*. The bioassays were performed for raw LLs and  
425 LLs treated with 0.5k BDD and 10k BDD electrodes. On the basis of the experimental data it was found that, among  
426 the tested LL samples, raw LLs were characterized by the strongest toxicity of all tested species (Fig. 4) probably as  
427 a synergistic toxic effect of different compounds present in the complex LL matrix (Wang et al. 2016). Toxicity of  
428 LLs after EO-treatment decreased but remained high, especially on *T. platyurus* and *D. magna* assays  
429 (Fig. 4).

#### 430 *Thamnotoxkit F* and *Rapidtoxkit F*

431 The most sensitive organism among those tested proved to be *T. platyurus*, which is prone to environmental  
432 contamination and frequently used in bioassays (Kalka 2012; Aydin et al. 2015). In this study, raw LLs indicated  
433 strong toxicity towards *T. platyurus* (Fig. 4a, Fig. 5a). In the case of treated LL samples, lower toxicity was observed  
434 (Fig. 4, Fig. 5b-c).

435 The samples treated with 10k BDD anode were less toxic towards the aforementioned organisms than were  
436 those treated with 0.5k BDD. A significant decrease in toxic effect was observed in samples at concentrations 0.4%  
437 and 0.8% – by 46% and 70%, respectively (Fig. 4). Detailed observations showed that in samples at concentration  
438 above 6.2%, *T. platyurus* individuals were dead after a 1-minute exposure. With decreasing sample concentrations  
439 (0.4–3.1%) toxic effects from 1.5 to 24 hours were observed (Supplementary Material, Fig. S5). Researchers  
440 Mavakala et al. (2016) and Melnyk et al. (2014) indicate that the main causes of *T. platyurus* mortality in LLs are  
441 extremely high concentrations of salts and COD (Melnyk et al. 2014; Mavakala et al. 2016). However, in such a  
442 complex LL matrix, it is difficult to indicate the direct cause of toxicity.

443 Additionally, a microbiotest for rapid detection of contamination was carried out using *Thamnocephalus*  
444 *platyurus*. Exposed to harmful substances, these organisms react by slowing their filtration rate. In this experiment,

445 the raw LL samples showed higher toxicity compared to leachates after EO (Fig. 5). Raw LL samples caused particle  
446 uptake inhibition at a concentration of 12.5%. In the case of treated samples the inhibition effect was only noted at the  
447 highest concentration (100%). During the test, inhibition was not observed to change with time of exposure. The  
448 results of the “rapid assay” correspond to those of the 24-hour test – i.e. the strongest toxicity was observed for highly  
449 concentrated samples.

#### 450 ***Daphtoxkit F. magna***

451 LLs were also toxic to the *Daphnia magna* species. The highest mortality of *D. magna* exposed to raw and  
452 treated LLs was observed in samples with concentrations ranging from 6.2 to 100% (Fig. 4b). Treated LLs at  
453 concentrations below 3.1% were less toxic than raw samples. Additional observations of the organisms showed that  
454 in the samples with concentrations above 6.2% crustaceans died with a 3-hour exposure. At sample concentrations of  
455 25%, 50% and 100%, all crustaceans died after 1–5 minutes.

456 According to Kalcikova et al. (2011), the toxic effects of LLs on daphnids are mainly attributed to high levels  
457 of ammonium compounds and COD. There are also publications in which no relationship between the mortality of  
458 daphnia and high levels of the aforementioned contaminants was found (Isidori et al. 2003; Kalcikova et al. 2011). To  
459 exactly determine the main factors responsible for the acute toxicity towards the selected organism, it would be  
460 necessary to include many chemical compounds potentially present in the LLs in a long-term monitoring programme.  
461 This would also allow the conditions and concentrations that cause death of the daphnia species to be determined with  
462 more confidence.

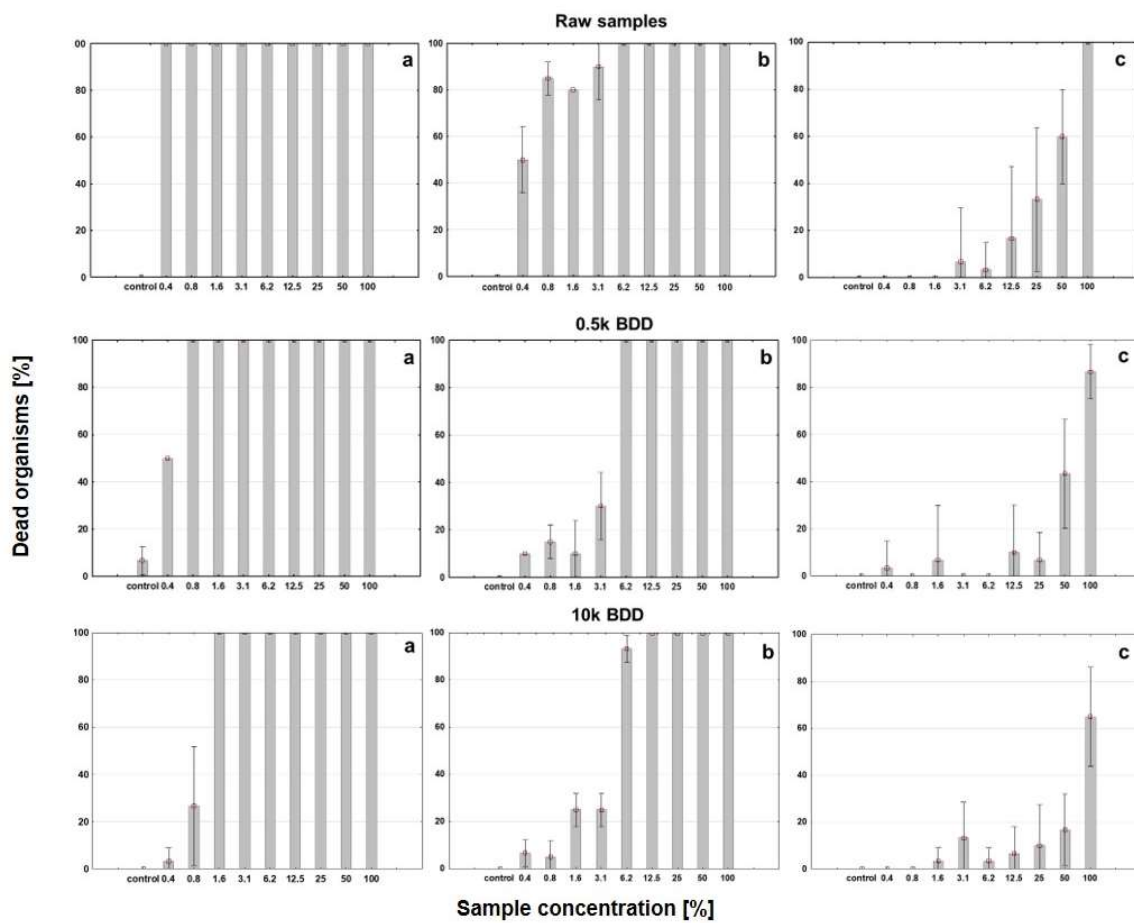
#### 463 ***Artoxkit M.***

464 The survival of *Artemia franciscana* in raw and treated LLs was also studied, and as for the *Daphnia magna*  
465 species and *T. platyurus*, it depended on the concentration of the samples. During 24-hour exposure to raw LLs, the  
466 strongest toxic effect was observed for the two most concentrated samples (50% and 100%) (Fig. 4c). In the samples  
467 treated by 10k BDD, crustacean mortality decreased by *ca* 40%. The most diluted samples of LLs slightly affected *A.*  
468 *franciscana* (Fig. 4c).

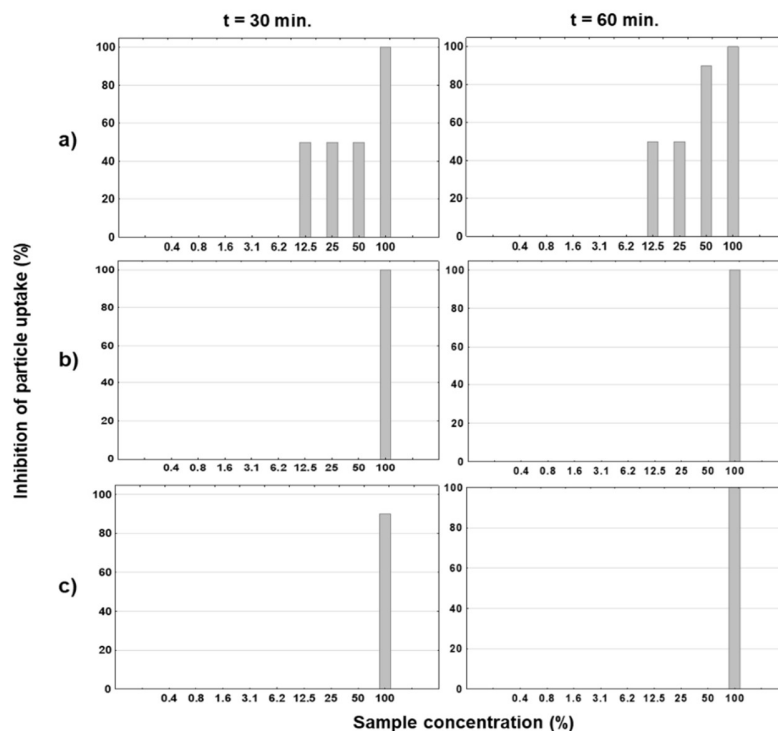
469 The observed response of aquatic crustaceans to LLs is in general species-dependent. In this work, the  
470 sensitivity of two species of crustaceans *T. platyurus* and *D. magna* was observed, while lower mortality was noted  
471 for *Artemia franciscana*, which lives naturally in inland saltwater lakes and tolerates a wide range of salinities (35–  
472 110%) (Vanhaecke et al. 1984). This makes *A. franciscana* a good indicator of LL toxicity, as compared to other  
473 compounds such as chlorine ions.

474 It can be concluded that LL toxicity is a very complex issue, and there remains insufficient knowledge about  
475 LL compounds and their toxicity. Thus, effective tools for estimating leachate strength and toxic potency are needed.  
476 This is of special concern if LL treatment is implemented, as treatment benefits connected with the effective removal  
477 of nutrients could be nullified by the generation of toxic compounds. In this study, EO-treated LLs were less toxic  
478 than raw samples, especially in the case of diamond electrodes with higher levels of boron doping.





479  
 480 **Fig. 4** (a) *Thamnocephalus platyurus*, (b) *Daphnia magna*, (c) *Artemia franciscana* and their mortality percentage to  
 481 raw and treated LL samples with 0.5k BDD and 10 k BDD Nb electrodes, 24-hour tests



**Fig. 5** (a) Effect of raw LL samples, (b) treated LLs with 0.5k BDD electrode and (c) treated LLs with 10k BDD electrode on *T. platyurus* inhibition of particle uptake, Rapidtoxkit test

#### 4. Conclusions

This study indicates the potential of EO by means of BDD electrodes technique as a promising method for remediating sanitary LLs. The effectiveness of removal of the selected macropollutants from LLs was tested by the EO method using three BDD electrodes with boron doping concentrations of 500, 10,000 and 15,000 ppm of B and applied current densities 25–100 mA cm<sup>-2</sup>. In general, the highest current density used ( $j = 100 \text{ mA cm}^{-2}$ ) resulted in the best pollutant-removal efficiency. Among the tested electrodes, the 0.5k BDD showed the best organic and N-NH<sub>4</sub><sup>+</sup> compound removal efficiency (97% COD, 90% BOD<sub>20</sub>, 62% N-NH<sub>4</sub><sup>+</sup>). Moreover, results demonstrated that most of the N-NH<sub>4</sub><sup>+</sup> was converted mainly to nitrate or nitrite forms: thus, the simultaneous removal of COD and N-NH<sub>4</sub><sup>+</sup> via BDD oxidation requires further investigation towards the total nitrogen removal. The EO method is also effective to mitigate the dissemination of LLs microorganism, reaching over 80% of mesophilic and up to 99% of psychrophilic bacterial cell inactivation within 2 h. It is suspected that in a such complex matrix as LLs, the EO process is based on combined effect of electrogenerated oxidants such as: hydroxyl radicals (<sup>•</sup>OH), active chlorine (HOCl, OCl<sup>-</sup>, Cl<sub>2</sub>) and sulphate radicals. Interestingly, the toxicity assays, indicated that EO-treated LLs were less toxic than raw ones, which confirmed that LL toxicity was more connected with the high concentration of salts and other pollutants, than with the presence of EO by-products. Thus, it is believed that by choosing appropriate electrolysis parameters the toxicity effect can be diminished, without compromising nutrient removal and disinfection capability.



503 **5. Declarations**

504 **Ethics approval and consent to participate:** Not applicable.

505 **Consent for publication:** Not applicable.

506 **Availability of data and materials:** All data generated or analyzed during this study are included in this published  
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508 **Competing interests:** The authors declare no competing interests.

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519

520 **6. References**

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