Article

Emerging Contaminants Decontamination of WWTP Effluents by BDD Anodic Oxidation: A Way towards Its Regeneration

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Abstract: Electrochemical oxidation using a boron-doped diamond anode (EO-BDD) was tested to remove emerging contaminants commonly present in wastewater treatment plant effluents (WWTPe). The main objective of the work was the regeneration of this water for its possible reuse in high-quality demanding uses. In the first part of the work, we investigated the potential of this technique for removing a group of neonicotinoid pesticides (thiamethoxam (TMX), imidacloprid (ICP), acetamiprid (ACP), and thiacloprid (TCP)) in a WWTP effluent. The influence of operating variables, such as current density, the conductivity of media, supporting electrolyte type (Na_2SO_4, NaCl or $NaNO_3$), or the natural aqueous matrix on target variables were fully established. Selected target variables were: (1) the percentage of pollutant removal, (2) the kinetics (apparent pseudo-first-order kinetic rate constant), (3) total organic carbon (TOC) removal, and (4) the specific energy consumption (SEC). A response surface methodology (RSM) was applied to model the results for all cases. In the paper's final part, this technology was tested with a more broad group of common emerging pollutants, including some azole pesticides (such as fluconazole (FLZ), imazalil (IMZ), tebuconazole (TBZ), or penconazole (PNZ)), antibiotics (amoxicillin (AMX), trimethoprim (TMP), and sulfamethoxazole (SMX)), and an antidepressant (desvenlafaxine (DVF)). The results confirm the power of this technology to remove this emerging contamination in WWTP effluents which supposes an interesting way towards its regeneration.

Keywords: anodic oxidation; BDD electrodes; emerging contaminants; neonicotinoid pesticides; azole pesticides; wastewater treatment plant effluent

1. Introduction

Water resources worldwide, in general, and in the European Union (EU) are under increasing pressure, leading to water scarcity problems and quality deterioration. Furthermore, climate change and droughts contribute significantly to a decrease in the volume of fresh water available. For specific uses, wastewater treatment plant (WWTPe) effluents have been subjected to a further treatment process (tertiary), allowing them to adapt their quality to different potential uses.

In this context, the European Commission has specified the minimum quality of regenerated water for agricultural use (EU Decision 2020/741). This regulation considers that reusing adequately treated water (from WWTP effluents) has less environmental impact than other water supply alternatives. This regulation aims to guarantee regenerated, safe water for agricultural irrigation and ensure a high level of protection for the environment, humans, and animals. Concerning organic contamination, this regulation is completed with EU Decision 2020/1161, which establishes a list of priority contaminants which includes: neonicotinoid pesticides (thiamethoxam, imidacloprid, acetamiprid, and thiacloprid), antibiotics (amoxicillin, sulfamethoxazole, trimethoprim, and ciprofloxacin), antifungals (clotrimazole, fluconazole, and imazalil), or antidepressants (such as venlafaxine). The final aim of this work is to provide a feasible technology to remove these micropollutants from WWTP effluents.

Among these organic contaminants, neonicotinoid pesticides represent the most widely used insecticide worldwide [1,2], accounting for >25% of the global insecticide market. Essential, since their properties include a broad spectrum of insecticidal activity, a persistent effect, and a systemic nature [3], their use is gradually increasing over the years, and they are currently one of the best-selling insecticides in the world [4]. These pollutants are relatively persistent and mobile and are easily transported through surface and groundwater [5]. Recent works have confirmed the presence of neonicotinoids in aquatic ecosystems [6] in concentrations that exceed the reference values established to protect these ecosystems. They exhibit slow dissipation rates (half-life = 0.5 to 0.7 years) [7]. The main transport routes to aquatic ecosystems are runoff, soluble or insoluble fractions transported by melting ice, contaminated dust, and leaching into groundwater [5]. Additionally, we include in this work the emerging pollutants present in the mentioned EU Decision, which are the group of azole pesticides (fluconazole (FLZ), imazalil (IMZ), tebuconazole (TBZ), and penconazole (PNZ)), antibiotics (such as amoxicillin (AMX), trimethoprim (TMP), and sulfamethoxazole (SMX)), and antidepressants (desvenlafaxine (DVF)).

In this context, studying more efficient technologies than the conventional ones used in wastewater treatment plants (WWTPs) is necessary. Among these processes, advanced oxidation processes (AOPs) may be a great alternative. For example, we can mention ozonation [8], UV photo-oxidation [9], UV/H_2O_2, UV/Persulphate [10], sonochemical oxidation [11], and electrochemical oxidation (EO) [12,13]. EO constitutes an attractive alternative to other systems due, fundamentally, to two factors: firstly, chemical reagents are not added in the medium, and secondly, there is a greater mineralization capacity. Some authoritative reviews about mechanisms and involved species of this oxidation system have been recently published [14–16].

The EO process allows the generation of hydroxyl radicals ($\cdot OH$) for organic matter oxidation to CO_2, H_2O, and inorganic salts. Some of these studies have already been published with the prospect of applying them shortly in pilot plants [14]. Due to its main properties, the boron-doped diamond (BDD) covering has emerged as a new anodic treatment. It has become the best-known electrode for degrading toxic and refractory organic compounds [17]. For this electrochemical technique, it is convenient to use an inert electrolyte that does not produce reactive species during electro-oxidation or generate them under specific conditions and that is harmless concerning the electrodes used. Various studies have verified that Na_2SO_4 is the supporting electrolyte that best degrades different pollutants/drugs [18,19]. On the other hand, due to the considerable energy costs associated with this technique, it is necessary to evaluate their viability and efficiency by determining the specific energy consumed (SEC) (amount of energy consumed per unit mass of pollutant removed (kW h g^{-1})) [19].

Regarding the potential of this technique, some exciting results were obtained in ultrapure-water (UPW), removing pharmaceuticals [20], neonicotinoid pesticides [13], and some antidepressants [21]. However, no results were found about the group of azole pesticides (present in the last EU Decision 2020/1161). Additionally, all the works mentioned here were carried out in UPW. In this case, all the experiments were carried out in natural water matrices.

The present work was divided into two parts. In the first part of the work, the EO of a mixture of neonicotinoid pesticides was carried out in the Badajoz-WWTP effluent. A design of experiments (DoE) was developed, taking as its target variables: (1) the percentage of removal of each pollutant (E, %), (2) the kinetics of the reaction (k_i, min^{-1}), (3) the removal of total organic carbon (TOC, %), and (4) the specific energy consumption (SEC, kWh μM^{-1}). The influence of different supporting electrolytes (Na_2SO_4, $NaNO_3$, and NaCl) and different aqueous matrices (Almendralejo-WWTP effluent, Peña del Águila-reservoir, and Guadiana-river) on target variables was also established. In the second part of the work, the potential of this technique was evaluated with one more broad group of emerging contaminants (azole pesticides, antibiotics, and antidepressants) in the same aqueous matrix (Badajoz-WWTP effluent).

2. Materials and Methods

2.1. Materials

The neonicotinoid pesticides (NCTs), thiamethoxam (TMX), imidacloprid (ICP), acetamiprid (ACP), and thiacloprid (TCP), added to natural water matrices were supplied by Sigma-Aldrich, Madrid, Spain, with a purity of >98% for all cases. The support electrolyte used was anhydrous sodium sulfate (Na_2SO_4) with a purity of >99%. Sodium chloride (NaCl) and sodium nitrate ($NaNO_3$) were provided by Panreac Química, Barcelona, Spain (purity >99%). The mobile phase used in the HPLC analysis was a mixture of acetonitrile (Panreac Química) and ultrapure water (Milli-Q Millipore, Madrid, Spain) acidified with formic acid (CH_2O_2) with a purity of 98–100% (supplied by Merck, Madrid, Spain).

The pharmaceutical products added to real water matrices were amoxicillin (AMX), trimethoprim (TMP), and sulfamethoxazole (SMX); all were provided by Sigma-Aldrich with a purity of 98%. Across Quimica, Madrid, Spain, supplied Desvenlafaxine (DVF) in 97% purity. The azole products, fluconazole (FLZ), imazalil (IMZ), tebuconazole (TBZ), and penconazole (PNZ), were all supplied by Sigma-Aldrich.

Electrochemical oxidation runs were carried out in a circular single-cell reactor consisting of two circular electrodes with a geometric area of 78 cm^2, with an electrode gap of 9 mm. Boron-doped diamond material (BDD) and a stainless-steel electrode (AISI 304) were used as anode and cathode, respectively. The BDD electrode was supplied by CSEM (Switzerland). Before experiments, the electrodes were polarised and cleaned with a 10 mM Na_2SO_4 solution at a current density (j) of 20 mA·cm^{-2} for 15 min. The electrolysis was carried out using the equipment detailed and shown in Figure 1.
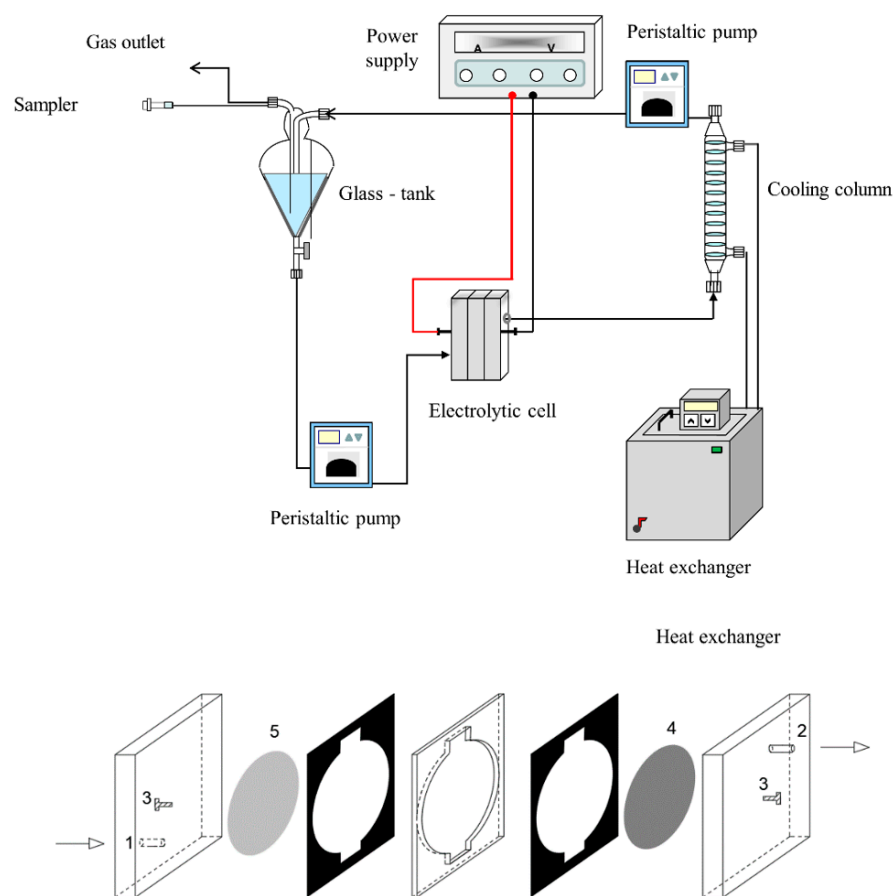

Figure 1. Electrochemical installation scheme for NCTs degradation (**top**) and electrolytic cell details (**bottom**): (1) gas inlet, (2) gas outlet, (3) power supply-electrodes connections, (4) Stainless Steel cathode, and (5) BDD anode.

2.2. Methods

The degradation of NCTs in a natural water matrix (Badajoz WWTP effluent) by electrochemical oxidation was followed by reverse-phase high-performance liquid chromatography (HPLC) using a method previously used [13,22].

Quantifications for azole pharmaceuticals (FLZ, IMZ, TBZ, and PNZ) were performed at 205 nm, 210 nm for AMX and TMP, 224 nm for DVF, and 265 nm for SMX. In all cases, we injected aliquots of 100 μL into the system. Well-defined peaks were obtained for FLZ, IMZ, TBZ, and PNZ at 7.68, 15.06, 24.24, and 25.17 min, respectively. Peaks were obtained for AMX, TMP, DVF, and SMX at 2.69, 4.86, 5.47, and 7.88 min, respectively. TOC content was determined using an Analytikjena Multi N/C® 3100 analyzer.

Real water matrices used in this investigation (Badajoz-WWTP effluent, Almendralejo-WWTP effluent, Peña del Águila-reservoir, and Guadiana-river) were thoroughly characterized (physicochemical characterization) in previous work [13]. The samples were filtered through a 0.45 μm filter and stored in the dark at 4 °C for later use. Before their use, these water matrices were dopped with the corresponding mixture of contaminants (concentration of each = 1 μM).

The study of the influence of variables on the electro-oxidation process was planned and statistically analyzed using Statgraphics Plus 5.1 for Windows with a randomized central composite orthogonal and rotatable design (CCORD). The target variables were the percentage of pollutant removal (E_i, %) (Equation (1)), the apparent pseudo-first-order kinetic rate constant (k_i) (Equation (2)), TOC removal (TOC, %), and the specific energy consumption (SEC, kWh μM^{-1}) (Equation (3)). After determining the essential factors, a response surface methodology model (RSM) was used. This method fits a second-order equation (Equation (4)) for predicting a theoretical response, where the quadratic terms model the curvature. The validity of the applied model was supported by the analysis of the variance (ANOVA test).

$$Ei = \left(\frac{N_o - N}{N_o} \right) 100 \tag{1}$$

$$ln\left(\frac{N_o}{N} \right) = k_i \cdot t \tag{2}$$

$$SEC = \frac{E_{cell} \cdot I \cdot t}{3600 \cdot V \cdot (N_o - N)} \tag{3}$$

N_o is the initial concentration of each contaminant (μM), N is the concentration at different reaction times (μM), t is the reaction time (min), E_{cell} is the applied cell potential (V), I is the supplied current intensity (A), and V is the volume of solution (dm^3).

$$Y = a + b\,C + c\,j + d\,C^2 + e\,C\,j + f\,j^2 \tag{4}$$

Y is the predicted response (E, k_i, TOC, or SEC) and a, b, c, d, e, and f are the polynomial coefficients of the fitting equation for the linear, quadratic, and second-order terms. The experimental conditions (coded variables-experimental variables) used for each run are shown in Table 1.

Table 1. Experimental conditions for electrochemical oxidation of neonicotinoid mixture (1 μM each). Aqueous matrix = Badajoz WWTP effluent.

Experiment	Coded Variables		Real Variables	
			j (mA·cm^{-2})	C (mS·cm^{-1})
EO-1	0	0	20	3.5
EO-2	0	0	20	3.5
EO-3	1.41	0	34.14	3.5
EO-4	1	−1	30	2.0
EO-5	0	0	20	3.5

Table 1. *Cont.*

Experiment	Coded Variables		Real Variables	
			j (mA·cm^{-2})	C (mS·cm^{-1})
EO-6	1	1	30	5.0
EO-7	0	0	20	3.5
EO-8	−1.41	0	5.6	3.5
EO-9	−1	1	10	5.0
EO-10	0	0	20	3.5
EO-11	0	−1.4142	20	1.4
EO-12	−1	−1	10	2.0
EO-13	0	0	20	3.5
EO-14	0	0	20	3.5
EO-15	0	1.4142	20	5.6
EO-16	0	0	20	3.5

3. Results and Discussion

3.1. Influence of Operating Variables on the Electrochemical Oxidation of Neonicotinoid Pesticides in a WWTP Effluent

The response surface methodology (RSM) has been used according to a Central Composite Design (DCC) [23]. The target variables were the percentage of pollutant removal (E, %) (Equation (1)), the apparent pseudo-first-order kinetic rate constant (k_i) (Equation (2)), TOC removal (TOC, %), and the specific energy consumption (SEC, kWh μM^{-1}) (Equation (3)).

3.1.1. Neonicotinoids Removal as the Target Variable

In this section, the influences of the current density (j) and the conductivity of the media (C) on neonicotinoids removal (TMX, ICP, ACP, and TCP) were evaluated. The conductivity of the media was adjusted by adding Na$_2$SO$_4$ for all cases. The removal percentages achieved for each contaminant at different reaction times (60 and 120 min) are shown in Table 2 (Ei, %). Obtained results agree with those obtained by Meijide et al. [24] for TMX degradation using Na$_2$SO$_4$ (0.01 M), BDD anode, and carbon-felt cathode. However, improved levels of degradation were obtained by Brahim et al. [25] for ICP oxidation using the same electrolyte with a Ta/PbO$_2$ anode and a Pt cathode.

Table 2. NCTs removal (%) at 60 and 120 min of electrochemical treatment time. Aqueous matrix = Badajoz WWTP effluent. See the experimental conditions for each experiment in Table 1.

Exp.	E$_{TMX,60}$ (%)	E$_{ICP,60}$ (%)	E$_{ACP,60}$ (%)	E$_{TCP,60}$ (%)	E$_{TMX,120}$ (%)	E$_{ICP,120}$ (%)	E$_{ACP,120}$ (%)	E$_{TCP,120}$ (%)
EO-1	96.0	97.3	85.1	99.0	100	100	97.5	100
EO-2	96.9	97.6	85.8	99.1	100	100	98.2	100
EO-3	100	100	97.8	100	100	100	100	100
EO-4	98.6	98.6	93.5	100	100	100	100	100
EO-5	97.1	98.2	88.1	100	100	100	98.4	100
EO-6	100	99.6	96.7	100	100	100	100	100
EO-7	95.9	97.5	84.1	99.0	100	100	97.3	100
EO-8	73.7	75.9	45.0	75.0	92.6	94.1	72.0	94.4
EO-9	86.9	89.6	65.4	94.2	98.0	98.7	87.9	100
EO-10	95.5	96.8	82.2	98.6	100	100	96.5	100
EO-11	95.6	96.3	82.1	98.5	100	100	96.1	100
EO-12	83.4	85.0	58.6	91.0	96.4	98.5	81.4	97.8
EO-13	95.7	97.1	85.3	99.1	100	99.6	97.7	100
EO-14	97.1	97.5	85.7	99.0	100	100	98.4	100
EO-15	98.8	98.9	93.2	100	100	100	100	100
EO-16	96.7	97.7	86.8	100	100	100	97.7	100

Figure 2 shows the response surface and level curves corresponding to ACP removal at 60 min of reaction time. These surfaces are convex within the study region. The percentage of neonicotinoids removal increases with current density (j). However, the curvature has an asymptotic tendency (less influential at longer treatment times), whereas conductivity's influence is positive but moderate.
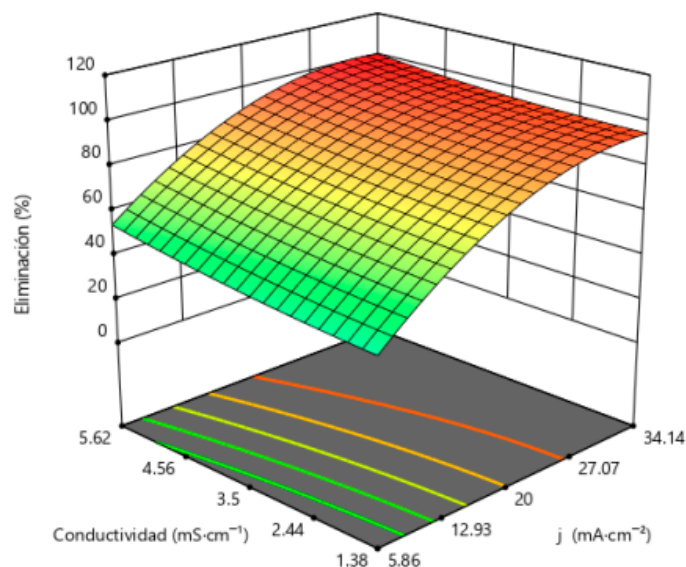

Figure 2. Estimated response surface and level curves for ACP removal at 60 min of reaction time. Aqueous matrix = Badajoz WWTP effluent.

The above trend was attributed to the proportional relationship between the hydroxyl radicals concentration ($\cdot$OH) generated on the electrode surface and the applied current density (j). Thus, these hydroxyl radicals can react with the neonicotinoid molecules and break them down. High j values increase the hydroxyl radical production rate and, thus, the pollutant removal rate [24]. However, the removal efficiency does not increase proportionally with the current density. The observed asymptotic trend (see Figure 2) is due to radical deactivation (see Equation (5)) at high current densities and other oxidation (parasite) reactions with other NCT oxidation intermediates (see Equation (6)) [25]. Additionally, at higher current densities, the high generation of hydrogen bubbles at the cathode negatively affects the oxidation process in the aqueous phase.

$$OH + \cdot OH \rightarrow H_2O_2 \tag{5}$$

Concerning the influence of reaction time, at low current density values (experiment EO-8, $j = 5.6 \text{ mA} \cdot \text{cm}^{-2}$), ACP removal increases from 45% (at 60 min) to 72% (at 120 min). In contrast, for high-density values (EO-1 experiment, $j = 20 \text{ mA} \cdot \text{cm}^2$), the pollutant removal increased softly from 85.1% to 97.5% (see Table 2). This was also attributed to secondary reactions with other oxidation intermediates.

$$OH + \cdot Pox1 \rightarrow Pox2 \tag{6}$$

3.1.2. Kinetics as the Target Variable

In this case, the target variable was the reaction kinetics measured by the pseudo-first-order kinetic rate constant (k_i) (see Equation (2)). The conductivity adjustment was carried out by adding Na_2SO_4 for all cases. The results after 120 min of reaction time are shown in Table 3 (see the experimental conditions in Table 1).

Table 3. Pseudo-first-order kinetic rate constant for the electrochemical oxidation of the different neonicotinoids. (Experimental conditions in Table 1). Aqueous matrix = Badajoz WWTP effluent.

Experiment	k_{TMX} (min^{-1})	k_{ICP} (min^{-1})	k_{ACP} (min^{-1})	k_{TCP} (min^{-1})
EO-1	0.0536	0.0593	0.0310	0.0800
EO-2	0.0560	0.0609	0.0330	0.0803
EO-3	0.0920	0.1062	0.0625	0.1438
EO-4	0.0731	0.0840	0.0457	0.1153
EO-5	0.0564	0.0638	0.0345	0.0911
EO-6	0.0894	0.0981	0.0523	0.1389
EO-7	0.0534	0.0592	0.0308	0.0804
EO-8	0.0220	0.0237	0.0104	0.0265
EO-9	0.0332	0.0368	0.0176	0.0451
EO-10	0.0542	0.0566	0.0285	0.0730
EO-11	0.0491	0.0531	0.0277	0.0750
EO-12	0.0287	0.0351	0.0143	0.0352
EO-13	0.0536	0.0611	0.0314	0.0819
EO-14	0.0574	0.0604	0.0336	0.0786
EO-15	0.0696	0.0755	0.0433	0.0885
EO-16	0.0544	0.0626	0.0325	0.0846

The experimental results of the design were fitted to an equation of type 4. Equations (7)–(10) show the adjustment coefficients for each factor for TMX, ICP, ACP, and TCP contaminants, respectively. These equations show a positive effect on the degradation rate of all operative variables (j and C), including their interactions.

$$k_{TMX} = 0.0549 + 0.0249 \cdot j + 0.0062 \cdot C + 0.0005 \cdot j^2 + 0.0029 \cdot j \cdot C + 0.0017 \cdot C^2 \tag{7}$$

$$k_{ICP} = 0.0605 + 0.0284 \cdot j + 0.0059 \cdot C + 0.0019 \cdot j^2 + 0.0031 \cdot j \cdot C + 0.0016 \cdot C^2 \tag{8}$$

$$k_{ACP} = 0.0319 + 0.0175 \cdot j + 0.0040 \cdot C + 0.0014 \cdot j^2 + 0.0008 \cdot j \cdot C + 0.0009 \cdot C^2 \tag{9}$$

$$k_{TCP} = 0.0812 + 0.0425 \cdot j + 0.0066 \cdot C + 0.0020 \cdot j^2 + 0.0034 \cdot j \cdot C + 0.0003 \cdot C^2 \tag{10}$$

For all cases, the values of the regression coefficients of k_i plots presented in Table 3 were greater than 0.990. As is shown in this Table, k_i values increase with current density, implying a more significant generation of ●OH radicals [12]. On the other hand, it is observed that the values of k_i corresponding to runs EO-1, EO-11, and EO-15 are very similar, indicating that the conductivity poorly influences the degradation rate (at least in this study region) in this aqueous matrix. However, a higher current density (see experiments EO-3 and EO-8) conducts a higher kinetic rate constant because of a higher ●OH radicals concentration on the electrode's surface [26].

3.1.3. TOC Removal as the Target Variable

In this section, the results are analyzed, taking as the target variable the removal of total organic carbon (TOC) expressed as a percentage (% E_{COT}) after 120 min of reaction time. As shown in Table 4, higher percentages of TOC removal were obtained when the current density increased. According to other authors, higher mineralization was reached under a higher current density [27]; however, the influence of the conductivity was softly positive in this study range (54.8–62.5%).

As shown the Figure 3, TOC removal efficiency depends more firmly on the current density (j). This fact is fundamental because we aim to degrade the pollutants and mineralize them to CO_2 and H_2O.

Table 4. Elimination of TOC in the electrochemical oxidation of the neonicotinoid mixture at 120 min of reaction time. Aqueous matrix = Badajoz WWTP effluent. (Experimental conditions see Table 1).

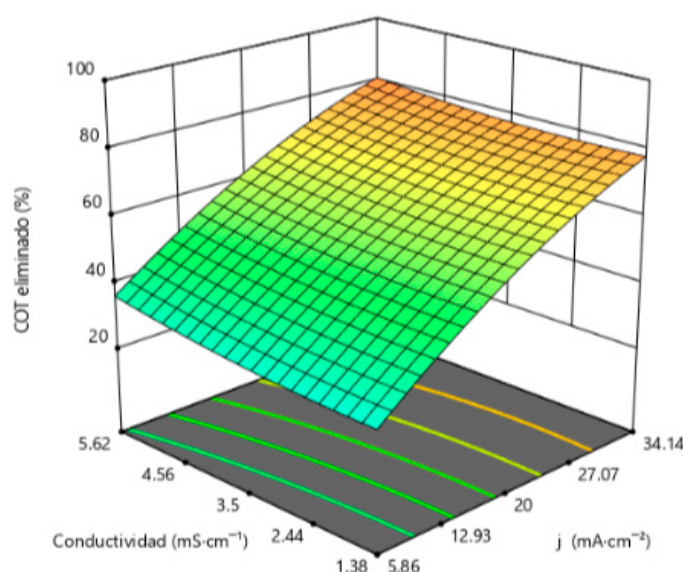| Experiment	E_{TOC} (%)	Experiment	E_{TOC} (%)
EO-1	58.37	EO-09	45.39
EO-2	59.11	EO-10	58.00
EO-3	77.09	EO-11	54.85
EO-4	74.91	EO-12	42.67
EO-5	60.00	EO-13	60.80
EO-6	75.47	EO-14	58.12
EO-7	60.26	EO-15	62.55
EO-8	27.33	EO-16	58.33

Figure 3. Response surface and contour curves for TOC removal in the electrochemical oxidation of the neonicotinoid mixture. Aqueous matrix = Badajoz WWTP effluent.

3.1.4. Energy Efficiency as the Target Variable

The specific energy consumed (SEC) was determined to evaluate the energetic and economic viability of the process (see Equation (3)). Table 5 shows the average values obtained after 120 min of treatment under different experimental conditions (see Table 1).

Table 5. Specific energy consumed (SEC) in the electrochemical oxidation process. Aqueous matrix = Badajoz WWTP effluent. Experimental conditions in Table 1.
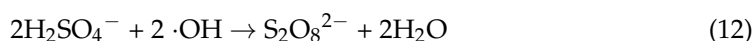
Experiment	SEC (kW·h·g^{-1})	Experiment	SEC (kW·h·g^{-1})
EO-1	0.0107	EO-9	0.0052
EO-2	0.0107	EO-10	0.0108
EO-3	0.0172	EO-11	0.0144
EO-4	0.0163	EO-12	0.0064
EO-5	0.0105	EO-13	0.0103
EO-6	0.0131	EO-14	0.0107
EO-7	0.0102	EO-15	0.0090
EO-8	0.0046	EO-16	0.0107

As is shown in Table 5, in the experiments carried out with a constant electrolyte conductivity (experiments EO-1, EO-3, and EO-8) (see Table 1), an increase in current intensity produces an increase in the SEC parameter (which measures energy efficiency), increasing the costs associated with the process. For the experiments carried out with a constant applied current intensity (experiments EO-1, EO-11, and EO-15) (see Table 1),
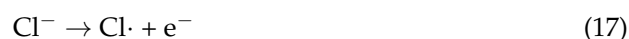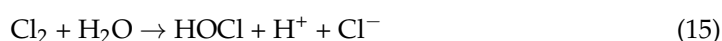
the cell's potential increases inversely proportional to the conductivity of the electrolyte, negatively influencing the energy efficiency of the process. Thus, we can constate a positive influence of the conductivity of media (C) on the SEC parameter, reducing the associated energy costs by up to 38%.

3.2. Influence of Supporting Electrolyte Type on WWTPe Treatment

The supporting electrolyte type is essential in the electrochemical treatment. The presence of these electrolytes increases conductivity, decreases resistance, and, therefore, reduces the energy cost of the process. In several cases, the electrochemistry of the electrolytes plays an essential role in the process due to the possible formation of secondary products that can increase or decrease the process's efficiency. Chloride and sulfate salts are two of the most widely used electrolytes. Rabaaoui et al. [18] stated that anodic oxidation of aqueous chloride or sulphate solutions promotes hypochlorite and persulfate species. Adding these electrolytes to the effluent should improve conductivity and increase electron mass transfer [28]. In this context, Na_2SO_4 is often used as a supporting electrolyte because it generates species of peroxy-disulfate ($S_2O_8^{2-}$) (see Equations (11)–(13)), a potent oxidant. Anions, in low concentrations, can trap photogenerated electrons more efficiently than O_2 and hinder the recombination of electrons and holes. A very detailed mechanism for the production of persulphate was proposed by Araujo et al. [29].

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \tag{11}$$

$$2H_2SO_4^- + 2 \cdot OH \rightarrow S_2O_8^{2-} + 2H_2O \tag{12}$$

$$SO_4^- + SO_4^- \rightarrow S_2O_8^{2-} \tag{13}$$

On the other hand, the case of NaCl was related to the existence of soluble Cl_2 and HClO, generated from the oxidation of chloride anions on the anode, which is shown in the following Equations (14)–(18) [16,19]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{14}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{15}$$

$$HOCl \rightarrow ClO^- + H^+ \tag{16}$$

$$Cl^- \rightarrow Cl\cdot + e^- \tag{17}$$

$$ClO_2^- \rightarrow ClO_2\cdot + e^- \tag{18}$$

Other studies analyzed the influence of $NaNO_3$ as a supporting electrolyte, concluding that it is an inert reagent in the chemical electro-oxidation process [30].

In the present work, three sodium salts (NaCl, Na_2SO_4, and $NaNO_3$) were used to investigate the influence of the electrolyte type on the process (in the Badajoz WWTP effluent). The removal percentages achieved for each pollutant (at 60 min of reaction time) are shown in Table 6 for experiment EO-4 (see conditions in Table 1). The conductivity adjustment has been made by adding the necessary amount of supporting electrolyte until it reaches 2 mS cm^{-1}. As shown in Table 6, the pollutant removal at 60 min was maximum when Na_2SO_4 was used as a supporting electrolyte.

These results are confirmed by the pseudo-first-order kinetic rate constants obtained for NCTs removal (experiment EO-4) using different electrolytes (see Table 7). The influence of the supporting electrolyte on TOC removal (EO-4 experiment) at 120 min of reaction time (Badajoz WWTP effluent) is practically negligible. These results follow the results of Velappan et al. [31] for other contaminants in other complex aqueous matrices.

Table 6. Neonicotinoids removal at 60 min of reaction time for experiment EO-4. Aqueous matrix = Badajoz WWTP effluent.

Electrolyte	$E_{TMX,60}$ (%)	$E_{ICP,60}$ (%)	$E_{ACP,60}$ (%)	$E_{TCP,60}$ (%)
EO-NaCl	83.1	91.1	64.8	100
EO-NaNO$_3$	92.0	91.4	79.7	90,6
EO-Na$_2$SO$_4$	98.6	99.3	93.5	100

Table 7. Pseudo-first-order kinetic rate constants for NCTs removal (experiment EO-4) with different supporting electrolytes. Aqueous matrix = Badajoz WWTP effluent.

Experiment	k_{TMX} (min^{-1})	R^2	k_{ICP} (min^{-1})	R^2	k_{ACP} (min^{-1})	R^2	k_{TCP} (min^{-1})	R^2
EO-NaCl	0.0312	0.99	0.0395	1.00	0.0216	0.976	0.0334	0.99
EO-NaNO$_3$	0.0410	1.00	0.0402	1.00	0.0259	0.999	0.0387	1.00
EO-Na$_2$SO$_4$	0.0731	1.00	0.0840	1.00	0.0457	0.999	0.1153	1.00

3.3. Influence of the Real Aqueous Matrix

Different aqueous matrices, such as surface water, groundwater, and WWTP effluents, contain different concentrations of inorganic and organic species. Species can interfere with or potentiate electrochemical treatment [12]. The role of chloride in the anodic oxidation of organics is of particular interest, as it is commonly present in wastewater [32]. In this sense, the aqueous matrix's complexity affects the process's efficiency.

NCTs removal was carried out in four real water matrices, that is, Guadiana-river (RW-1), Villar del Rey-reservoir (RW-2), Almendralejo-WWTP effluent (RW-3), and Badajoz WWTP effluent (RW-4). Aqueous matrices were filtered through a 0.45 μm filter and stored in the dark at 4 °C for later use. A complete physicochemical characterization of these different water matrices was carried out (see Table 8) [13]. The mixture of NCTs (concentration of each = 1 μM) was added to each real matrix.

Table 8. Physico-chemical characterization of different real aqueous matrices.

Parameter	RW-1 (Guadiana River)	RW-2 (Reservoir Villar del Rey)	RW-3 (Almendalejo WWTP)	RW-4 (Badajoz WWTP)
pH	7.95	8.11	8.72	7.57
Conductivity (μS·cm^{-1})	641	151	2332	538
Turbidity (NTU)	0.58	0.44	0.98	0.61
TOC (mg·L^{-1})	7.04	8.69	20.04	9.66
COD (mg O$_2$·L^{-1})	22.4	26.8	60.7	29.7
Total phosphorus (mg P·L^{-1})	0.06	0.05	0.99	1.27
Total nitrogen (mg N·L^{-1})	2.3	1.6	11.6	12.1
Nitrate (mg NO$_3^-$·L^{-1})	8.5	1.3	30.5	23.7
Nitrite (μg NO$_2^-$·L^{-1})	51	634	57	621
Ammonium (mg NH$_4^+$·L^{-1})	0.23	0.78	1.17	3.87
A$_{254nm}$ (cm^{-1})	0.135	0.140	0.559	0.183
Total solids (mg·L^{-1})	360	250	1690	410
Fixed solids (mg·L^{-1})	285	175	1390	325
Volatile solids (mg·L^{-1})	75	75	300	85

Table 9 shows the elimination percentage of each neonicotinoid (Ei, %) in each aqueous matrix (RW-1, RW-2, RW-3, and RW-4) at 60 min of reaction time. The experiments were carried out under the same conditions (see EO-4 experiment in Table 1). The conductivity adjustment was carried out by adding the amount of Na$_2$SO$_4$ (supporting electrolyte) necessary to reach 2.0 mS·cm^{-1}. A significant increase in the degradation level for all neonicotinoids was found with the following sequence: RW-1 > RW-4 > RW-2 > RW-3.

This fact is attributable to anionic species acting as ·OH radical scavengers (such as NO_3^-, HPO_4^{2-}, or HCO_3^-) [13]. Another factor that can influence efficiency is pH. All the experiments were carried out with the natural pH of the sample (pH_0), which presented a basic initial pH, obtaining similar pH values at the end of each experiment.

Table 9. NCTs removal at 60 min in different real aqueous matrices.

Exp.	$E_{TMX,60}$ (%)	$E_{ICP,60}$ (%)	$E_{ACP,60}$ (%)	$E_{TCP,60}$ (%)
RW-1	100	100	97.4	100
RW-2	97.1	97.6	88.7	99
RW-3	74.9	86,0	55.4	100
RW-4	98.6	98.6	93.5	100

This reactivity sequence was also corroborated by the pseudo-first-order kinetic rate constants obtained for this experiment (EO-4) in the different aqueous matrices (see Table 10).

Table 10. Pseudo-first-order kinetic constant in the electro-oxidation of neonicotinoids for different aqueous matrices.

Experiment	k_{TMX} (min^{-1})	R^2	k_{ICP} (min^{-1})	R^2	k_{ACP} (min^{-1})	R^2	k_{TCP} (min^{-1})	R^2
RW-1	0.0908	1.00	0.1005	1.00	0.0600	1.00	0.1745	1.00
RW-2	0.0567	1.00	0.0577	1.00	0.0353	1.00	0.0765	1.00
RW-3	0.0202	1.00	0.0376	0.99	0.0126	0.99	0.3643	0.96
RW-4	0.0731	1.00	0.084	1.00	0.0457	1.00	0.1153	1.00

Regarding TOC removal, after 120 min of reaction in the different aqueous matrices, we reached values of 17.91%, 28.21%, 78.43%, and 74.91% for RW-1, RW-2, RW-3, and RW-4, respectively.

In this sense, humic and fulvic acids represent up to 80% of natural waters' TOC (as dissolved organics). Humic substances are weak acidic electrolytes with carboxylic and phenolic groups with a micelle-like structure and molecular weights between 500 (fulvic) and 100,000 (humic). Degradation is usually inhibited by the presence of humic acids [12]. The inhibitory effect of humic acids can be attributed to two facts [33,34]: the removal of reactive species by humic acids and the appearance of a competitive reaction between humic acid and NCTs for reactive ·OH species [13].

3.4. Electrochemical Oxidation of a Broad Group of Emerging Pollutants in a WWTP Effluent

This final section investigates the potential of this technique with a broad group of emerging contaminants in the same aqueous matrix (Badajoz-WWTP effluent). The contaminants chosen for this study are divided into three groups: azole pesticides (fluconazole (FLZ), imazalil (IMZ), tebuconazole (TBZ), and penconazole (PNZ)), antibiotics (amoxicillin (AMX), trimethoprim (TMP), and sulfamethoxazole (SMX)), and antidepressants (desvenlafaxine (DVF)). These compounds are included in the substance observation list for monitoring at the European Union, following Directive 2008/105/EC of the European Parliament [35]. All these compounds were added to the Badajoz-WWTP effluent at a concentration of each = 1 μM.

The experimental conditions were the same as those in the previous sections (see experiment EO-4 of Table 1). The conductivity adjustment was carried out by adding Na_2SO_4 until reaching 2.0 mS·cm^{-1}. The elimination percentages achieved for azole pesticides at different reaction times (10 and 60 min) are shown in Table 11. As was previously mentioned, no investigations were found about the EO of this group of azole pesticides in real effluents.

Table 11. Azole pesticide removals. Experiment EO-4 (see Table 1). Reaction time (10 and 60 min). Aqueous matrix = Badajoz-WWTP effluent. Initial contaminants concentration of each = 1 μM.

Experiment	$E_{FLZ,10}$ (%)	$E_{IMZ,10}$ (%)	$E_{TBZ,10}$ (%)	$E_{PNZ,10}$ (%)	$E_{FLZ,60}$ (%)	$E_{IMZ,60}$ (%)	$E_{TBZ,60}$ (%)	$E_{PNZ,60}$ (%)
Azole pesticides	23.9	96.3	73.8	77.5	80.6	100	100	100

The removal percentages achieved for antibiotics and antidepressants at different reaction times (5 and 10 min) are shown in Table 12 (experiment EO-4). These results agree with those obtained by Murillo-Sierra et al. [36] for SMX degradation using Na_2SO_4 (0.05 M), a BDD anode, and a carbon-felt cathode. However, these results improve the degradation levels obtained by Brito et al. [37] for AMX oxidation using the same electrolyte (0.1 M) with a TiO_2-modified carbon anode and a steel wire cathode.

Table 12. Antibiotics removal. Experiment EO-4 (see Table 1). Reaction times (5 and 10 min). Aqueous matrix = Badajoz-WWTP effluent. Initial contaminants concentration of each = 1 μM.

Experiment	E_{AMX5} (%)	E_{TMP5} (%)	E_{DVF5} (%)	E_{SMX5} (%)	E_{AMX10} (%)	E_{TMP10} (%)	E_{DVF10} (%)	E_{SMX10} (%)
Antibiotics/ Antidepressants	98.2	57.8	100	98.2	100	88.8	100	100

We can conclude that there is a higher reactivity for antidepressants (antidepressants > antibiotics > azole pesticides > neonicotinoids). This observation supports the assertion that this technique suits NCTs and a large group of emerging contaminants in this effluent type (WWTP effluent) for regeneration purposes.

4. Conclusions

Electrochemical oxidation with boron-doped diamond anodes demonstrated a great potential to remove a broad group of emerging contaminants (antidepressants, antibiotics, azole pesticides, and neonicotinoids) in a WWTP effluent aqueous matrix. While other advanced oxidation techniques achieve similar levels of degradation in similar treatment times, none achieves the mineralization levels achieved through this oxidation system.

Total contaminant removal (100%) of each contaminant and TOC removals between 27–77% were obtained. The energy consumption ranged between $4.60 \cdot 10^{-3}$–$1.44 \cdot 10^{-2}$ kW·h·g^{-1} in this WWTP effluent.

Regarding the influence of operating variables, the applied current density positively affects the contaminant removal, TOC removal, and kinetics but considerably worsens the energy consumption and, therefore, the associated costs. The influence of the conductivity of media was positive (but very soft) on all target variables except for energy consumption, which strongly influences reducing the associated costs by up to 38%.

Concerning the electrolyte type, the best results were obtained by using Na_2SO_4. The aqueous matrix significantly influences the degradation rate of contaminants with the following ranking sequence: Guadiana-river > Badajoz-WWTP effluent > Villar del Rey-reservoir > Almendalejo-WWTP effluent. These results were attributable to anionic species acting as ·OH radical scavengers (such as NO_3^-, HPO_4^{2-}, or HCO_3^-). The process kinetics fit well to a pseudo-first-order pattern, following a reactivity ranking (in WWTP effluent): antidepressants > antibiotics > azole pesticides > neonicotinoids.

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