ARTICLE

Groundwater treatment using a solid polymer electrolyte cell with mesh electrodes

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Abstract: This article reports the high performance of a solid polymer electrolyte cell, equipped with a Nafion® N117 membrane packed between a Nb/BDD mesh anode and a Ti/RuO$_2$ mesh cathode, to degrade the insecticide imidacloprid spiked at 1.2 - 59.2 mg L^{-1} into low conductivity groundwater by electrochemical oxidation. The natural water matrix was first softened using valorized industrial waste in the form of zeolite as reactive sorbent. Total removal of the insecticide, always obeying a pseudo-first-order kinetics, and maximum mineralization degrees of 70%-87% were achieved, with energy consumption of 26.4±1.6 kWh m^{-3}. Active chlorine in the bulk and •OH at the BDD surface were the main oxidants. Comparative studies using simulated water with analogous anions content revealed that the natural organic matter interfered in the groundwater treatment. Trials carried out in ultrapure water showed the primary conversion of the initial N and Cl atoms of imidacloprid to NO$_3^-$ and Cl$^-$ ions, being the latter anion eventually transformed into ClO$_3^-$ and ClO$_4^-$ ions. 6-Chloro-nicotinonitrile, 6-chloro-pyridine-3-carbaldehyde, and tartaric acid were identified as oxidation products.

Introduction

Over the last decade, great progress has been made to address the removal of recalcitrant organic pollutants from urban and industrial wastewater thanks to the development of more suitable technologies, in particular the so-called electrochemical advanced oxidation processes (EAOPs).[1-4] These are considered environmentally friendly treatments that are easy to operate and maintain, also being safe, readily scalable and relatively cost-effective, typically involving the use of ambient pressure and temperature. Electrochemical oxidation (EO),[1,5-8]

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electro-Fenton (EF),[2,9-13] and photoelectro-Fenton (PEF),[2,14-16] are ubiquitous EAOPs for effective wastewater treatment in which organics pollutants are mainly destroyed by the strong oxidant hydroxyl radical (•OH). This radical is generated in situ at the anode surface and/or in the bulk from Fenton reaction, being assisted by the photocatalytic action of UV radiation in PEF. The simplest method is EO in inert electrolytes (e.g., sulfate, nitrate, perchlorate), since organic molecules are only attacked by the species generated at the anode. In the absence of Cl$^-$ ion, the non-active boron-doped diamond (BDD) thin films are the best anodes for EO. The H$_2$O oxidation at the BDD surface via Equation (1) produces larger amounts of physisorbed •OH, denoted as BDD(•OH), as compared to other anodes.[1,6,17-19] In contrast, the presence of Cl$^-$ ion in the reaction medium complicates the situation because it can be easily oxidized at the BDD anode, giving rise to competing oxidizing agents like active chlorine species (Cl$_2$, HClO, and/or ClO$^-$, depending on pH) from Equations (2)-(4).[20-23] HClO and ClO$^-$ can then evolve to other oxychlorine ions like ClO$_2^-$, ClO$_3^-$, and ClO$_4^-$ from Equations (5)-(7), with a conversion degree that depends on the initial Cl$^-$ and organics concentration, the applied current and the flow rate.

$$BDD + H_2O \rightarrow BDD(•OH) + H^+ + e^- \qquad (1)$$

$$2Cl^- \rightarrow Cl_2(aq) + 2e^- \qquad (2)$$

$$Cl_2(aq) + H_2O \rightarrow HClO + Cl^- + H^+ \qquad (3)$$

$$HClO \leftrightarrows ClO^- + H^+ \qquad pK_a = 7.56 \qquad (4)$$

$$HClO + H_2O \rightarrow ClO_2^- + 3H^+ + 2e^- \qquad (5)$$

$$ClO_2^- + H_2O \rightarrow ClO_3^- + 2H^+ + 2e^- \qquad (6)$$

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^- \qquad (7)$$
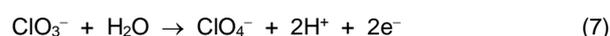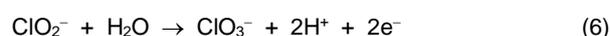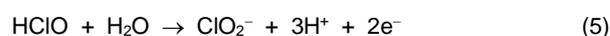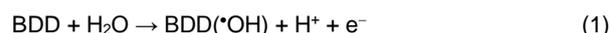
The EO treatment is typically applied over a long period of time. The major impact on the energy consumption of this process is exerted by the solution conductivity. High values of this parameter are usually recommended, because it is directly correlated with a lower cell voltage and hence, with a smaller energy requirement. Unfortunately, natural water, urban wastewater, and many industrial and hospital effluents present very low conductivities, which may prevent the direct application of EO for their decontamination. This is the main reason to explain the scarce expansion of EO as a technology for natural water treatment. The most common approach to overcome this limitation is the addition of supporting electrolyte, typically Na$_2$SO$_4$ and/or NaCl. Less explored alternatives have considered the direct application of EO to raw low conductivity aqueous matrices using microfluidic

reactors,[24,25] or solid polymer electrolyte (SPE) cells.[26-32] An SPE cell presents a sandwich configuration, i.e., anode/polymer electrolyte/cathode, which ensures an appropriate current flux when immersed in a low conductivity medium. The cost of the membrane and its potential fouling, have been described as possible drawbacks for this cell.[32] SPE cells have been mainly employed in the electrochemical production of ozone.[26-28] They have also offered good performances for water treatment, although only synthetic solutions prepared with deionized water have been tested so far.[29-32] For example, the successful mineralization of benzyl alcohol using a BDD/Nafion®/BDD cell,[29] and the dyes Safranin T [31] and Crystal Violet [32] using a BDD/Nafion®/RuO$_2$ cell has been described. However, no previous studies have reported the use of SPE cells to decontaminate natural wastewater.

An important parameter to keep under strict control for the electrochemical decontamination of groundwater is water hardness, since calcium and magnesium ions can induce cathode scaling upon precipitation in the form of hydroxides and carbonates. In order to avoid the electrode passivation, some kind of softening pre-treatment is required.[33] Within the context of circular economy, the valorization of industrial waste to yield added-value products is of major interest nowadays. Reactive powdered sorbents like Na$^+$- and K$^+$-loaded synthetic zeolites can be prepared from coal combustion fly ash.[34] Further, they can be added to the natural water matrix to trap calcium and magnesium cations, prior to subsequent electrochemical treatment.

Imidacloprid (C$_9$H$_{10}$ClN$_5$O$_2$, M = 255.66 g mol^{-1}) is a widely used neonicotinoid insecticide in agriculture. It is classified as moderately toxic by the USEPA, with tolerance from 0.02 m kg^{-1} in eggs to 3.0 mg kg^{-1} in hops. Its ingestion by animals can produce pre-eminently hepatotoxicity, along with immunotoxic, nephrotoxic, and oxidative stress effects.[35] Imidacloprid is highly resistant to degradation and, consequently, it has been detected at concentrations up to 52 μg L^{-1} in agricultural water[36] and 0.36 μg L^{-1} in urban wastewater.[37] The destruction of this pollutant was feasible using ultrasounds combined with UV radiation and H$_2$O$_2$,[38] as well as EAOPs like EO[39,40] and EF.[41-43] In these electrochemical treatments, large mineralization (> 80%) was attained from highly conductive synthetic solutions containing pure water, sulfate and 0.1-10 mM imidacloprid, using anodes of BDD, PbO$_2$, and mixed metal oxides of Ru, Ir, and Ti (i.e., dimensionally stable anodes, DSA®). However, the use of low conductivity media and natural water has not been described yet.

This work reports the destruction of imidacloprid, spiked into groundwater, by EO using an SPE cell composed of a Nafion® membrane in contact with a Nb/BDD mesh anode and a Ti/RuO$_2$ mesh cathode. Mesh electrodes were employed to ensure the H$^+$ passage through the membrane. Comparative experiments were performed with simulated water whose anions content was similar to that of groundwater, in the absence of natural organic matter (NOM). The effect of applied current and pesticide concentration was examined. The action of active chlorine was assessed from a comparative treatment in pure water. The transformation of the

N atoms and the fate of Cl$^-$ released or present in the medium were analyzed, and the main oxidation products were identified.

Results and Discussion

Comparative imidacloprid treatment in different aqueous matrices

First assays were carried out by electrolyzing 500 mL of 23.7 mg L^{-1} imidacloprid (i.e., 10.0 mg C L^{-1} total organic carbon (TOC)) spiked into the raw groundwater at pH 6.9, using the SPE cell at 0.50 A and 25 ºC. However, a gradual increase of cell voltage with time was observed, also resulting in a slower pesticide abatement and a lack of reproducibility upon successive trials. These findings were attributed to the passivation of the cathode, which became coated with a grey jelly film due to the precipitation of hydroxides and carbonates of alkaline earth metal ions (Ca^{2+} and Mg^{2+}) present in the matrix. On the other hand, preliminary assays allowed discarding any adsorption of the insecticide on the electrodes or membrane. To prevent the cathode fouling, the raw groundwater was softened using a Na$^+$-loaded zeolite, as explained in the Experimental Section. Table 1 collects the physicochemical characteristics of the raw and pre-treated groundwater. Upon softening, an increase of pH up to 9.8, conductivity up to 2.95 mS cm^{-1}, and Na$^+$ concentration up to 780 mg L^{-1} was found, whereas Ca^{2+} and Mg^{2+} concentrations were drastically reduced down to 12.3 and 2.3 mg L^{-1}, respectively. The rise in Na$^+$ content, with much higher molar conductivity than replaced Ca^{2+} and Mg^{2+}, explains the greater conductivity of the

Table 1. Physicochemical characteristics of the groundwater used as real water matrix, before and after softening with zeolite.

Parameter (units)	Raw groundwater	Softened groundwater
pH	6.9±0.1	9.8±0.1
Conductivity (mS cm^{-1})	1.87±0.07	2.95±0.12
TC (mg C L^{-1})	67.2±1.0	143.2±1.6
TOC (mg C L^{-1})	2.6±0.1	2.8±0.1
NO$_3^-$ (mg L^{-1})	107±3	107±3
NO$_2^-$ (mg L^{-1})	n.d.[a]	n.d.[a]
Cl$^-$ (mg L^{-1})	458±20	473±19
SO$_4^{2-}$ (mg L^{-1})	90±4	110±4
Ca^{2+} (mg L^{-1}	240±10	12.3±0.5
Mg^{2+}(mg L^{-1})	55±2	2.3±0.1
K$^+$(mg L^{-1})	4.5±0.2	60±3
Na$^+$(mg L^{-1})	80±2	780±31
NH$_4^+$(mg L^{-1})	n.d.[a]	n.d.[a]

[a] Not detected.
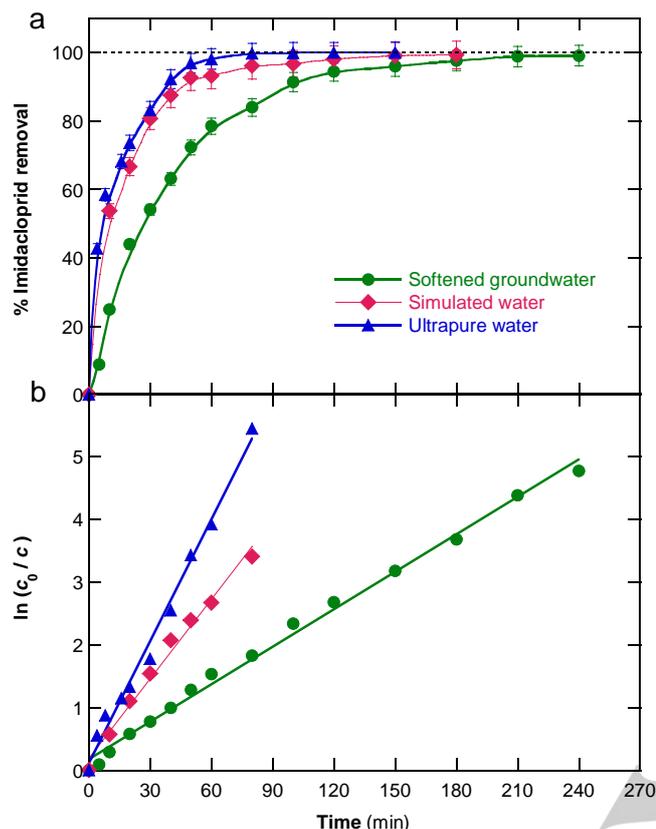
Figure 1. (a) Percentage of imidacloprid removal and (b) pseudo-first-order kinetic analysis of each decay trend at increasing electrolysis time for the electrochemical oxidation of 500 mL of 23.7 mg L^{-1} of the insecticide in several aqueous matrices at pH 9.8 and 25 ºC using an SPE cell with a Nb/BDD mesh anode and a Ti/RuO$_2$ mesh cathode at 0.50 A.

softened groundwater. The content of significant anions such as NO$_3^-$, Cl$^-$, and SO$_4^{2-}$ remained practically constant during the pre-treatment. The softened groundwater was employed in all further EO treatments focused on real matrix since a stable current and cell voltage were obtained, without any additional fouling. For comparative degradation studies, two synthetic aqueous matrices of very low conductivity were also employed: a simulated water matrix with anions composition similar to that of the softened groundwater, and an ultrapure water matrix (see Experimental Section). The pH of these two matrices was adjusted to 9.8 to mimic that of the pre-treated groundwater. All the experiments were run at this pH, aiming at simplifying and making less expensive the conditioning process in future applications of this technology.

Figure 1a depicts the change of the percentage of imidacloprid removal with electrolysis time for the EO treatment of solutions containing 23.7 mg L^{-1} insecticide in the three matrices at 0.50 A for 240 min. Total disappearance was achieved after 150 min in ultrapure water, 180 min in simulated water, and 240 min in groundwater. This trend is indicative of a quicker attack of BDD($^\bullet$OH), originated from Equation (1), as single oxidant over

the organic molecule in the former matrix, as compared to its combined attack with active chlorine, formed from Equations (2)-(4), in the two latter matrices. It is also worth mentioning that the scavenging effect of the inorganic carbon, present in such alkaline media, causing some BDD($^\bullet$OH) consumption that can diminish the oxidation power of the EO process.[23] The faster insecticide removal in the simulated water matrix compared to that obtained in groundwater can be explained by the simultaneous destruction of the NOM contained in the real sample, thus reducing the amount of available oxidants to attack the insecticide.

The excellent linear trend lines found from the pseudo-first-order kinetic analysis of the concentration decays in the above trials are presented in Figure 1b. From their slopes, decreasing apparent rate constants (k_1) of $(6.4\pm0.3)\times10^{-2}$ min^{-1} ($R^2 = 0.990$) in ultrapure water, $(4.2\pm0.2)\times10^{-2}$ min^{-1} ($R^2 = 0.986$) in simulated water, and $(2.0\pm0.1)\times10^{-2}$ min^{-1} ($R^2 = 0.994$) in groundwater were determined. This behavior suggests the reaction of imidacloprid with a constant amount of BDD($^\bullet$OH) and/or active chlorine in each case.

Figure 2a shows the percentage of TOC removal vs. electrolysis time for the assays of Figure 1. Again, the most powerful EO treatment was achieved in ultrapure water, giving rise to 88% mineralization, whereas the oxidation ability of the SPE cell was
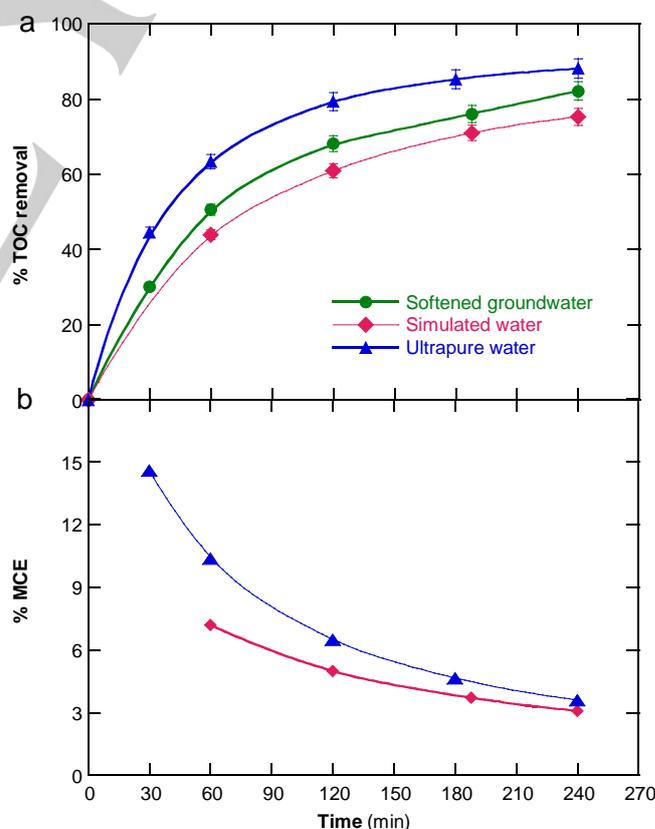
Figure 2. Change of the percentage of (a) TOC removal and (b) mineralization current efficiency with electrolysis time for the assays of Figure 1.

inverted for the other two matrices as compared to the insecticide removal. A greater mineralization rate can be observed in Figure 2a for the trial in groundwater (12.8 mg C L^{-1} of initial TOC), attaining 82% mineralization, as compared to that in simulated water (10.0 mg C L^{-1} of initial TOC) where only 75% mineralization was reached. This accounts for a larger destruction of a quantity of about 2.8 mg C L^{-1} TOC in groundwater, which means that the NOM content was completely mineralized in the SPE cell (see Table 1) under the action of BDD($^\bullet$OH) and active chlorine. On the other hand, the superior mineralization of the insecticide in ultrapure water is due to the action of BDD($^\bullet$OH) as single oxidant, in contrast to the simultaneous attack of active chlorine over the organics in the two chlorinated matrices, yielding chloroderivatives that are more recalcitrant and hence, less prone to transformation into CO_2.[3,4,22,23] It should be noted that the solution pH did not vary when the degradation was studied in groundwater, whereas it decayed from 9.8 to 7.5 in the case of simulated water. In contrast, this pH change was found after 150 min of treatment in ultrapure water, whereupon it continuously dropped down to pH near 5. These results suggest the formation of acidic products, whose effect was much less evident in groundwater probably because of the buffering capacity conferred by the large amount of HCO_3^-/CO_3^{2-} concentration (see Table 1).

During the above mineralization assay in ultrapure water, the fate of the N and Cl atoms of imidacloprid was assessed. The results obtained are shown in Figure 3a and b, respectively. Figure 3a highlights that the initial N was pre-eminently mineralized to NO_3^- ion, although its content gradually increased to attain only 27.1% conversion. In contrast, the conversion of N to NO_2^- ion was very low, dropping from 1.1% at 30 min to 0.3% at 240 min because it became oxidized to NO_3^- ion as the solution pH decreased. A small content of NH_4^+ ion was also accumulated, with a maximum final conversion of 3.8%. At the end of the EO treatment with 88% mineralization, a small proportion of 31.0% of initial N was released as nitrogenated ions. This can be explained by the loss of volatile nitrogenated products, probably N_2, N_xO_y, and chloramines, as typically reported for other organics.[4,22,23] Figure 3b highlights that the Cl atom of the insecticide was initially released as Cl^- ion, attaining a maximal of 32.0% at 60 min, whereupon it decreased dramatically down to a final value of 9.7%. This decay was due to its oxidation to active chlorine (Cl_2/HClO/ClO$^-$) from Equations (2)-(4), but such species were not detected since they were partially oxidized to ClO_3^- and ClO_4^- ions via Equations (5)-(7), reaching final conversions of 7.1% and 20.6%, respectively. Since only a 37.4% of the initial Cl was detected in the form of chloride and oxychlorine ions, one can infer that most of the active chlorine reacted either with organics to form chloro-organics or with NH_4^+ ion to form chloramines.[20-23] However, the amount of lost chlorine was so small (0.06 mM as maximal) that, in practice, in this matrix imidacloprid and its oxidation products were more rapidly oxidized and to much larger extent by BDD($^\bullet$OH), giving rise to the quickest insecticide and TOC decays as compared to those in the two chlorinated matrices, as shown in Figures 1a and 2a. On the other hand, the final concentration of the above species after the EO treatment in simulated water and groundwater were also quantified. In the

case of nitrogenated ions, neither NO_2^- nor NH_4^+ ions were detected, whereas the initial 107±3 mg L^{-1} of NO_3^- ion rose up to 125±5 mg L^{-1}, meaning that its surplus (18 mg L^{-1}) came from the initial N of imidacloprid (6.49 mg L^{-1}). This represents a conversion of 62.6% into this ion, much superior to 27.1% found in ultrapure water, suggesting that the pathway originating NO_3^- is favored in the chlorinated matrices. SI Table S1 confirms the oxidative transformation expected for the Cl contained in both chlorinated matrices (i.e., Cl of the insecticide + Cl$^-$ in the medium). So, in both cases, the Cl$^-$ concentration initially accumulated was dramatically reduced, being transformed into active chlorine that was further oxidized to ClO_3^- ion and, to a smaller proportion, to ClO_4^- ion. Note that the production of ClO_3^- and ClO_4^- ions is likely dependent on the applied current, diminishing as current decreases.[3] Moreover, active chlorine reacts with organics to yield, in many cases, chloroderivatives that release Cl$^-$ ion when they became mineralized.[2-4] A simple mass balance of the data of Table S1 reveals that < 2% of initial Cl was lost from each medium, probably due to the release of volatile chloramines causing that the small NH_4^+ content expected from the initial N of imidacloprid (see Figure 3a) was not detected.

From the aforementioned findings, the mineralization reaction of imidacloprid involves the formation of CO_2, Cl$^-$ as primary ion and
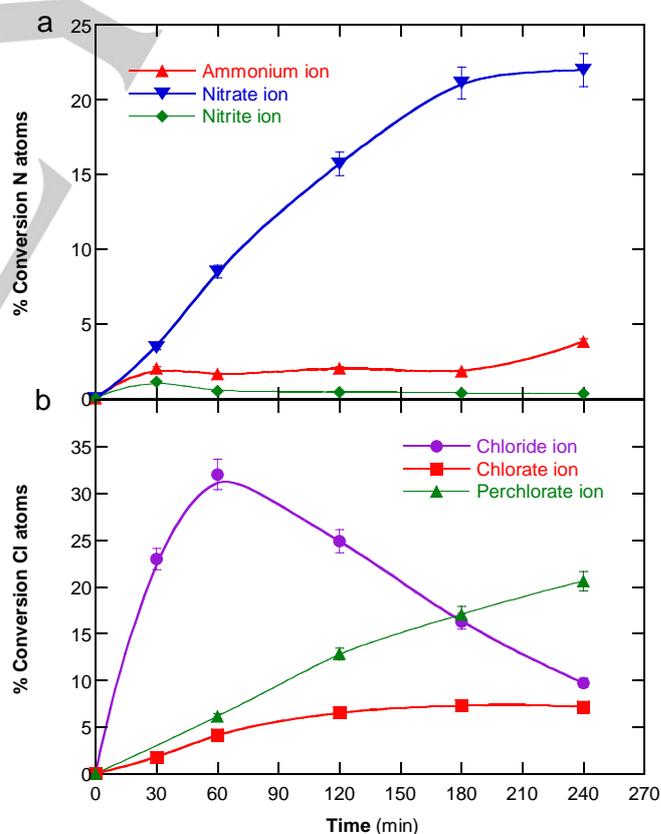
Figure 3. Evolution of (a) nitrogenated and (b) chloride and oxychlorine ions percentages during the experiment shown in Figure 2 carried out in ultrapure water as aqueous matrix.

NO_3^-, as shown in Equation (8), with a number of consumed electrons $n = 66$:

$$C_9H_{10}ClN_5O_2 + 31H_2O \rightarrow 9CO_2 + Cl^- + 5NO_3^- + 72H^+ + 66e^- \quad (8)$$
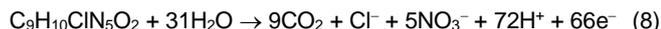
On this basis, the percentage of mineralization current efficiency (MCE) for a TOC decay (ΔTOC, in mg C L^{-1}) in a given assay at current I (A) and time t (h) was estimated from Equation (9):[2,3]

$$\% \ \mathbf{MCE} = \frac{n \, F \, V \, \Delta \mathbf{TOC}}{4.32 \times 10^7 \, m \, I \, t} \, \mathbf{100} \quad (9)$$

where F is the Faraday constant, V is the solution volume (L), 4.32×10^7 is a factor for units homogenization (s mg C h^{-1} mol^{-1}), and m is the number of carbon atoms of the insecticide.

Figure 2b shows the MCE values calculated for the EO experiments in ultrapure and simulated water, which did not contain NOM, depicted in Figure 2a. According to Equation (9), greater ΔTOC yields higher MCE and, for this reason, the current efficiency was greater for the process using ultrapure water, decaying from 14.6% at 30 min to a final value of 3.6%. The same profile can be observed in the simulated water, where the MCE value dropped from 7.2% at 30 min to 3.1% at 240 min. The progressive decrease of MCE can be ascribed to the loss of organic matter, along with the formation of more refractory products that impede the achievement of total mineralization of the insecticide.[1,2]

Imidacloprid treatment in simulated water

The influence of the applied current on the oxidation ability of EO to remove imidacloprid in simulated water using the SPE cell was assessed because this parameter determines the amount of generated oxidizing agents as well as the resulting cell voltage, which is of paramount importance in low conductivity media. To do this, 500 mL of 23.7 mg L^{-1} of the insecticide (10.0 mg C L^{-1} of TOC) in this matrix at pH 9.8 and 25 °C were treated at a constant current between 0.10 and 1.50 A for 240 min. Figure 4a illustrates a rapid and continuous removal of imidacloprid in all cases, whose rate is enhanced as the applied current is increased. Total removal was reached at shorter times of 240, 210, 180, and 120 min at 0.10, 0.25, 0.50, and 1.00 A, respectively. Similar degradation rates with disappearance at the same time can be observed at 1.00 and 1.50, being slightly quicker than the degradation at 0.50 A. This means that the process attained the maximum degradation power. The enhancement of the insecticide decay at higher current can be associated with the concomitant acceleration of all electrode reactions. Greater amounts of BDD($^{\bullet}$OH) from Equation (1) and active chlorine from Equations (2)-(4) are then produced, allowing a faster attack over the target organic pollutant.

The imidacloprid concentration decay in the above trials always obeyed a pseudo-first-order kinetics, as shown in Figure 4b. SI Table S2 shows that the k_1-values obtained from this analysis gradually increased from $(2.4 \pm 0.1) \times 10^{-2}$ min^{-1} at 0.10 A to
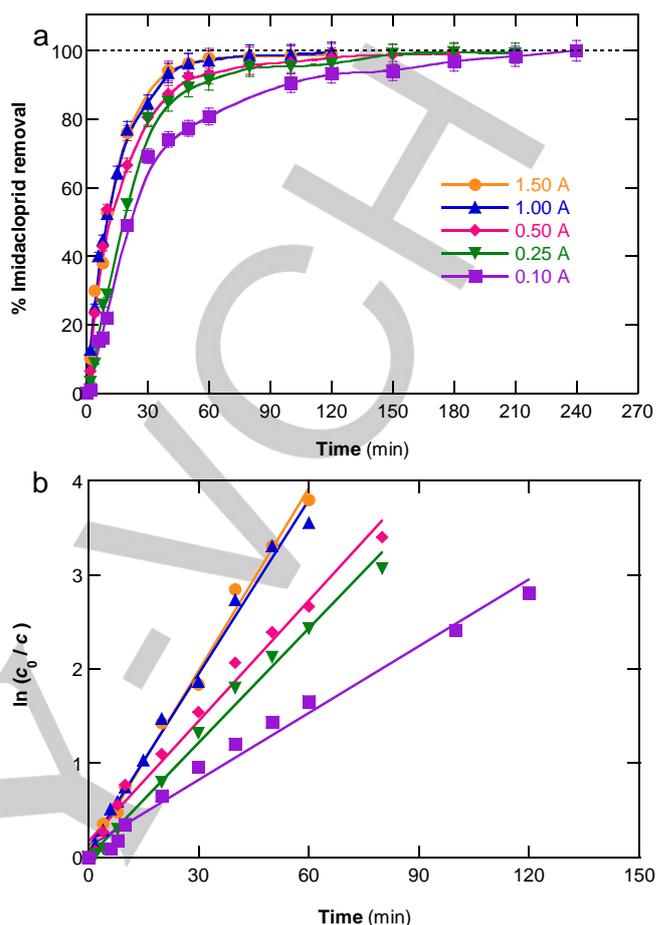
Figure 4. Effect of applied current on the (a) percentage of imidacloprid removal and the (b) pseudo-first-order kinetic analysis of each decay trend vs. electrolysis time for the electrochemical oxidation of 500 mL of 23.7 mg L^{-1} of the insecticide in simulated water at pH 9.8 and 25 °C using an SPE cell with a Nb/BDD mesh anode and a Ti/RuO$_2$ mesh cathode.

$(6.5 \pm 0.2) \times 10^{-2}$ min^{-1} at 1.50 A. The analogous k_1-value determined for the two latter currents confirms the limitation of the degradation ability of the electrolytic setup from 1.00 A, at least for the removal of this pesticide. The pseudo-first-order reaction found at each current can be related to the attack of a constant, but different, quantity of BDD($^{\bullet}$OH) and active chlorine over the insecticide molecules, despite the simultaneous destruction of its oxidation products, as will be discussed below.

The variation of the percentage of TOC removal with electrolysis time during the above experiments is depicted in Figure 5a. A progressively larger mineralization as the electrolyses were prolonged can be seen in all cases, showing a higher rate as current was increased. After 240 min of EO treatment, TOC was reduced by 65%, 69%, 75%, 80%, and 86% at 0.10, 0.25, 0.50, 1.00, and 1.50 A, respectively. This tendency is analogous to that described for imidacloprid removal, meaning that the rise in concentration of generated oxidants was able to destroy more rapidly all the organics present in the medium, not just the parent compound. Note that the TOC removal reached at 1.50 A was
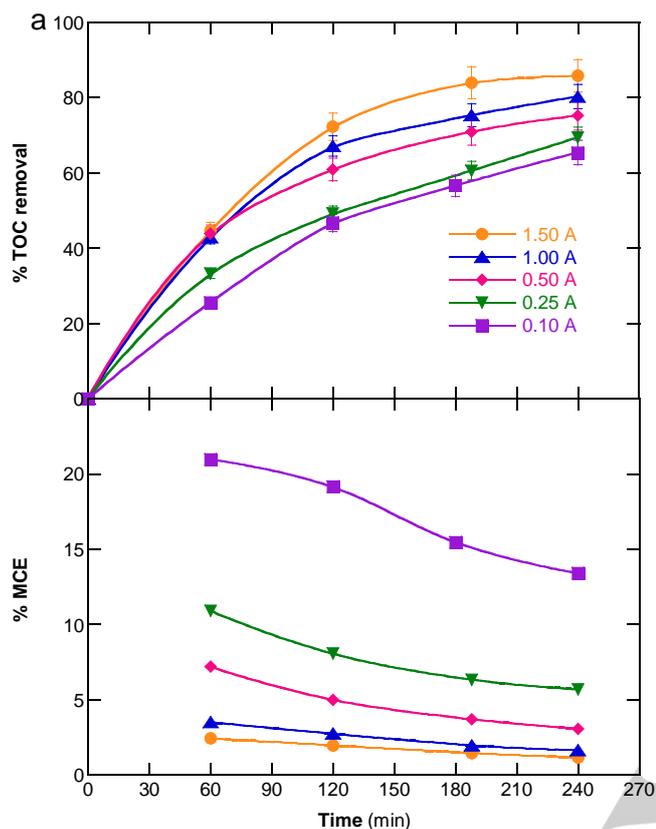
Figure 5. Variation of the percentage of (a) TOC removal and (b) mineralization current efficiency with electrolysis time for the trials of Figure 4.

Figure 6. Time course of the concentration of active chlorine generated during the assays of Figure 4 and 5.

clearly higher than that at 1.00 A, which differs from the similar degradation profile of the insecticide at both current values. This points to consider that the mineralization power of the EO process in the SPE cell was not really limited at such high current. This suggests that the excess of generated oxidants at 1.50 A were actually able to destroy preferentially some oxidation products that were less recalcitrant than the pesticide.

The percentage of MCE calculated from Equation (9) at each time for the trials of Figure 5a is depicted in Figure 5b. In contrast to the greater mineralization achieved at higher current, a progressive decrease of MCE can be observed. This is not surprising because a high increase of I in the denominator of Equation (9) involves a much lower MCE. So, the greatest MCE values were determined at 0.10 A, decreasing from 20.9% at 60 min to 13.4% at 240 min as a result of the loss of organic matter and the generation of more recalcitrant products, as pointed out above. This informs about a relative loss of the oxidation power of the EO process, because an increasing amount of oxidizing agents are wasted when current increases and hence, a much lower relative proportion of oxidants is available to attack the organics, decreasing the MCE value. In the case of BDD($^{\bullet}$OH), the main waste reaction is its oxidation to O_2 from Equation (10).[1] Other reactions are the dimerization to yield H_2O_2 from Equation (11), and the reaction between the two latter species to yield the

weak oxidant hydroperoxyl radical (HO$_2^{\bullet}$) from Equation (12).[3,22]

$$2BDD(^{\bullet}OH) \rightarrow 2BDD + O_2 + 2H^+ + 2e^- \tag{10}$$

$$2BDD(^{\bullet}OH) \rightarrow 2BDD + H_2O_2 \tag{11}$$

$$BDD(^{\bullet}OH) + H_2O_2 \rightarrow BDD + HO_2^{\bullet} + H_2O \tag{12}$$
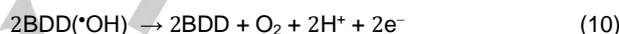
The waste reactions of active chlorine include its consecutive oxidation to ClO_2^-, ClO_3^-, and ClO_4^- ions from Equations (5)-(7), as experimentally confirmed for the simulated water during EO (see Table S1). Figure 6 evidences a greater initial production of active chlorine as current was increased, attaining maximum concentrations of 29.5, 44.8, 78.6, 94.9, and 121.7 mg L^{-1} after 30-60 min. However, a decay of the accumulated active chlorine concentration can be observed at longer electrolysis time, to larger extent as the current rose, except at 0.10 A. This decrease was slow at 0.25 and 0.50 A, whereas complete disappearance of active chlorine species occurred after 240 min at 1.00 A and 180 min at 1.50 A. These findings are indicative of the initially higher production of active chlorine by the acceleration of Cl$^-$ oxidation from Equation (2) at higher current, which enhanced imidacloprid destruction, but also of its greater destruction from Equations (5)-(7), thus decreasing its relative content and MCE. Therefore, the use of lower current favors the accumulation of a lower quantity of undesirable oxychlorine ions, although at the expense of a slower degradation and lower mineralization ability.

Detection of oxidation products

The oxidation products originated after 30 min of EO treatment of 23.7 mg L^{-1} imidacloprid at 0.50 A were identified by gas chromatography-mass spectrometry (GC-MS). Two stable heteroaromatic intermediates, namely 6-chloro-nicotinonitrile (m/z 140 (^{37}Cl)/138 (^{35}Cl)) and its derivative 6-chloro-pyridine-3-carbaldehyde (m/z 142 (^{37}Cl)/140 (^{35}Cl)), were identified. The former product is originated from the cleavage of the imidazole

ring of the parent molecule, which is subsequently oxidized with transformation of the nitrile group into a carbaldehyde one. These products differ from 6-chloronicotinic acid, 6-chloronicotinaldehyde, and 6-hydroxynicotinic acid identified by the same technique when imidacloprid was treated in sulfate medium by EO with a Pt or BDD anode and EF with the same anodes and a carbon felt cathode.[42]

Operating with 23.7 mg L^{-1} of the insecticide at 0.50 A, the feasible generation of final short-chain linear aliphatic formed from the cleavage of the pyridine and imidazole moieties of imidacloprid during the EO treatment in simulated water as well as in groundwater, was evaluated by ion-exclusion HPLC.[40] In both media, traces of oxalic and formic acids, which are directly transformed into CO_2,[2-4] were found, suggesting that they are oxidized as they are formed. Only large contents of tartaric acid were detected. SI Figure S1 illustrates that this acid was released rapidly at the beginning of the treatment, attaining 3.2 mg L^{-1} at 40 min in simulated water and 5.1 mg L^{-1} at 20 min in groundwater. At longer time, it decreased progressively to disappear at 120 min in the former matrix and to be reduced down to 0.6 mg L^{-1} at 240 in the latter one. This suggests that the contribution of final carboxylic acids to the residual TOC in both media (see Figure 2a) is insignificant, as expected if the undetected final organics products are even more recalcitrant than those ones.

EO treatment in softened groundwater

The oxidation ability of EO using the SPE cell was assessed within a large range of insecticide concentrations, from 1.2 to 59.2 mg L^{-1}, spiked into softened groundwater. Lower concentrations were assayed but no accurate results could be obtained. Figure 7a highlights that overall removal of imidacloprid was reached after 210-240 min of electrolysis, regardless of its initial concentration. Note that, in a pure electrolyte, a gradual decrease in rate of pollutant removal is typically observed because of the presence of a larger organic load under the action of similar amounts of generated oxidants. However, this trend is not observed in Figure 7a, since the degradation rate decreased from 1.2 to 4.8 mg L^{-1}, whereupon gradually rose up to 59.2 mg L^{-1}. This is corroborated from the pseudo-first-order kinetic analysis depicted in Figure 7b. A fluctuating k_1-value was determined, varying between $(2.1\pm0.1)\times10^{-2}$ min^{-1} at 1.2 mg L^{-1} and $(2.5\pm0.2)\times10^{-2}$ min^{-1} at 59.2 mg L^{-1}, as can be seen in SI Table S2. This anomalous behavior can be related to the simultaneous oxidation of the NOM contained in the matrix, which consumes part of the generated BDD($^{\bullet}$OH) and active chlorine. Up to 4.8 mg L^{-1}, it seems that the NOM interference is very significant and largely reduces the insecticide removal, whereas at higher content, the attack of the oxidants over imidacloprid became predominant and its destruction was gradually enhanced. These results allow concluding that the EO process is very efficient to remove organics from pre-treated groundwater, despite the negative influence of NOM on the degradation rate, especially at small organic loads.
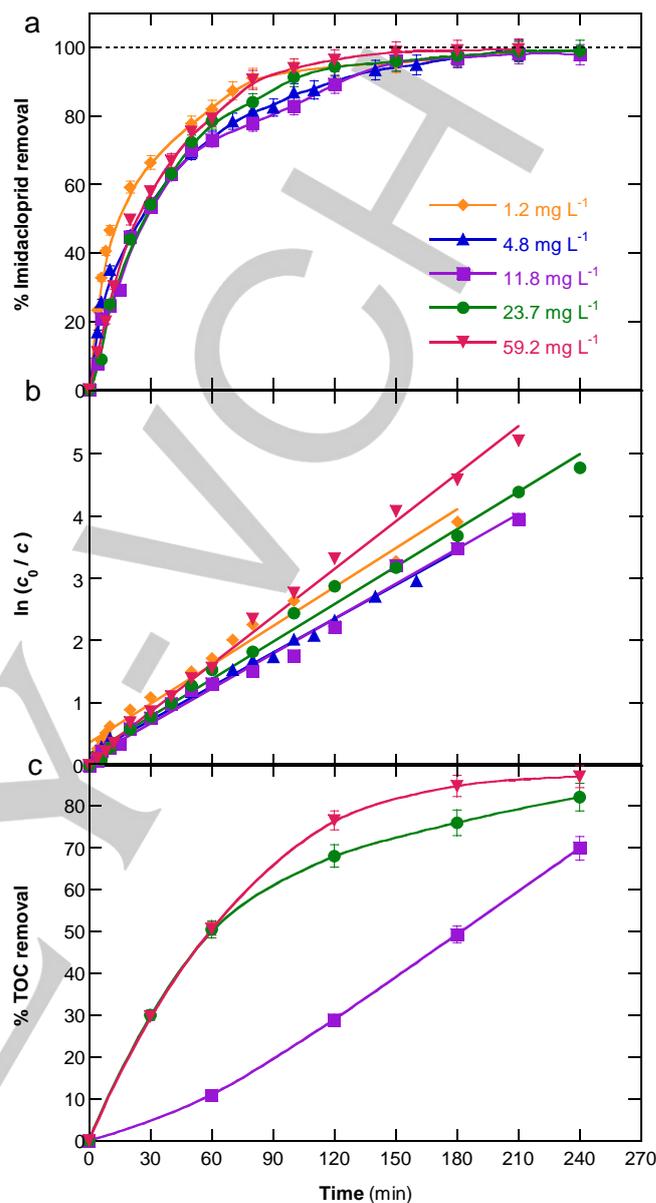
Figure 7. Effect of insecticide concentration on the variation of the (a) percentage of imidacloprid removal, (b) pseudo-first-order decay kinetics, and (c) percentage of TOC removal with time for the electrochemical oxidation of 500 mL of the insecticide spiked into softened wastewater at pH 9.8 and 25 °C using an SPE cell with a Nb/BDD mesh anode and a Ti/RuO$_2$ mesh cathode at 0.50 A.

Figure 7c evidences the NOM interference when evaluating the percentage of TOC decay of the above solutions. Only accurate TOC measurements were possible for pesticide contents ≥11.8 mg L^{-1} (7.8 mg C L^{-1} of initial TOC). At this concentration, an exponential profile can be observed in Figure 7c, meaning that imidacloprid mineralization was progressively accelerated as NOM was converted into CO_2, attaining 70% TOC reduction. This effect was less evident at 23.7 and 59.2 mg L^{-1} of insecticide,

corresponding to initial TOC of 12.8 and 27.8 mg C L^{-1}, due to the smaller proportion of NOM and thus, TOC was reduced by 82% and 87%, respectively. This confirms again the high oxidation power of the electrolytic system to destroy imidacloprid and its oxidation products. In these trials, the cell voltage (E_{cell}) remained very stable, ca. 6.6±0.4 V, which corresponded to a low energy consumption (= E_{cell} I t V^{-1}) of 26.4±1.6 kWh m^{-3}, being very appealing for future scale-up of EO technology with SPE cell.

Conclusions

It has been shown that the use of zeolites obtained from valorized industrial waste ensures sufficient groundwater softening, further allowing its effective electrochemical decontamination. Imidacloprid concentrations between 1.2 and 59.2 mg L^{-1}, spiked into pre-treated groundwater at pH 9.8, were degraded at a similar rate until 100% removal was reached by EO using an SPE cell with mesh electrodes at 0.50 A. High mineralization degrees up to 87% were achieved, with energy consumptions as low as 26.4±1.6 kWh m^{-3}. Comparative studies in simulated water revealed a quicker removal of the target pollutant, but with slower mineralization, due to the absence of NOM. Organics were destroyed by BDD($^{\bullet}$OH) at the anode surface and active chlorine formed in the bulk. The greater production of both oxidants as the applied current was increased from 0.10 to 1.50 A accounted for by the quicker degradation and mineralization, in concomitance with a progressive decay in MCE. Analogous trials using ultrapure water without any dissolved electrolyte showed a quicker destruction of all organics due to their efficient oxidation by BDD($^{\bullet}$OH). It was found that the initial N atoms were mainly as NO$_3^-$ ion, with only minor accumulation of NO$_2^-$ and NH$_4^+$ ions. The initial Cl was transformed into Cl$^-$ ion, which was further transformed into ClO$_3^-$ and ClO$_4^-$ ions. All the imidacloprid decays obeyed a pseudo-first-order kinetics. 6-Chloro-nicotinitrile, 6-chloro-pyridine-3-carbaldehyde, and tartaric acid were detected as stable oxidation products. This work demonstrates the feasibility of electrochemical groundwater treatment with BDD anode, although low current should be applied to minimize the formation of undesirable oxychlorine ions.

Experimental Section

Analytical standard imidacloprid (*N*-{1-[(6-Chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl}nitramide, PESTANAL®) was purchased from Sigma-Aldrich. Analytical grade H$_2$SO$_4$ (95-98%) and NaOH (98-100%) were purchased from Panreac. The salts used for the preparation of the simulated water were: Na$_2$SO$_4$ (99.9%) from BDH PROLABO®, KNO$_3$ (98%) from Panreac and NaCl (99%) from Panreac, all of analytical grade. Carboxylic acids and other chemicals were of either analytical or HPLC grade provided by Merck, Fluka, and Probus. Synthetic and analytical solutions were prepared with Milli-Q water (resistivity > 18.2 MΩ cm).

Three different aqueous matrices were employed:

(i) A real groundwater sample, which was obtained from a water well in an agricultural area near Barcelona (Spain). Upon collection, the raw sample was preserved at 4 ºC in a refrigerator. Table 1 shows its main characteristics: circumneutral pH, low conductivity, large amount of inorganic carbon (i.e., HCO$_3^-$ and CO$_3^{2-}$), as well as NO$_3^-$, Cl$^-$, and SO$_4^{2-}$ ions, and alkaline earth metal ions (Ca^{2+} and Mg^{2+}). Before the EO treatments in the SPE cells, the groundwater sample was conveniently softened by adding 20 g L^{-1} of a Na$^+$-zeolite (NaP1-NA), synthesized by a hydrothermal method from coal combustion fly ash (CFA).[44] The properties of this material have been well characterized in earlier work.[45] Softening was completed upon vigorous magnetic stirring at 1100 rpm for 24 h, at room temperature. Decalcified samples were finally obtained after vacuum filtration using 0.22 μm cellulose acetate filters from Frisenette. Analysis of these samples (Table 1) revealed a drastic reduction of the alkaline earth metal ions content, with concomitant accumulation of the alkali metal ions (Na$^+$ in particular). This enhanced the solution conductivity and, even more significant, caused the alkalization of the groundwater to reach pH 9.8. Solutions with this initial pH were always employed in the EO assays.

(ii) Simulated water mimicking the anions content of the softened groundwater. It was prepared with Milli-Q water and contained 1.70 mM KNO$_3$, 12.52 mM NaCl, and 0.92 mM Na$_2$SO$_4$. The pH was adjusted to 9.8 with 1 M NaOH, yielding a conductivity of about 1.8 mS cm^{-1}.

(iii) Ultrapure (i.e., Milli-Q) water adjusted to pH 9.8 with 1 M NaOH.

An open, cylindrical glass tank, jacketed to circulate thermostated water from a water bath at 25 ºC, was used to keep 500 mL of solution under stirring with a magnetic stirrer at 1100 rpm. It became operative when the SPE cell, i.e., the anode/membrane/cathode sandwich, was immersed in it. The cell was composed of mesh electrodes of 3.5 cm (width) × 7.5 cm (height). The thickness was 0.90 and 0.20 mm for BDD and Ti/RuO$_2$, respectively, yielding approximate surface areas of 34 and 21 cm^2. Their separation was 0.15 mm, which corresponded to the thickness of the Nafion® N117 ion exchange membrane. The anode was a BDD thin film (3500 ppm of boron/carbon ratio) of 1.5 mm thickness deposited onto a Nb mesh, purchased from Condias. The cathode was a Ti/RuO$_2$ mesh provided by De Nora Industries. More information about the characteristics of the SPE cell is given in previous work.[31,32] All the electrolytic assays were performed at constant current using an EG&G Princeton Applied Research 273A potentiostat/galvanostat, whereas the cell voltage was measured on a Demestres 601BR digital multimeter.

The solution pH was monitored with a Crison 2200 pH-meter, whereas a Metrohm 644 conductometer was employed for the conductance measurement. The *N*,*N*-diethyl-*p*-phenylenediamine colorimetric method was utilized to determine the active chlorine content, using a Shimadzu 1800 UV/Vis spectrophotometer set at λ = 515 nm.[46] For all the analyses in matrices containing chloride ion, a small volume of thiosulfate solution was added to the aliquots just after withdrawal from the reactor in order to neutralize the remaining active chlorine, thus stopping the degradation process. All the aliquots were filtered with 0.45 μm PTFE membrane filters from Whatman before further analysis.

The imidacloprid concentration was monitored by reversed-phase high-performance liquid chromatography (HPLC). This analysis was carried out by injecting 20 μL aliquots into a Waters 600 LC fitted with a Thermo BDS Hypersil C-18 5 μm (250 mm × 4.6 mm (i.d.)) column at 35 ºC. It was coupled to a Waters 996 photodiode array detector selected at λ = 270 nm and controlled by Millennium-321 software. The mobile phase was a 50:50 (v/v) acetonitrile/0.02 M phosphate buffer mixture, at pH 3, which was eluted at 1.2 mL min^{-1}. The chromatograms displayed a well-defined peak for the pesticide at retention time (t_r) of 3.2 min, with L.O.D. = 0.090 mg L^{-1} and L.O.Q. = 0.298 mg L^{-1}. The same equipment, with a Bio-Rad Aminex HPX 87H (300 mm × 7.8 mm (i.d.)) column at 35 ºC, the photodiode array selected at λ = 210 nm, and a 4 mM H$_2$SO$_4$ solution at 0.6 mL min^{-1} as mobile phase was employed to detect and quantify the produced carboxylic acids by ion-exclusion HPLC. Tartaric acid exhibited a well-defined peak at t_r = 8.4 min.

The solution TOC was obtained with a Shimadzu VCSN TOC analyzer by adding 50 μL aliquots into it and using the non-purgeable organic carbon

(NPOC) method, with L.O.D. = 0.211 mg L^{-1} and L.O.Q. = 0.708 mg L^{-1}, showing ±1% accuracy. NH_4^+, NO_3^-, NO_2^-, Cl^-, SO_4^{2-}, ClO_3^-, and ClO_4^- concentrations were determined as reported elsewhere.[22,47] Alkaline earth metal and alkali metal ions in the raw and softened groundwater were measured by inductively coupled plasma with optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 8300 spectrometer.

All the assays were performed at least in duplicate and average values with error bars within a 95% confidence interval are given.

Heteroaromatic products formed after 30 min of EO treatment of 500 mL of a 23.7 mg L^{-1} imidacloprid solution in the simulated matrix at 0.50 A were detected by GC-MS and identified using the NIST05 database. Organics were extracted from the treated solution with CH_2Cl_2 (6x15 mL) and the resulting organic sample was dried with anhydrous Na_2SO_4, filtered, and its volume reduced to about 2 mL under N_2 stream for analysis. The GC-MS procedure used is analogous to that detailed in earlier work.[47]

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

ARTICLE

A solid polymer electrolyte (SPE) cell with a Nb/BDD mesh anode, a Ti/RuO$_2$ mesh cathode, and a Nafion® N117 membrane was used to effectively degrade and mineralize the drug imidacloprid spiked into softened groundwater with very low conductivity under galvanostatic conditions.
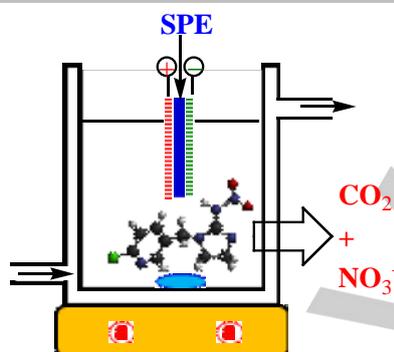
Roger Oriol, Davide Clematis, Enric Brillas, José L. Cortina, Marco Panizza*, and Ignasi Sirés*

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Groundwater treatment using a solid polymer electrolyte cell with mesh electrodes

Layout 2:

ARTICLE

((Insert TOC Graphic here))

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Title

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SUPPORTING INFORMATION

Groundwater treatment using a solid polymer electrolyte cell with mesh electrodes

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Table S1. Distribution of chlorinated species after 240 min of electrochemical oxidation of 500 mL of 23.7 mg L^{-1} imidacloprid in simulated water and softened groundwater at pH 9.8 and 25 ºC using a stirred reactor with an SPE cell composed of a Nb/BDD mesh anode and a Ti/RuO$_2$ mesh cathode, at 0.50 A.

Chlorinated species	Concentration (mg L^{-1})	
	Simulated water	Softened groundwater
Cl$^-$	82.7±2.7 [a]	92.1±2.8 [b]
Active chlorine as ClO$^-$	69.2±2.5	22.3±0.9
ClO$_3^-$	435.9±13.1	522.3±22.8
ClO$_4^-$	346.1±10.7	381.7±14.4

Initial Cl$^-$ concentration: [a] 442.8±15.4 mg L^{-1}; [b] 476.8±18.8 mg L^{-1}

Table S2. Apparent rate constant determined for the degradation of imidacloprid in different aqueous matrices at pH 9.8 and 25 °C using a stirred reactor with an SPE cell composed of a Nb/BDD mesh anode and a Ti/RuO$_2$ mesh cathode under selected conditions.

[Imidacloprid] (mg L^{-1})	Current (mA)	k_1 (10^{-2} min^{-1})	R^2
Simulated water			
23.7	0.10	2.4±0.1	0.982
	0.25	4.0±0.2	0.992
	0.50	4.2±0.2	0.986
	1.00	6.2±0.2	0.991
	1.50	6.5±0.2	0.994
Softened groundwater			
1.2	0.50	2.1±0.1	0.980
4.8	0.50	1.8±0.1	0.994
11.8	0.50	1.9±0.1	0.989
23.7	0.50	2.0±0.1	0.990
59.2	0.50	2.5±0.2	0.995
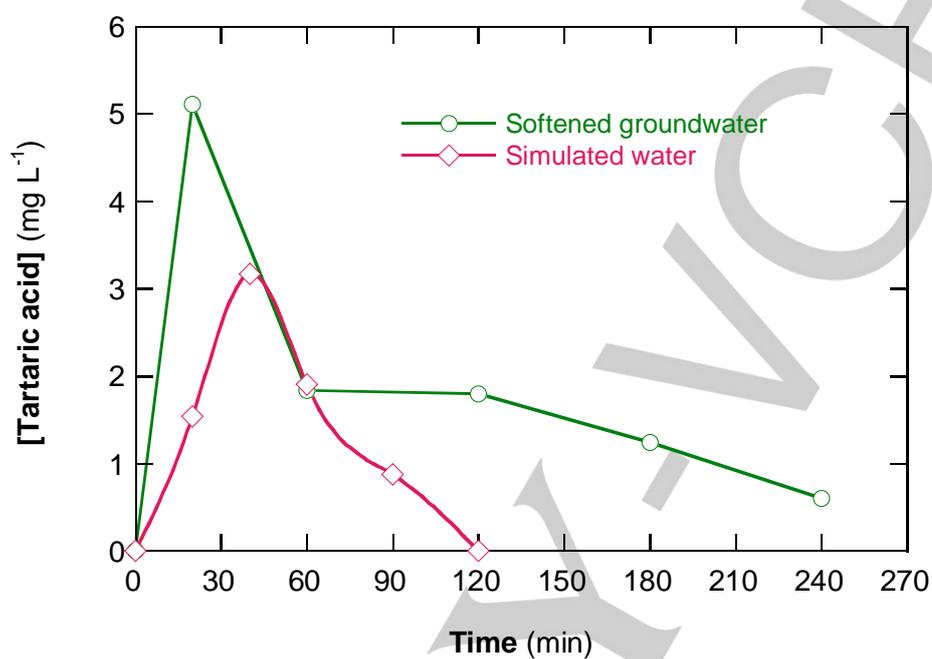
Figure S1. Time course of tartaric acid detected during the electrochemical oxidation of 500 mL of 23.7 mg L^{-1} imidacloprid spiked into simulated water and softened groundwater at pH 9.8 and 25 °C using an SPE cell with a Nb/BDD mesh anode and a Ti/RuO$_2$ mesh cathode, at 0.50 A.