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Original scientific paper

Near-complete atrazine mineralization in an electro-Fenton--boron-doped diamond electrochemical system

El Habib El Azzouzi, Ayoub Ait Bella✉ and Mohamed Azzi

Geo-Biodiversity and Natural Patrimony Laboratory, GEOPAC Research Center, Scientific Institute, Mohammed V University in Rabat, Av. Ibn Battota, BP. 703, Rabat-Agdal, Morocco

Corresponding Author: ✉Ayoub_aitbella3@um5.ac.ma; Tel.: +212618303486

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Abstract

The complete mineralization of atrazine beyond dealkylation and dechlorination is still difficult and advanced oxidation technologies are being tested. In this work, we used the electro-Fenton (EF) process, with a carbon-felt cathode and either boron-doped diamond (BDD) or Pt as the anode, to investigate atrazine degradation and mineralization in aqueous solution. The experiments were carried out in an undivided electrochemical cell filled with a solution containing atrazine, Fe^{2+} and Na_2SO^4 as the supporting electrolyte. Disappearance of atrazine was pseudo-first order. Applied current densities of 2, 10, and 20 mA cm-2 (based on the 25 cm2 geometric BDD area) completely eliminated the parent herbicide after 40, 20 and 10 min in the EF-BDD system, respectively, while 50, 30, and 15 min were required for the EF-Pt system. The most interesting one was the nearly complete mineralization realised with BDD (97.06 % total organic carbon (TOC) removal after 8 h at 40 mA cm^{-2}) in comparison to EF-Pt (81.03 %) and EF-BDD (96.29 %) and anodic oxidation with BDD (96.29 %). Desethylatrazine, deisopropylatrazine, hydroxyatrazine and desethylhydroxyatrazine were detected as early intermediates by chromatographic monitoring, followed by detection of the presence of cyanuric acid, carboxylic acids, and finally inorganic ions. Cyanuric acid TOC removal reached 77 % after 3 h in EF-BDD, while EF-Pt achieved only 4.2 % after 10 h at the same applied current; EF-BDD achieved almost 90 % mineralization of cyanuric acid after 10 h. The absolute rate constant of the reaction between cyanuric acid and hydroxyl radicals was 1.53×10^{-8} M^{-1} s^{-1}. These results show that homogeneous Fenton chemistry, combined with the high oxidation power of the BDD anode, is key to achieving near-complete atrazine mineralization despite the cyanuric-acid bottleneck.

Keywords

Atrazine remediation; electrochemical treatment; advanced oxidation; cyanuric acid; hydroxyl radicals; pseudo-first-order kinetics

Introduction

One of the most common s-triazine herbicides is atrazine, 2-chloro-4-ethylamino-6-isopropyl-amino-1,3,5-triazine. Atrazine is highly persistent in water and produces transformation products that can remain environmentally relevant long after application. Although atrazine was banned in the EU in 2003, its metabolites are still found in surface water and groundwater, and it remains a significant global model pollutant for testing the effectiveness of new treatment technologies [1,2]. The concentration of the parent compound can be decreased by conventional methods like biological degradation, adsorption on activated carbon and membrane filtration, but these methods generally cannot provide for deep oxidation and can merely move pollution from one phase to another.

The diversity of contaminated matrices in Morocco has been further illustrated by recent environmental studies that highlight the need for efficient solutions to the treatment of persistent pollutants. The studies focused on hospital effluents in Marrakech, peri-urban soils in the Kenitra region, and surface water and groundwater upstream of the Merja Zerga lagoon [3-8]. The results showed that persistent contaminants can be found in environmentally diverse matrices, and that treatment technologies should be assessed not only on removal of the parent contaminant, but also on reducing contamination from persistent transformation products.

Electrochemical advanced oxidation processes (EAOPs) stand out as a promising option among the advanced oxidation technologies, as they produce the reactive species *in situ*, offer control over the process through the applied current, and do not require storage or dosing issues like in the case of large quantities of externally added oxidants [9]. In this family, the electro-Fenton process (EF) is one of the most powerful methods for degrading persistent organic contaminants in water. Its main characteristic is the *in situ* production of hydroxyl radicals, formed by the reaction between Fe^{2+} in the bulk solution and electrogenerated H_2O_2 at the cathode [10]. Hydroxyl radicals are highly non-selective oxidants with a standard reduction potential of 2.80 V *vs.* SHE, and they can react with a wide variety of organic molecules, ultimately mineralizing them into CO_2, water, and inorganic ions.

Previous studies on herbicide adsorption by mineral-organic sorbents show that herbicide retention and mobility can change through adsorption onto mineral/organic surfaces, but this does not indicate complete elimination of the herbicide [11]. This differs from separation-based approaches and oxidative technologies specifically developed for deep oxidation and, ideally, full mineralization.

The choice of anode material is especially important for atrazine and other recalcitrant compounds treated by EF. Recent studies show that boron-doped diamond (BDD) has the largest potential window, high oxygen-evolution overpotential, and a high capacity to generate hydroxyl species on the electrode surface (BDD(·OH)), which support extensive mineralization during electrochemical water treatment [12]. Therefore, the BDD anode complements homogeneous hydroxyl-radical oxidation in the bulk solution by providing an additional surface-mediated oxidation pathway. Mechanistic studies combining compound-specific isotope analysis and density functional theory have shown that both direct charge transfer and hydroxyl-radical attack contribute to atrazine oxidation on the BDD anode, and that hydroxyl-radical attack becomes increasingly important as degradation proceeds [13]. At the same time, recent analytical research has validated atrazine as a convenient model compound for evaluating oxidation rates and degradation products in complicated water matrices [14,15].

Atrazine is known to be more difficult to mineralize completely than to transform. Earlier research has consistently shown efficient atrazine degradation in both Fenton and electro-Fenton processes, with only limited TOC degradation, due to several relatively stable intermediates, particularly cyanuric acid (1,3,5-triazine-2,4,6-triol) [16-18]. Therefore, rapid disappearance of the parent herbicide does

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not necessarily indicate effective remediation. To date, no advanced oxidation process has reported atrazine mineralization efficiency above approximately 80 % TOC removal [18].

The present study carries out a detailed study of atrazine degradation and mineralization by EF with a BDD anode. Four major objectives were investigated: (i) study of the effects of current intensity and anode material on the degradation rate of atrazine, (ii) evaluation of the potential for near-complete mineralization, (iii) determination of the major intermediates generated during the oxidation of atrazine, and (iv) elucidation of the role of cyanuric acid in the mechanism of atrazine oxidation and the reason why it acts as a barrier to complete mineralization. To reveal the special function of the BDD anode in overcoming the limitations that are frequently encountered in the EF treatment process of atrazine, the comparative performance of EF-BDD, EF-Pt and anodic oxidation with BDD was analysed.

Experimental

Reagents and electrochemical system

The pollutant of interest was atrazine (purity > 98 %, Acros Organics) and the solutions were prepared using ultrapure water (Milli-Q, Millipore Simplicity 185, resistivity > 18 MΩ cm). The concentration of atrazine added to the degradation tests was 0.1 mM (21.57 mg L^{-1}). An undivided electrochemical cell with a nominal capacity of 250 mL was used for electrolysis, and a working solution of 220 mL was used. The supporting electrolyte Na_2SO_4 was added at 50 mM (0.05 mol L^{-1}). For electro-Fenton experiments, $FeSO_4{\cdot}7H_2O$ (99.5 %, Acros Organics) was added to a concentration of 0.10 mM. To ensure the iron remains soluble and to ensure optimum pH for the Fenton reaction [19,20], the initial pH was adjusted to 3.0 with H_2SO_4.

A carbon-felt electrode (Carbone Lorraine, 14×5×0.5 cm) was placed against the inner wall of the cell as the cathode. The following two anode materials were tested: a cylindrical Pt grid (3 cm diameter and 5 cm height) and a BDD electrode (active surface area of 25 cm^2). A HAMEG HM8040 triple power supply was used for constant current electrolysis. The applied currents for the degradation-kinetics experiments were 50, 250 and 500 mA, which translates to 2, 10 and 20 mA cm^{-2}, respectively, on the basis of the BDD electrode area of 25 cm^2. In the experiments with high mineralization, the applied current was 1000 mA (40 mA cm^{-2}). We first bubbled compressed air through the solution for 10 min before electrolysis, then bubbled it continuously during treatment through a fritted-glass diffuser to ensure continuous generation of H_2O_2 at the carbon-felt cathode. It is not possible to quantify the accumulation of electrogenerated H_2O_2 at the various current densities in separate blank experiments without Fe^{2+} or without atrazine; thus, H_2O_2 accumulation curves are not reported here. The reaction medium was kept under magnetic stirring at ambient temperature (25 ± 2 °C). For anodic oxidation tests, Fe^{2+} was not added to the electrolyte so that the oxidation was mostly anodic with the BDD anode. A summary of the experimental conditions is given in Table 1.

Table 1. *Principal experimental conditions used for the atrazine treatment experiments*

Parameter	Condition
Target pollutant	Atrazine, 0.1 mM (21.57 mg L^{-1})
Working volume	220 mL in a 250 mL undivided cell
Supporting electrolyte	Na_2SO_4, 0.05 mol L^{-1}
Catalyst for EF	Fe^{2+}, 0.1 mM (as $FeSO_4{\cdot}7H_2O$)
Initial pH	3.0 (adjusted with H_2SO_4)
Cathode	Carbon felt, 14×5×0.5 cm
Anodes	Pt grid (3 cm diameter, 5 cm height) or BDD (25 cm^2)
Applied current density	2, 10 and 20 mA cm^{-2} (kinetics); 40 mA cm^{-2} (mineralization)
Gas supply	Compressed air, 10 min pre-saturation + continuous bubbling
Temperature	Ambient (25 ± 2 °C)

Analytical methods

The disappearance of atrazine and aromatic intermediates was monitored by high-performance liquid chromatography (HPLC) with diode-array detection (DAD) on a 40 °C Merck LaChrom-Hitachi HPLC system with a Purospher RP-18 column (5 µm, 250×4.6 mm). The mobile phase consisted of 40:60 (v/v) methanol/water containing 1 % acetic acid and was delivered isocratically at 0.8 mL min^{-1}. Carboxylic acids and cyanuric acid were individually separated on Supelcogel H (9 µm, 250×4.6 mm) with 4 mM H_2SO_4 as mobile phase and UV detection at 210 nm. Ion chromatography was used to determine mineral ions. Anions (Cl^-, NO_3^-, SO_4^{2-}) were determined with a Dionex ICS-1000 system with an IonPac AS4A-SC anion exchange column and a carbonate/bicarbonate eluent (1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3). The NH_4^+ was analysed separately with an IonPac CS12A cation exchange column with methanesulfonic acid as the eluent. Thus, cyanuric acid was not analysed by the RP-18 method for atrazine and the aromatic intermediates and was instead quantified by the dedicated Supelcogel H/4 mM H_2SO_4 method at 210 nm as described above.

The samples were filtered through 0.22 µm membrane filters, acidified with 1 % HCl and then analysed for total organic carbon (TOC) using a Shimadzu TOC-VCHS analyzer. Potassium hydrogen phthalate standards were used to calibrate. Aliquots of 0.5 mL were removed at desired time intervals for HPLC analysis and 5 mL samples were taken for TOC measurements. The efficiency of mineralization was expressed as TOC abatement, $[(TOC_0 - TOC_t)/TOC_0]\times100$, where TOC_0 and TOC_t are TOC values at time zero and time *t,* respectively.

Kinetic analysis

The disappearance of atrazine was analysed under the assumption that the concentration of the hydroxyl radical did not change significantly during the early phase of oxidation due to the excess of pollutant concentration over the hydroxyl-radical flux, which led to the use of a pseudo-first-order kinetic model. With this assumption, the rate of the reaction can be expressed as $dC/dt = -k_{app}C$, with k_{app} being the apparent pseudo-first-order rate constant. Here, C / mM is the atrazine concentration at the electrolysis time t / min and C_0 / mM is the initial atrazine concentration. $C_0/C = k_{app}t$ and the slope of the linear plot of ln C_0/C *vs.* time gave the value for k_{app}. The absolute rate constant of the reaction between hydroxyl radicals and cyanuric acid, k_{abs}(CA), was obtained by competition kinetics with 4-hydroxybenzoic acid (4-HB) as reference, for which k_{abs}(4-HB) is 1.80×10^{10} M^{-1} s^{-1} [21].

Results and discussion

Effect of current intensity and anode material on atrazine disappearance

Under all the electro-Fenton conditions studied, the atrazine concentration was found to decrease rapidly with time, and the plots of ln(C_0/C) *versus* time were linear, suggesting pseudo-first-order reaction (Figures 1 and 2). Complete removal of atrazine was achieved within 50, 30 and 15 min at 2, 10 and 20 mA cm^{-2}, respectively, in the EF-Pt system. These times decreased to 40, 20, and 10 min, respectively, when the Pt anode was replaced with a BDD anode, demonstrating the positive effect of the BDD anode. Both systems showed that the degradation rate increased with current density, and the improvement was always greater for BDD than for Pt, suggesting that atrazine oxidation is current-density- and anode-material-dependent. This enhancement aligns with the wide anodic potential window and strong oxidizing character of BDD, which promotes the combination of homogeneous ·OH in solution and surface-bound BDD(·OH) species [12,13].

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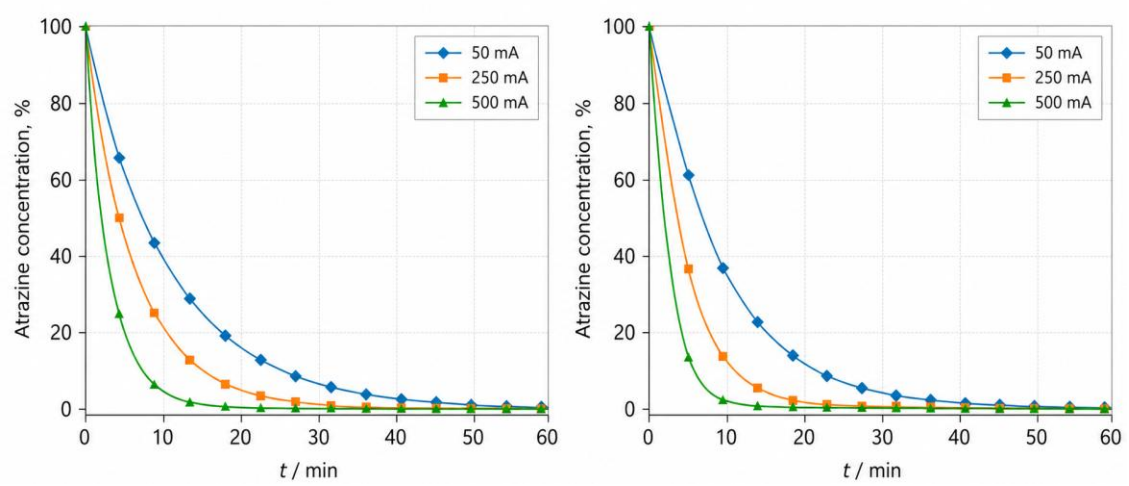

***Figure 1**. Atrazine concentration decay during electro-Fenton treatment at different applied currents: (a) EF-Pt and (b) EF-BDD. Conditions: $C_{atrazine}$ = 0.1 mM (21.57 mg L^{-1}), $C_{Fe^{2+}}$ = 0.1 mM, $C_{Na_2SO_4}$ = 50 mM, pH 3.0, V = 220 mL*

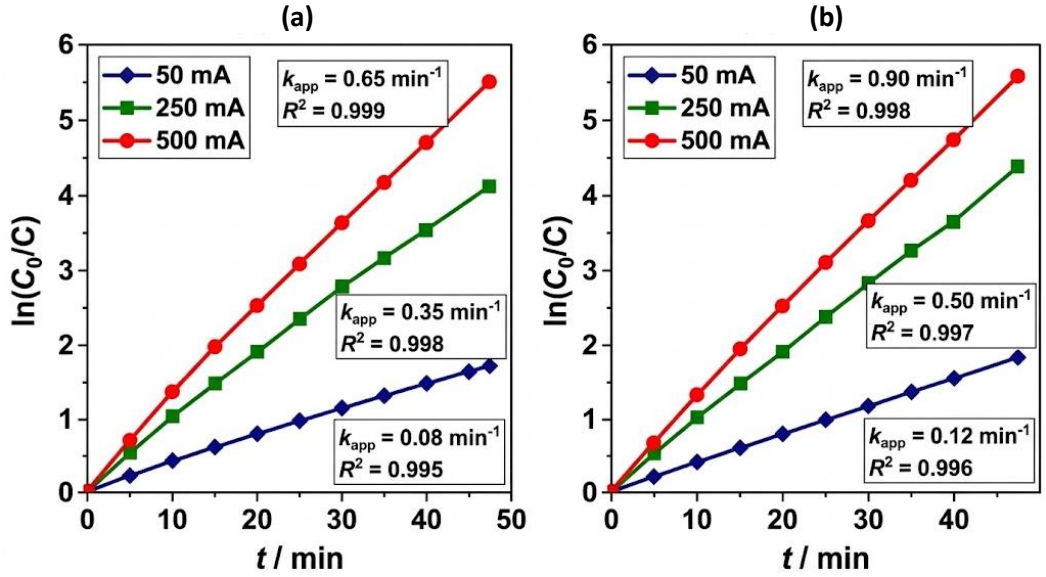

***Figure 2.** Linearized kinetic plots of ln C_0/C) vs. time for atrazine degradation at different applied currents: (a) EF-Pt and (b) EF-BDD*

Mechanistically, the main oxidation pathway is the homogeneous reaction of hydroxyl radicals formed on the Pt anode in the bulk solution via the electro-Fenton cycle, whereas the Pt anode surface is a relatively inert current feeder [22] and is more susceptible to the competing oxygen-evolution reaction. In contrast, oxidation with the BDD anode occurs via a combination of homogeneous ·OH in solution and weakly adsorbed BDD(·OH)/direct anodic oxidation at the diamond surface, which explains the faster disappearance of atrazine. Linear regression of the pseudo-first-order plots in Figure 2 gave k_{app} values of about 0.10, 0.16 and 0.32 min^{-1} for EF-Pt and 0.11, 0.22 and 0.43 min^{-1} for EF-BDD at 2, 10 and 20 mA cm^{-2}, respectively, with R^2 values ranging from 0.994 to 1.000. The high R^2 values also support pseudo-first-order atrazine disappearance over the range studied, while the systematically higher k_{app} values from EF-BDD indicate that the BDD anode reaction contributes to atrazine disappearance in addition to the homogeneous Fenton reaction.

Parent-compound disappearance occurred quickly in the short electrolysis runs, but complete mineralization took longer than atrazine removal. The longer experiments (discussed below) are therefore most relevant for comparing mineralization performance, and they show that EF-BDD

ultimately removes much more TOC than EF-Pt. The difference between the two proves that disappearance of the parent herbicide is not enough to measure treatment efficiency, and that continued oxidation is required to transform the stable intermediate(s) to the final mineralization product(s).

To evaluate the effect of supplied current using a single descriptor, the apparent pseudo-first-order rate constant k_{app} was used throughout the kinetic analysis. In both EF-BDD and EF-Pt conditions, k_{app} was found to be greater with higher current density, which indicates that higher current results in faster disappearance of atrazine. However, the systematically higher k_{app} values in the presence of EF-BDD show that the current response depends strongly on the anode material. Therefore, current efficiency for TOC removal and mineralization is used to complement the analysis of current efficiency for degradation kinetics, providing a basis to compare the overall mineralization extent driven by current effects.

Mineralization performance and significance of the BDD anode

The most significant result from this study is not just the rapid removal of atrazine but the degree of "total mineralization" of the oxidation sequence. The results showed that EF-BDD was able to remove 97.06 % TOC after 8 h of electrolysis at 40 mA cm^{-2}, while EF-Pt was able to remove only 81.03 % under the same conditions (Figure 3). Anodic oxidation in BDD without Fe^{2+} (*i.e.* without Fenton chemistry) also yielded 96.29 % TOC removal. The results show that the BDD anode can achieve nearly 100 % removal of organic carbon with electro-Fenton chemistry or in standalone anodic oxidation mode. The EF-BDD configuration remains appealing, as it provides rapid degradation of the parent compound and near-complete mineralization.

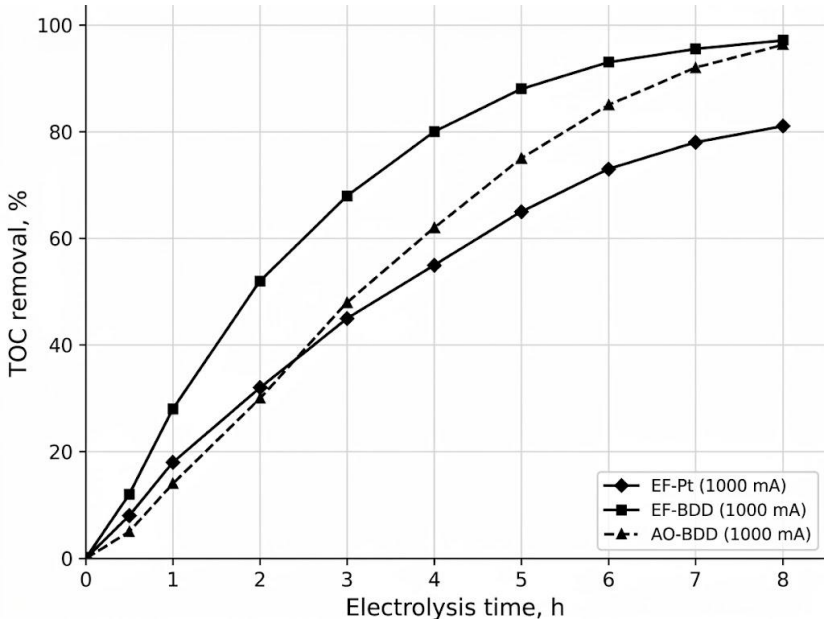

***Figure 3**. TOC removal during treatment of 0.1 mM atrazine solution at 1000 mA (40 mA cm^{-2}). Comparison of EF-Pt, EF-BDD, and anodic oxidation with BDD (AO-BDD). Conditions:* $C_{Fe^{2+}}$ *= 0.1 mM for EF experiments,* $C_{Na_2SO_4}$ *= 50 mM, pH 3.0,* V *= 220 mL*

To check the efficiency of the electric charge used for the mineralization of atrazine, the mineralization current efficiency (MCE, %) was calculated for each of the long-duration experiments at 40 mA cm^{-2} with the standard expression (Equation (1)) used in electrochemical advanced oxidation research:

$$MCE = n\,F\,V_s\,\Delta TOC\,100 / MIt \quad (1)$$

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where n is the number of electrons exchanged in the complete mineralization of one atrazine molecule (n = 42 for the oxidation of $C_8H_{14}ClN_5$ to CO_2, Cl^-, NO_3^- and NH_4^+), F is the Faraday constant (96,485 C mol^{-1}), V_s is the solution volume (220 mL), ΔTOC, mg L^{-1} is the experimental TOC decay, M is the molar mass of carbon (12 g mol^{-1}), I / A is the applied current and t / s is the electrolysis time.

The TOC decay measured after 8 h of electrolysis at 40 mA cm^{-2} (I = 1.0 A, t = 28,800 s) was 9.32 mg L^{-1} for the EF-BDD system and 7.78 mg L^{-1} for the EF-Pt system (97.06 and 81.03 % of the initial TOC of 9.6 mg L^{-1}, respectively), giving MCE(EF-BDD) ≈ 2.4 % and MCE(EF-Pt) ≈ 2.0 %. The low absolute values likely reflect slow mineralization of dissolved organic carbon, which requires longer treatment times, as well as current losses from the competing oxygen evolution reaction and other side reactions at the anode. The small absolute efficiencies, although not that impressive, are systematically higher for the BDD anode than for the Pt anode under the same conditions, and it is the high oxygen evolution overpotential of BDD that enables the applied current to be directed more effectively towards organic-carbon oxidation and ultimately towards near-complete mineralization of atrazine.

This level of mineralization is remarkable in the atrazine literature. Earlier studies on atrazine oxidation by advanced oxidation processes consistently documented efficient transformation of the parent herbicide but substantially lower final TOC removal because stable triazine-derived products, principally cyanuric acid, persisted in solution [16-18]. The highest previously reported TOC removal for atrazine by an advanced oxidation process was approximately 80 % after 10 h of treatment [18]. The present results therefore indicate that BDD does more than accelerate primary degradation; it allows the oxidation sequence to proceed past the stable intermediates that usually cap the mineralization yield. The corresponding journal article reporting these data reached the same conclusion, describing the EF-BDD configuration as yielding 97 % TOC removal for atrazine and efficient destruction of cyanuric acid [23].

Intermediates and proposed degradation pathway

Chromatographic analysis revealed that the oxidation of atrazine proceeds by a complicated series of dealkylation, hydroxylation and dechlorination reactions. Desethylatrazine (DEA), deisopropylatrazine (DIA), hydroxyatrazine (HA), desethylhydroxyatrazine (DEHA), desethyldeisopropylatrazine (DEIA), deisopropylhydroxyatrazine (DIHA) and desethyldeisopropylhydroxyatrazine (DEIHA) were the main aromatic intermediates identified by HPLC-DAD. Stepwise release of chlorinated and nitrogen-containing substituents from the triazine ring was further confirmed by progressive increases in chloride, nitrate and ammonium concentrations. The pathway shown in Figure 4 can be summarized as follows: Initial hydroxyl-radical attack leads to the formation of both side-chain and ring-retaining oxidized, dealkylated and dechlorinated products, and the mono-dealkylated products, DEA and DIA, are the first to appear, followed by the more highly oxidized and hydroxylated triazine species; continued oxidation results in the formation of cyanuric acid ($C_3H_3N_3O_3$), which is the most stable ring-retaining intermediate. They undergo further ring opening and oxidation to form short-chain carboxylic acids (oxalic, formic, acetic and glycolic acids), which are subsequently mineralized to CO_2, water and inorganic ions (Cl^-, NO_3^- and NH_4^+). This pathway is similar to previously reported mechanistic studies on atrazine oxidation under electrochemically generated hydroxyl-radical conditions [18] and to more recent isotope-based studies indicating that C-N bond cleavage and side-chain oxidation become more important on BDD anodes [13].

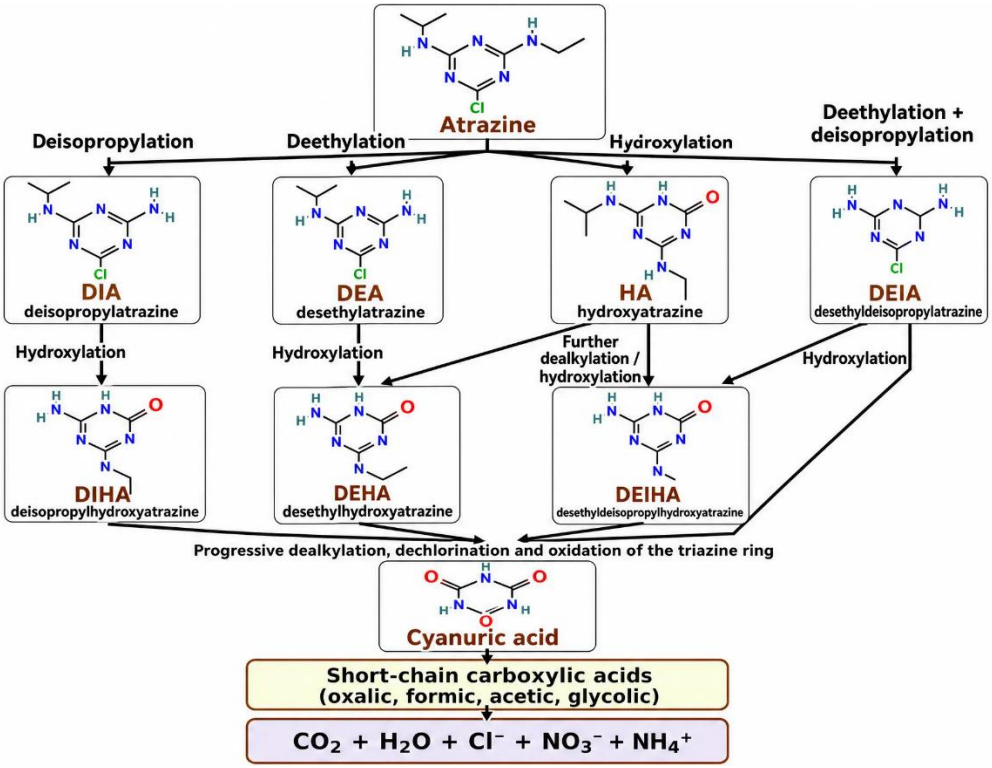

Figure 4. *Proposed degradation pathway of atrazine by hydroxyl radicals generated in the EF-BDD process*

Cyanuric acid as the mineralization bottleneck

Cyanuric acid is the most stable end product of the oxidative chain that results in atrazine mineralization and is therefore an important intermediate in mechanistic discussions of the process. Even if mineralization were limited to cyanuric acid, the theoretical TOC removal would be far from complete, as the cyanuric acid molecule contains 3 carbon atoms that would remain in solution. The high TOC removal (97 %) achieved here therefore indicates not only cyanuric acid formation, but also its subsequent oxidation to lower-molecular-weight products and eventual mineralization. This discovery is especially important because cyanuric acid is generally considered one of the main rate-limiting steps in atrazine oxidation, as it is not easily oxidized under less severe conditions. The atrazine RP-18 method was not used for measuring the cyanuric acid concentrations mentioned in this section; the dedicated Supelcogel H method (4 mM H_2SO_4, UV at 210 nm) was used.

This interpretation was confirmed by dedicated experiments on cyanuric acid oxidation, and a significant difference between the two anode materials was revealed. In the EF-BDD system, the removal rate of cyanuric acid TOC reached approximately 77 % after 3 h, and TOC removal from 0.2 mM cyanuric acid solution reached almost 90 % after 10 h (Figure 5). In contrast, under the same operating conditions, the EF-Pt system removed only 4.2 % TOC from the same recalcitrant intermediate after 10 h, showing that a Pt anode is not suitable for mineralizing this intermediate. The oxidation of cyanuric acid was also highly efficient by BDD without the addition of Fe^{2+} and anodic oxidation alone resulted in almost 82.4 % TOC removal after 10 h.

The results provide a clear mechanism to explain the better performance of EF-BDD in atrazine remediation. Unlike classical EF-Pt, which depends primarily on hydroxyl radical production in the bulk solution, the EF-BDD system combines homogeneous Fenton chemistry with strong oxidizing species present on the BDD surface. This dual oxidation process allows efficient attack on both cyanuric acid and the carboxylic-acid intermediates resulting from ring opening. Therefore, the cyanuric acid barrier can be overcome only by combining bulk-solution oxidation with heterogeneous oxidation at the BDD anode.

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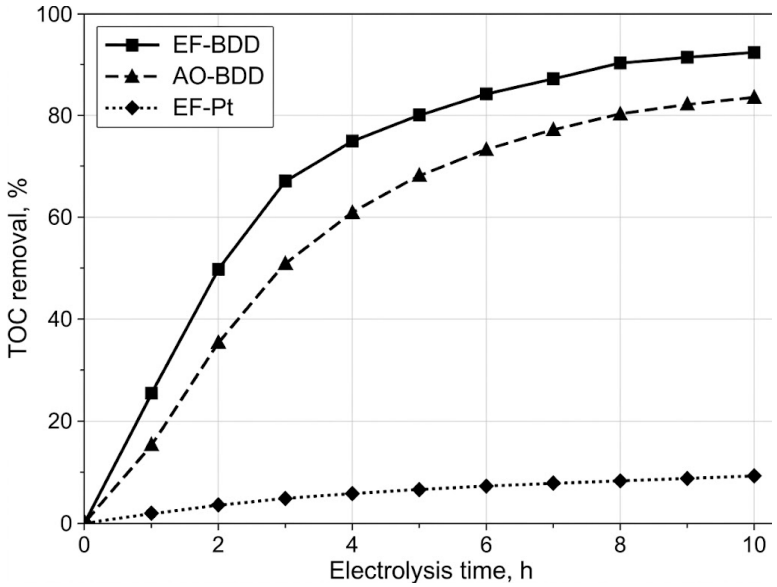

***Figure 5**. Comparison of cyanuric acid mineralization (TOC removal) by EF-BDD, EF-Pt and AO-BDD at 1000 mA (40 mA cm⁻²). Conditions: $C_{cyanuric\ acid}$ = 0.2 mM, $C_{Na_2SO_4}$ = 50 mM, pH = 3.0, V = 220 mL*

A further mechanistic contribution of this study is the determination of the absolute rate constant for cyanuric acid oxidation by hydroxyl radicals. Using the competition kinetics method with 4-hydroxybenzoic acid as the reference compound, the value k_{abs} = 1.53×10^8 M^{-1} s^{-1} was obtained. This result matters because it quantifies the intrinsic reactivity of a compound often regarded as highly refractory toward advanced oxidation. The determined rate constant indicates that cyanuric acid is not unreactive in absolute terms; rather, its effective oxidation requires sufficiently powerful and sustained hydroxyl radical fluxes, such as those achieved when electro-Fenton chemistry is coupled with a BDD anode. The comparatively low rate constant relative to typical aromatic pollutants also explains why efficient cyanuric acid mineralization demands the high radical generation rates provided by the EF-BDD configuration.

Relevance in light of recent literature

The findings of the present study align with recent studies published after 2020. Wang *et al*. [13] reported that atrazine oxidation on a BDD anode occurs via both direct charge transfer and hydroxyl-radical attack, the latter increasing as degradation proceeds. In another CSIA study, Liang *et al*. [24] showed that the relative importance of direct electron transfer and hydroxyl-mediated pathways for atrazine oxidation on BDD changes with applied current density. In general, Oturan [12] pointed out that the remarkable efficiency of the electro-Fenton on a BDD film anode results from a combination of homogeneous reactions in the bulk solution and heterogeneous oxidation at the electrode surface. Deng *et al*. [25] also emphasized the need for effective Fe^{2+} regeneration to sustain the electro-Fenton cycle, whereas Brosler *et al*. [26] showed that both in-house and commercial BDD electrodes can achieve high pollutant removal efficiency, but reproducibility and stability remain significant practical challenges. Additional studies have further demonstrated the broader implications of these findings through herbicide treatment in a real matrix [27], tracking of atrazine transformation products [14,15], and the persistence and remediation of s-triazine herbicides in general [28]. However, the following limitations should be noted: experiments were conducted in a synthetic aqueous medium with controlled concentrations; future studies should examine the effects of real-water components (natural organic matter and inorganic radical scavengers) and monitor ecotoxicity during treatment. Recently, the toxicity of the atrazine degradation mixtures generated by AOPs was evaluated by Hong

et al. [29], Zeng *et al.* [30] and Luo and Zheng [31], who further demonstrated the search for efficient atrazine removal and degradation of recalcitrant cyanuric acid. Overall, the near-complete carbon abatement reported here (~97 %) serves as a helpful benchmark for electrochemical treatment of atrazine-contaminated waters.

In addition to its mechanistic importance, EF-BDD is also interesting for water-management applications which require the use of complex environmental matrices, for which a high mineralization efficiency is essential. Contamination of hospital effluents, peri-urban soils and surface and groundwater impacted by organochlorine pesticides was recently documented in Morocco [3-8]. This finding highlights the importance of remediation technologies that can remove contaminants from one phase to another. In this way, EF-BDD is more beneficial than separation-based methods, as it promotes transformation and mineralization of the pollutant rather than simple immobilization. This is particularly significant in adsorption studies, such as those reported for imazethapyr on montmorillonite or humic materials [11], which show that retention does not ensure permanent pollutant removal.

Conclusions

The electro-Fenton process (EF) was used to mineralize atrazine in water, which was quickly broken down and almost completely mineralized when a boron-doped diamond (BDD) anode was employed with a carbon felt (CF) cathode. At current densities between 20 and 2 mA cm^{-2} (corresponding to 500 to 50 mA in the present cell configuration), EF-BDD completely removed atrazine in 10 to 40 min, compared with EF-Pt. Moreover, EF-BDD achieved 97.06 % TOC removal after 8 h of electrolysis at 40 mA cm^{-2}, which is 16.03 % higher than the EF-Pt result. This reaction pathway involved sequential dealkylation, hydroxylation and dechlorination to produce a series of partially oxidized triazine intermediates (DEA, DIA, HA, DEHA, DEIA, DEIHA and DIHA), followed by cyanuric acid, ring opening to short-chain carboxylic acids, and final mineralization to CO_2, H_2O and inorganic ions (Cl^-, NO_3^-, NH_4^+). Cyanuric acid was determined to be the major limiting compound for full mineralization of atrazine. This intermediate was successfully removed in the EF-BDD system, but not in the EF-Pt system. This could be attributed to the strong oxidizing species generated at the BDD anode surface, as well as those produced by Fenton chemistry in the bulk solution. This mechanistic interpretation is supported quantitatively by the rate constant of the oxidation of cyanuric acid by hydroxyl radicals (1.53×10^8 M^{-1} s^{-1}). Overall, EF-BDD is a very effective approach to decontaminating atrazine from polluted water and provides a good mechanistic explanation for the excellent mineralization rationalized by this electrode setup.

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