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Electrochemical degradation of aqueous alachlor and atrazine: products identification, lipophilicity, and ecotoxicity

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ABSTRACT: This work studied the electrochemical degradation of alachlor and atrazine (alone and mixed with each other) using a filter-press cell, a dimensionally stable anode (DSA Ti/Ru0.3Ti0.7O2), initial pH 3.0, and temperature at 25 °C. The best operational conditions for alachlor (0.33 mmol L⁻¹) degradation were obtained by a 3² factorial design, in which the factors/levels were: NaCl concentration (0.05, 0.1, and 0.15 mol L⁻¹) and current density (10, 30, and 50 mA cm⁻²). Thus, 93.1% alachlor removal and 71.2% mineralization were achieved using 0.15 mol L⁻¹ NaCl and 30 mA cm⁻². In addition, the initial degradation products (DPs) of alachlor and atrazine were identified by liquid chromatography coupled to mass spectrometry (LC-MS). Acute and chronic ecotoxicities for three trophic levels (fishes, daphnids and green algae) and lipophilicity (log D, pH 7.4) of the DPs were also estimated using the ECOSAR 1.11 and ChemAxon Calculator software, respectively. The present study showed that the electrochemical degradation is an efficient method for removing the herbicides alachlor and atrazine from water and that the DPs formed have lower pollution potential than their original compounds.

1. Introduction

Alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide) is one of the most frequently used herbicides in weed control, early inhibiting their development. This compound belongs to the chloracacetamide class and it is widely used to protect corn, rice, soybean, peanut, and cotton crops. Alachlor can be degraded by microorganisms present in soils. Therefore, both alachlor and its main metabolite, 2,6-diethylaniline, are ubiquitous in the environment and cause serious ecological and physiological problems. Alachlor is a toxic, carcinogenic, persistent organic compound (with a half-life of 70 days in soil and 30 days in water), and an endocrine disruptor. The contamination of water resources by alachlor occurs due to runoff and infiltration, causing it to be frequently detected in surface and groundwater samples. Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine), as well as alachlor, is widely used in weed control in maize, sugarcane, and soybean crops. This herbicide belongs to the triazines group, and it is the most important chemical of this family as well as one of the most used herbicides in the world due to its high phytotoxic activity. Among its main characteristics are: low vapor pressure, moderate solubility in water, slow hydrolysis, and the ability
of leaching\textsuperscript{13,14}. Besides that, atrazine is also a carcinogenic compound and an endocrine disruptor. For human consumption, atrazine concentration in water shall not exceed 3 µg L\textsuperscript{-1}. However, higher concentrations are frequently detected in surface and groundwater\textsuperscript{15,16}.

Alachlor and atrazine are the main active ingredients in many commercial herbicide formulations, which may, in some cases, consist of a mixture of atrazine and alachlor\textsuperscript{17}. These formulations have their selective action due to the mixture of the two herbicides that complement each other. The intensive use of these compounds associated with their persistence in the environment and their low biodegradability has contributed to their frequent detection in water. Therefore, it is necessary to develop new methodologies capable of removing those compounds from aqueous systems, since conventional water and sewage treatment plants are inefficient in doing so\textsuperscript{18-21}.

Among the available methodologies for the treatment of wastewaters containing organic compounds such as alachlor and atrazine, the electrochemical method is very promising. It has been gaining prominence in scientific community due to its versatility, easy automation, high organic removal rate, immobilization of the catalyst in the electrode, and the formation of reactive species on the surface of the electrode\textsuperscript{13,22-26}.

In electrochemical oxidations, the choice of the material with which the anode is made is of fundamental importance, because the efficiency and selectivity of the process depends on it. Among the most frequently used anodes for the removal of organic compounds is the dimensionally stable anode (DSA) with a nominal composition Ti/Ru\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2}.\textsuperscript{27} It has been used in the chlor-alkali industry for several years due to its mechanical stability and catalytic activity\textsuperscript{28,29}. Several studies report the successful use of the DSA anode\textsuperscript{28,30-34}.

The feasibility of a treatment technology should not be assessed only by its potential for degrading a pollutant, but also by the generation of less ecotoxic and more hydrophilic compounds (less prone to bioaccumulation and biomagnification).

Partition coefficients (log P) and distribution coefficients (log D) are the ratios of the concentrations of a compound in a mixture of two immiscible solvents at equilibrium. Log P generally refers to the non-ionized compound, whereas log D refers to the concentration ratio of all species of the compound (ionized and non-ionized). Therefore, the latter coefficient is pH-sensitive. Typically, the most useful pH is 7.4, the physiological one\textsuperscript{35,36}. When one of the solvents is water and the other is a nonpolar solvent (usually n-octanol), then those coefficients are a measure of lipophilicity (or hydrophobicity).

Finally, the objective of this work was to study the electrochemical degradation of the herbicides alachlor and atrazine, in a flow cell, using a DSA anode (Ti/Ru\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2}), assessing the influence of different concentrations of electrolyte and current densities on the removal and mineralization of the organic compounds, besides proposing their respective routes of degradation. The ecotoxicity and lipophilicity of the identified degradation products (DPs) were also estimated.

2. Materials and methods

2.1. Cyclic voltammetry

Cyclic voltammetry (CV) was used to obtain qualitative information about the reaction on the electrode/solution interface. Cyclic voltammograms were obtained using a potentiostat/galvanostat (Autolab, PGSTAT128) and a conventional electrochemical cell composed of: (a) working electrode: circular, dimensionally stable anode plate (DSA) manufactured by De Nora do Brasil Ltda. (nominal composition: Ti/Ru\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2}; exposed geometric area: 1 cm\textsuperscript{2}); (b) counter electrode: titanium plate (2 cm\textsuperscript{2}) parallel to the working electrode; and (c) reference electrode: normal hydrogen electrode (NHE). The assays were performed using 50 mL of 0.05, 0.1, and 0.15 mol L\textsuperscript{-1} NaCl as the supporting electrolyte. Cyclic voltammograms of atrazine and alachlor (both at 0.33 mmol L\textsuperscript{-1}) in NaCl 0.15 mol L\textsuperscript{-1} were also obtained. The potential window was 0.4-1.6 V versus NHE, with scanning speed of 50 mV s\textsuperscript{-1}.

2.2. Electrochemical degradation experiments

The degradation experiments were performed in a filter-press flow-cell using: (a) a commercial DSA Ti/Ru\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2} with surface area equal to 14 cm\textsuperscript{2} (working electrode); (b) a titanium plate with area equal to 14 cm\textsuperscript{2} (counter electrode); (c) a normal hydrogen electrode (NHE) (reference electrode), and (d) a commercial cationic membrane strip (Ionac, MC-3470), immersed in 0.5 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4}, providing the electric contact.
between the electrochemical cell and the reference electrode (Fig. 1). Besides that, a centrifugal pump drove the electrolytic solution through the flow-cell. This solution was magnetically stirred.

Initial pH 3, temperature 25 °C, flow rate 130 mL min⁻¹ and solution volume 200 mL were held constant throughout the experiments.

Initially, only alachlor (0.33 mmol L⁻¹) was degraded. The experiments followed a 3² full factorial design with the central point in triplicate (Statistica 7 software). The studied factors and levels were supporting electrolyte sodium chloride concentration (0.05, 0.1, and 0.15 mol L⁻¹) and current density (10, 30, and 50 mA cm⁻²).

2.3 Analytical procedures

Total organic carbon analyses (TOC, Shimadzu TOC-VCPH Total Organic Carbon Analyzer) were performed to determine the amount of organic matter in solution, before and after the treatment.

The concentrations of alachlor and atrazine were measured in a high-performance liquid chromatograph (HPLC, Shimadzu LC-10AD VP) equipped with a UV detector (Shimadzu LC-10AVP) and a C₁₈ reversed-phase column (Zorbax SB-C₁₈, 5 μm, 25 cm × 4.6 mm). 20 μL were isocratically eluted using a mobile phase composed of acetonitrile and water 70:30 (in volume), flow rate 1 mL min⁻¹, temperature 40 °C and UV detection at 210 nm.

The degradation products (DPs) were identified in a high-performance liquid chromatograph (HPLC, Thermo Scientific Accela 1250 Pump) coupled with a LTQ-Orbitrap Velos spectrometer (HPLC-MS, Thermo Fisher Scientific), operating under the following conditions: positive ion mode electrospray ionization (ESI), electrospray voltage 3.7 kV, nebulization gas pressure 75 psi, heater temperature 500 °C, capillary temperature 400 °C, and injection volume 10 μL. A C₁₈ reversed phase column (Zorbax SB-C₁₈, 5 μm, 25 cm × 4.6 mm) and a mobile phase composed of acetonitrile and formic acid 0.1% (70:30 in volume), isocratic mode, and flow rate 1 mL min⁻¹ were used.

2.4 Calculations

Ecotoxicities were estimated for three trophic levels (fishes, daphnids and green algae) using the ECOSAR 1.11 software (USEPA, 2017). The acute indicators: LC₅₀ (lethal concentration to 50% of the tested organisms) and EC₅₀ (effect concentration to 50% of the tested organisms) were estimated. Chronic ecotoxicities were estimated as the geometric mean of the LOEC (lowest-observed-effect concentration) and the NOEC (no-observed-effect concentration). Lipophilicity (log D) values were calculated with the aid of the ChemAxon Calculator.

3. Results and discussion

3.1 Cyclic voltammetry of atrazine and alachlor

Figure 2a shows the cyclic voltammograms of the commercial DSA electrode using NaCl as the supporting electrolyte in the following concentrations: 1) 0.05, 2) 0.1 and 3) 0.15 mol L⁻¹. Figure 2b shows the voltammetric behavior of the commercial DSA electrode with solutions 0.15 mol L⁻¹ NaCl in the presence of 4) alachlor (0.33 mmol L⁻¹) and 5) atrazine (0.33 mmol L⁻¹). One can observe that from 0.4 to 1.2 V vs. NHE, no significant increase of the density current occurs; however, for potentials above 1.2 V, there was a fast increase in density current, characterized by the oxygen evolution reaction (OER) and chlorine evolution (Eqs. 1 and 2)²⁷,²⁹.

\[ \text{2H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \quad (1) \]
\[ \text{2Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^- \quad (2) \]
Figure 2. Cyclic voltammograms of the commercial DSA electrode (Ti/Ru0.3Ti0.7O2) recorded between 0.4 and 1.6 V vs. NHE at 50 mV s⁻¹ in aqueous solutions containing: (a) 0.05, 0.1, and 0.15 mol L⁻¹ NaCl (lines 1, 2, and 3, respectively) and (b) alachlor 0.33 mmol L⁻¹ (line 4) and atrazine 0.33 mmol L⁻¹ (line 5).

In Figure 2a, it can be observed that oxygen and chlorine evolution reactions became more evident with increasing concentrations of NaCl. However, when the herbicides were added to the 0.15 mol L⁻¹ NaCl solution (Fig. 2b), a gradual decrease in current density was noticed for potentials over 1.2 V. That may happen because the adsorption of the herbicides and/or electrogenerated DPs on the anode surface, blocks the electrode active sites.³⁹,³⁰

3.2 Electrodegradation study

3.2.1 Study of the alachlor electrochemical degradation by factorial design

Table 1 shows the obtained results for alachlor degradation after 120 min of electrolysis (as alachlor was harder to degrade than atrazine, the best operational conditions for the former were also used with the latter).

Table 1. Alachlor removal and mineralization obtained after the electrochemical treatment (3² full factorial design with the central point in triplicate).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>j/ mA cm⁻²</th>
<th>CNaCl/mol L⁻¹</th>
<th>Alachlor removal/%</th>
<th>TOC/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.05</td>
<td>85.0</td>
<td>19.4</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.10</td>
<td>88.0</td>
<td>20.4</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.15</td>
<td>89.5</td>
<td>21.7</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>0.05</td>
<td>86.5</td>
<td>45.2</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>0.10</td>
<td>87.4</td>
<td>70.1</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>0.15</td>
<td>93.1</td>
<td>71.2</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>0.05</td>
<td>88.0</td>
<td>67.5</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>0.10</td>
<td>91.7</td>
<td>70.4</td>
</tr>
<tr>
<td>9</td>
<td>50</td>
<td>0.15</td>
<td>93.5</td>
<td>71.6</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>0.10</td>
<td>88.0</td>
<td>67.7</td>
</tr>
<tr>
<td>11</td>
<td>30</td>
<td>0.10</td>
<td>87.0</td>
<td>68.7</td>
</tr>
<tr>
<td>Experimental Error/%</td>
<td>0.5</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It was possible to assess the effect of the investigated factors on the response-variables (removal evaluated by HPLC and the respective mineralization expressed by TOC values) to determine which of them were statistically significant with a 95% confidence interval (within tested levels). Both factors were significant, and the best tested treatment condition was 0.15 mol L⁻¹ NaCl and current density equal to 50 mA cm⁻², since the higher the current density and the electrolyte concentration, the higher the removal (93.5%) and the mineralization (71.6%). However, 0.15 mol L⁻¹ NaCl and current density equal to 30 mA cm⁻² were chosen as the actual treatment conditions due to lower electric energy requirements and to the fact that the removal (93.1%) and the mineralization (71.2%) obtained were quite close to the ones at the best tested conditions.

3.2.1.1 Effect of electrolyte concentration and current density

The NaCl concentration affects the production of radicals (and therefore, the oxidation capacity) and current density. These are important parameters for the electrodgradation of any organic compound.⁴⁰,⁴⁷ The obtained results (Table 1) show that increasing current density with a fixed NaCl concentration led to higher removal and mineralization. This same behavior was observed for a fixed current density while increasing the electrolyte concentration. Under all studied conditions, alachlor removals were greater than 80%. However, in none of them the complete removal or mineralization were achieved.

Degradation may take place by two mechanisms: i) the organic compound is adsorbed on the anode surface and then oxidized by anodic electron transfer reaction – direct oxidation; and ii) it reacts with generated active chlorine species with high oxidizing power, according to Eqs. 2, 3 and 4 – indirect oxidation.²⁸,³⁹

\[
\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}_3\text{O}^+ + \text{Cl}^- \tag{3}
\]

\[
\text{HClO} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}^- \tag{4}
\]

Hypochlorous acid (E° = 1.49 V vs. NHE) acts as the main oxidizing agent in the degradation reactions due to its greater oxidation power in comparison to the other electrochemically generated active chlorine species like ClO (E° = 0.89 V vs. NHE) and Cl₂ (1.36 V vs. NHE).²²,⁴⁰,⁴¹ As the pKa of HClO is 7.5, the protonated species predominates when pH < 7.5. For this reason, all experiments were performed in acidic medium in order to guarantee that the organic compounds were preferably oxidized by HClO, in order to achieve higher rates of removal and mineralization. Scialdone et al. emphasize that intermediates of the OER can react with adsorbed chlorine on the electrode, favoring the oxidation of the organic compound (Eqs. 5 and 6).

\[
\text{MO}_{x} (\text{OH}) + \text{Cl}^- \rightarrow \text{MO}_{x+1} (\text{HClO}) + e^- \tag{5}
\]

\[
\text{Organics} + \text{MO}_{x+1} (\text{HClO}) \rightarrow \text{Intermediates} \rightarrow \text{MO}_x + \text{CO}_2 + \text{Cl}^- + \text{H}_2\text{O} + \text{H}_3\text{O}^+ \tag{6}
\]

Therefore, increasing sodium chloride concentration increases the formation of electrogenerated chlorine species (Cl₂/HClO/ClO⁻) and the use of high current densities leads to an increase in the amount of these species, allowing alachlor degradation. For this reason, the highest removal and mineralization of alachlor was achieved with 0.15 mol L⁻¹ NaCl and current density equal to 50 mA cm⁻². However, regardless of the tested NaCl concentrations and current densities, alachlor mineralization was not complete due to the formation of recalcitrant DPs.

3.2.1.2 Determination of the energy consumption

The electric energy consumption may be estimated by the Electric Energy per Order (EEO in kWh m⁻³ order⁻¹). The EEO is defined as the electric energy in kilowatts per hour (kWh) required to degrade a contaminant (C) by one order of magnitude in 1 m² (1,000 L) of water or air, as shown in Eq. 7⁴⁶-⁴⁹, where

\[
P = \text{nominal cell power/kW},
\]

\[
t = \text{time/h},
\]

\[
V = \text{volume/L},
\]

\[
C_0 \text{ and } C_I = \text{initial and final concentrations of the contaminant, respectively.}
\]
It is important to notice that Eq. 7 is multiplied by 1,000 to convert volume from L into m$^{-3}$ and that it can only be used if the chemical reaction follows a pseudo-first order kinetics, as was the case of alachlor$^8$.

$$E_{EO} (kWh \ m^{-3} \ order^{-1}) = \frac{P \times 1000}{V \times \log(C_0/C_t)} \quad (7)$$

According to Thiam et al.$^{50}$, the energy consumption can also be expressed per unit of TOC mass, as shown in Eq. 8, where

$$E_{cell} = \text{average cell voltage (V)},$$

$I = \text{applied current (A)},$

$t = \text{electrolysis time (h)},$

$V = \text{volume (L)},$ and

$\Delta(\text{TOC})_{exp}$ is the observed TOC decrease (mg L$^{-1}$).

$$E_{CTOC} (kWh \ g_{TOC}^{-1}) = \frac{E_{cell} \times I \times t}{V \times \Delta(\text{TOC})_{exp}} \quad (8)$$

Figure 3 shows $E_{EO}$ and $E_{CTOC}$ as a function of the applied current density, calculated for the alachlor degradation experiments. In Fig. 3a, one can notice that, for a fixed current density, as the NaCl concentration increases, energy consumption decreases. This is because the conductivity of the medium also increases, decreasing cell potential, which leads to lower values of energy consumption, as previously described$^{28,44}$. In addition, for the same concentration of the supporting electrolyte, there is a concomitant increase in energy consumption, due to the cell operational potential increase and the competition between $O_2$ and $Cl_2$ formation at higher potential values$^{44}$. Comparing Fig. 3a and 3b, one can observe that the behavior of the energy consumption calculated by Eq. 8 is very similar.

![Figure 3](image)

**Figure 3.** Dependence of energy consumption (kWh m$^{-3}$ order$^{-1}$ and kWh g$^{-1}$) with applied current density in NaCl solution: (●) 0.05, (○) 0.10 and (▲) 0.15 mol L$^{-1}$. Electrolysis performed using a commercial Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ DSA anode.

### 3.2.2 Electrochemical degradation of atrazine and alachlor-atrazine mixture

Some of the major companies producing agrochemicals trade alachlor in mixture with atrazine as a way to enhance the action of both herbicides. One of the usual compositions is the ratio of 1:1 (in volume) and, for this reason, the mixture employed in the present work was composed of 0.33 mmol L$^{-1}$ of each substance.

One can observe that atrazine was removed after 45 min of electrolysis (Fig. 4), while alachlor took more than 120 min of treatment to reach a similar degradation.
Figure 4. Variation of atrazine and alachlor concentrations with treatment time: (○) alone and (●) in the mixture.

Energy consumption, TOC, and obtained removals are given in Table 2. One can observe that alachlor alone required more energy to be degraded. In none of the applied conditions the complete mineralization of the compounds was achieved, which can be attributed to the formation of recalcitrant DPs during electrolysis.

Another finding is that, apparently, there is some kind of synergism between alachlor and atrazine. When those two substances were degraded together, alachlor removal and, mainly its mineralization, were increased. Also, energy consumption significantly decreased. The reasons for that behavior are not yet understood. However, that it is a true advantage, as alachlor and atrazine are usually employed together.

Table 2. Results obtained for the removals of alachlor, atrazine and their mixture, mineralization, and energy consumption estimated after electrochemical degradation (120 min, 30 mA cm\(^{-2}\), and 0.15 mol L\(^{-1}\) NaCl).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Removal/%</th>
<th>TOC/%</th>
<th>(E_{\text{EO}})/kWh m(^{-3}) order(^{-1})</th>
<th>(E_{\text{TOC}})/kWh gTOC(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor only</td>
<td>93.1</td>
<td>71.0</td>
<td>12.1</td>
<td>0.35</td>
</tr>
<tr>
<td>Atrazine only</td>
<td>100</td>
<td>70.4</td>
<td>5.0</td>
<td>0.20</td>
</tr>
<tr>
<td>Alachlor-Atrazine (1:1)</td>
<td>99.6</td>
<td>82.8</td>
<td>7.1</td>
<td>0.22</td>
</tr>
</tbody>
</table>

3.3 Alachlor electrochemical degradation mechanism proposition

Fig. 5 shows a proposition for the alachlor electrochemical degradation route. The m/z ratios here refer to the compounds in their protonated form, [M+H]\(^+\). Initially, the molecular ion that characterizes alachlor was identified with m/z = 270. Partial oxidative cleavage of the bond in the –OCH\(_3\) group connected to N, followed by dehalogenation and subsequent hydroxylation leads to the formation of the DP with m/z = 222. This compound also was identified by Pipi et al.\(^8\) and Wang and Zhang\(^5\). In addition, this DP was also detected in water samples in Massachusetts\(^3\).

According to Pipi et al.\(^8\), the formation of the DP with m/z = 284 is characterized by a purely oxidative mechanism due to hydroxyl radicals. Hydroxyl radicals can also convert lipophilic into
hydrophilic compounds. That is, from the structural point of view, the DP with m/z = 284 is more soluble in water than its parent compound due to an increased number of polar groups in its structure. The subsequent demethylation followed by the addition of H⁺ leads to the formation of another DP with m/z = 270. DPs with m/z = 158, 176, and 224 were also identified in this work. These compounds are quinoline and indoline derivatives, obtained by the complex cleavage of certain bonds followed by cyclization.

Figure 5. Proposition of the initial mechanism for the electrochemical degradation of alachlor using a commercial Ti/Ru0.3Ti0.7O2 DSA anode in aqueous medium containing 0.15 mol L⁻¹ NaCl.

3.4 Atrazine electrochemical degradation mechanism proposition

Fig. 6 shows a proposition for the atrazine electrochemical degradation route. The m/z ratios of the structures also correspond to the protonated forms, [M+H]^+.

The molecular ion of atrazine has m/z = 216. Dechlorination of atrazine followed by hydroxylation led to the formation of the DP with m/z = 198. This is the main degradation product of atrazine. According to Chen, Yang et al., the C–Cl bond in atrazine is the lengthiest one, approximately 1.73 Å, making it easier to undergo some sort of cleavage. The subsequent deamination with the total loss of the side chain (–NHCH2CH3), followed by hydroxylation forms the DP with m/z = 171.

Two other DPs were identified. The first one, with m/z = 218, was formed by atrazine demethylation followed by hydroxylation. The DP with m/z = 232 was formed due to the abstraction of a hydrogen atom followed by hydroxylation.
3.5 Lipophilicity and ecotoxicity of alachlor, atrazine, and their degradation products

The distribution coefficients (log D, pH 7.4) of alachlor, atrazine, and their degradation products (DPs) are presented in Fig. 7.

It is possible to observe that alachlor and its DPs have log D > 0. This is an indication that those compounds preferentially dissolve in non-polar media, representing a risk factor for living beings due to their bioaccumulation potential. The log D of all alachlor DPs are smaller than that of alachlor (3.59) due to the insertion of polar groups into their structures during electrolysis, which contribute to the increase in their aqueous solubility, and to smaller carbon chains compared to alachlor.

Among alachlor DPs, those formed by hydroxylation produced, in average, DPs with lower lipophilicity. DP3 is the compound with the lowest calculated lipophilicity (log D ≈ 1.55), due to the insertion of a carbonyl in one of the ethyl groups bonded to the aromatic ring and to the replacement of a methoxy group by a hydroxyl one, in one of the carbon chains bonded to the nitrogen atom. Its log D is twice as lower as that of alachlor.

In relation to the DPs formed by cyclization, from DP4 (3.09) to DP5 (2.61), log D decreases by one order of magnitude, due to the loss of aromaticity in one of the rings. From DP5 (2.61) to DP6 (1.56), log D decreases another order of magnitude, due to the loss of the ethyl group bonded to the aromatic ring and dechlorination. DP3 and DP6 have similar lipophilicities.

The lipophilicity of atrazine (2.20) is an order of magnitude lower than that of alachlor (3.59). Atrazine and its DPs have also log D > 0, indicating that they preferably dissolve in non-polar media. The log D of all atrazine DPs are smaller than that
of atrazine, in average one order of magnitude lower. The chemical features that make those compounds more water-soluble compared to atrazine are the smaller carbon chains and the increased number of polar groups in their structures.

Figure 8 shows the estimated acute and chronic ecotoxieties for freshwater organisms at three trophic levels (fishes, daphnids and green algae) of alachlor, atrazine and their DPs. It is important to observe that acute toxicity is usually observed within the first 24-48 h after exposure to the deleterious substance(s), whereas the chronic one is later observed (sometimes weeks or months after the exposure). In this context, the lower the concentration of those compounds that causes harmful effects, the greater their ecotoxicity.

Alachlor acute and chronic estimated ecotoxities were high for all tested organisms (fishes, daphnids and green algae) (Fig. 8). This could be attributed to: (i) alachlor is a compound with high log D value (3.59), which is an indication of its ability to dissolve in fat tissues of animals (fishes and daphnids) and (ii) as alachlor is a herbicide, whose main function is to prevent photosynthesis from happening, it is expected to be quite toxic to green algae. Approximately, the DPs formed from alachlor are equally toxic to fishes and daphnids. That is probably because all degradation products, as well as alachlor, have high lipophilicity.

Among the DPs formed from alachlor, the least toxic is DP6, which is the compound that presented the lowest lipophilicity. Therefore, increased concentrations of those compounds are necessary to harm fishes and daphnids, since they are easier to be eliminated by the organisms. Alachlor is much more toxic than atrazine (16, 4 and 26 times more toxic to fishes, daphnids and green algae, respectively).

**Figure 8.** Estimated acute and chronic ecotoxities of alachlor, atrazine, and their degradation products, using the ECOSAR 1.11 software (USEPA), for three trophic levels: fishes, daphnids and green algae. Chronic ecotoxities are the geometric mean between the lowest-observed-effect concentration (LOEC) and the no-observed-effect concentration (NOEC).
Atrazine and its DPs also have high acute ecotoxicities towards green algae due to their herbicidal action, preventing photosynthesis to happen. The atrazine DPs are less toxic to daphnids and fishes compared to atrazine, in the order DP7 > DP8 > DP9 > DP10. This may be ascribed to the partition coefficients of these compounds, which are lower than that of atrazine, making it necessary to increase the DPs concentration to cause fishes and daphnids mortality. In addition, all of atrazine DPs are more toxic to daphnids than to fishes.

Over time, the difference between the ecotoxicities of alachlor and atrazine decreased, so that their chronic ecotoxicities are similar. In addition, it is possible to observe that alachlor (atrazine) concentrations that cause chronic ecotoxicity are on average 10 (40) times lower than those that cause acute ecotoxicity. It is important to emphasize that atrazine and corresponding DPs ecotoxicity profile is quite similar, whether acute or chronic ecotoxicities are considered.

4. Conclusions

The DSA in the presence of chloride, led to high removals of alachlor and atrazine due to the formation of active chlorine species with high oxidant power (Cl₂/HOCl/ClO₂) and the generation of chemically adsorbed hydroxyl radicals on the surface of the electrode. However, in none of the experiments, it was possible to achieve complete mineralization of the organic compounds, due to the formation of recalcitrant DPs (some of which were identified in this work) and to the short electrolysis time (120 min).

The identified DPs of alachlor and atrazine in this work have already been reported in the literature; however, the electrolysis was performed under different conditions. Based on the structures of the DPs identified in this work, it was possible to estimate their acute and chronic ecotoxicities towards three different trophic levels (fishes, daphnids and green algae) and their distribution coefficients (log D). Those parameters allow one to conclude that all formed DPs have lower pollution potential than their original compounds, although they still pose threats to the environment.

In this context, the present study showed that the electrochemical degradation is effective and can be used for the treatment of residues of pesticides in formulations containing alachlor and atrazine.

References


