Removal of clomazone herbicide from a synthetic effluent by electrocoagulation
Cristina Benincá, Fernanda T. Vargas, Manoel L. Martins, Fábio F. Gonçalves, Rodrigo P. Vargas, Flavio B. Freire and Everton F. Zanoelo

ABSTRACT
The aim of this work was to investigate the kinetics of removal of clomazone herbicide from an aqueous solution by electrocoagulation. The experiments were performed in a cylindrical batch reactor with six aluminum electrodes in monopolar mode, arranged in series and connected to a digital DC power. The aqueous solution (tap water + clomazone) with initial pH close to 7.9 was always treated at ambient temperature (≈20°C) and atmospheric pressure for 5,400 s. For a confidence level of 95% the rate constant of electrocoagulation and the efficiency of removal of clomazone at equilibrium were $2.1 \times 10^{-3} \pm 0.5 \times 10^{-3}$ s$^{-1}$ and $97.7 \pm 2.2\%$, respectively. The final chemical oxygen demand was 88% lower than that measured initially, while turbidity and apparent color were totally removed from the synthetic solution at a rate close to that of formation of aluminum hydroxides. Some reaction intermediates, such as benzonitrile-2-chloro and 2-chloro-hex-2,4-diene-1,6-dioic-acid determined by gas chromatography mass spectrometry (GC-MS) analysis, explain the ratio of equilibrium to initial total organic carbon approximately between 0.6 and 0.8 at a probability of 95%.

Key words | aluminum electrodes, chemical kinetics, clomazone, electrocoagulation, herbicide, oxidation

INTRODUCTION

Pesticide contamination of ground and surface water has been a matter of great public concern for decades. However, the scarce control of destination and trading of these agrochemicals, which increased at a worrying global rate of ≈9.8% per year between 2007 and 2013 (Global Research & Data Services 2014), have recently made the problem of use of insecticides, herbicides and fungicides even more critical. Only in Brazil, the trade of chemicals for such a purpose reached the level of approximately 500 thousand tons in 2013 (IBAMA 2014). Clomazone is one of the most used (≈2,700–6,200 tons per year between 2009 and 2012), but still a long way behind glyphosate, 2,4-D and atrazine that together account for almost 50% of the total Brazilian market of pesticides (IBAMA 2014).

Clomazone is a herbicide extensively used in rice fields, but also in soybean, tobacco, pepper, pumpkin, and sugarcane growing areas (Lee et al. 2004; Li et al. 2004; Zanella et al. 2008). Clomazone suppresses the synthesis of chlorophyll and carotenoid pigments whose practical consequence is the efficient and selective control of many grass and weeds (Mervosh et al. 1995; Li et al. 2004). However, as clomazone is moderately toxic and it presents high solubility in water (1,100 mg L$^{-1}$), its use may represent a potential risk of contamination of water resources (CONAMA 1986; WHO 2010; Pereira et al. 2013; Menezes et al. 2014).

Traditional technologies for water and wastewater treatment have proven to be markedly ineffective for handling water contaminated with herbicides and recalcitrant compounds in general (Mir et al. 2012). Among the many innovative methods suggested to reduce the detrimental effects of such kinds of contaminant on environment (Chiron et al. 2000; Esplugas et al. 2007; Arslan-Alaton et al. 2010), electrocoagulation has received much attention (Emamjomeh & Sivakumar 2009; Nourozi et al. 2011;
For instance, it has been successfully applied for removal of atrazine, malathion, imidacloprid, chlorpyrifos, methyl parathion, monocrotophos and abamectin from water (Ghalwa et al. 2015).

Electrocoagulation is a low-cost operation process that basically requires a vessel where aluminum, copper, iron or stainless steel electrodes are immersed into the contaminated solution (Amani et al. 2014). The electrolysis is responsible for the production of metal hydroxides that neutralize the charges of particles dispersed in the solution, so particles agglomerate and form flocs that may be more easily removed by sedimentation/flotation (Gregory & Duan 2001; Holt et al. 2004; Mouedhen et al. 2008; Emamjomeh & Sivakumar 2009; Brillas & Martínez-Huitle 2015). Its extensive and efficient use for removal of many different pollutants from water, simplicity of operation, no need for chemicals except the products of electrolysis, and reduced amount of produced sludge are the most important alleged advantages of such a procedure for treatment of wastewater (Emamjomeh & Sivakumar 2009; Amani et al. 2014). Electrolytes may be used many times as additives, mainly ‘to adjust the electrical conductivity of the fluid to be treated’, but their use is not mandatory (Trompette & Vergnes 2009).

In this framework, the current study aims to investigate experimentally the kinetics of removal of clomazone herbicide from an aqueous solution (tap water + clomazone) by applying electrocoagulation with aluminum electrodes (Al-Al). The chemical oxygen demand (COD), total organic carbon (TOC), turbidity and apparent color of the examined synthetic solution, as well as the formation of reaction intermediate products were also periodically monitored. Although clomazone is widely used around the world, studies about its degradation are limited in the literature (Gara et al. 2009; Abramović et al. 2013; Feng et al. 2015), or even nonexistent for the particular case of involving electrocoagulation. Aluminum electrodes were preferred because they have been successfully used to reduce all the pollutant parameters currently considered (contaminant concentration, COD, TOC, color and turbidity) from different wastewater (Emamjomeh & Sivakumar 2009; Brillas & Martínez-Huitle 2015; Dermici et al. 2015; Yehya et al. 2015).

**MATERIALS AND METHODS**

**Chemicals**

The herbicide clomazone [2-[(2-chlorophenyl)-methyl]-4,4-dimethyl-3-isoxazolidinone] (99.8% purity) and the triphenyl phosphate (99.5% purity, internal standard (IS) for gas chromatography (GC) analysis) were from Dr. Ehrenstorfer (Augsburg, Germany). Standard aqueous solutions were always prepared with Milli-Q water (Millipore, Bedford, USA). Helium (99.9997% purity, White Martins, Brazil) and iso-octane (HPLC grade, JT Baker, Center Valley, USA) were used as carrier gas and solvent, respectively.

**Electrocoagulation experiments**

The electrocoagulation tests were carried out in an experimental apparatus schematically shown in Figure 1. It basically consists of a 5,000 mL cylindrical glass reactor filled with a clomazone solution (500 mg L$^{-1}$) prepared with tap water. The reactor was always operated batchwise at ambient temperature ($\approx$20°C) and atmospheric pressure for 5,400 s. The initial pH of the herbicide aqueous solution (tap water + clomazone) was 7.9. A submersible pump placed at the bottom of the vessel was used to promote good mixing between the contaminant and the aluminum hydroxides formed by electrolysis ($<$180, Sarlo Better, São Caetano do Sul, Brazil). It was particularly done by bubbling air through the synthetic solution and by circulating water at a volumetric flow rate of 5 L min$^{-1}$.

The used electrodes were cylinders 5 $\times$ 10$^{-3}$ m diameter and 0.1 m long made of aluminum. A set of six of those electrodes (interelectrode gap = $3 \times 10^{-2}$ m) was distributed over the cross sectional area of the cylindrical reactor. They were arranged in series and in monopolar mode, and connected to a digital DC power supply (24 V, 25 W and 1 A) (S25-24 V Sibratec, Rio do Sul, Brazil). A digital multimeter was used for measurements of voltage and current loads (100V06, Worker, Curitiba, Brazil). The current density was 106 A m$^{-2}$.

The sampling procedure consisted of transferring 40 mL of effluent from the reactor (where a suspension was formed) to an external sedimentation vessel, where it was left for 10 min. Only the supernatant was taken for analyses in order to determine the concentration of aluminum, color,
turbidity COD, and TOC. In the case of gas chromatography mass spectrometry (GC-MS) analyses to determine the concentration of clomazone and formed by-products, 1 mL of suspension was directly removed from the reactor and placed in a 10 mL volumetric flask with 1 mL of iso-octane and 8 mL of distilled water. The mixture was stirred vigorously for 1 min and sonicated for further 5 min in an ultrasonic bath (Sanders, Santa Rita da Sapucaí, Brazil). Then, it was left in repose, and a sample of 1 mL from the less dense formed phase rich in iso-octane was removed for analysis. Both the sampling procedures were repeated six or seven times at different times for the entire period of electrocoagulation.

Analysis

The mineralization of the synthetic solution was monitored from the decay of TOC by using a TOC-VCPH analyzer (Shimadzu, Kyoto, Japan). For this purpose samples were preliminary taken to filtration through a 0.45 μm cellulose acetate filter and their pH was adjusted to approximately 2 with sulfuric acid.

The COD removal was according to standard methodology (APHA 1995, method 5220D). To determine the apparent color (APHA 1995, method 2120C) and turbidity (APHA 1995, method 2130B) the absorbance of the sample was recorded with a photometer (Spectroquant NOVA 60, Merck, Darmstadt, Germany). The apparent color was expressed in terms of mg PtCo L⁻¹. The concentration of aluminum compounds was determined colorimetrically with a spectrophotometer (Pharo 100, Merck, Darmstadt, Germany) by applying the Eriochrome Cyanine-R method (APHA 1995, method 3500-Al B). The pH of solution was measured using a pH meter (UB-10, Denver Instrument, Bohemia, USA), while the removal of clomazone was followed by GC-MS analyses.

All the GC-MS analyses were made with a Clarus 680 gas chromatograph combined with a Clarus 600 T quadrupole mass spectrometer (Perkin Elmer, Waltham, USA). The GC-MS was operated in the electron impact ionization mode at 70 eV and scanned from 50 to 600 Da. A total of 1 μL of prepared extract solution was injected in a split/splitless injector held at 250 °C for 30 min. GC separations were performed on a capillary column CP-VF-5 MS (30 m × 0.25 mm × 0.25 μm film thickness, Agilent, Palo Alto, USA). The carrier gas was maintained at a constant flow rate of 1 mL min⁻¹. The oven temperature program was as follows: 45 °C kept for 1.5 min, then ramped to 260 °C at 10 °C min⁻¹ kept for 7.0 min. The total runtime was 70 min, and the solvent delay was 30 min. Transfer line and MS temperatures were set at 300 °C and 250 °C, respectively.

The data were stored and processed with software Turbo Mass (version 5.4.2.1617, Perkin Elmer, Waltham, USA) and NIST mass spectral Search Program (version 2.0f, NIST, DC, USA). The full scan chromatograms were integrated without noise reduction, and smoothed 2 × 2 by Savitzky-Golay algorithm with a threshold of 1,000 counts for peak area and a signal-to-noise ratio higher than 100. The mass spectra of identified peaks were automatically compared with a NIST mass spectral library by a reverse fit method with a match limit higher than 700. For the unknown mass spectra mass spectrometric identification was based on a comparison with a database for clomazone degradation (Zanella et al. 2008). IS peak areas were used to correct signals of each sample.

RESULTS AND DISCUSSION

Table 1 presents a summary of the initial examined properties of the synthetic solution of clomazone. They are the initial conditions used to compute the single integration constant of a first-order differential equation (ODE) (Equation (1)) suggested to describe the kinetics of the electrocoagulation operation:

\[
\frac{dy}{dt} = -k(y - y_e)
\]  

where \(dy/dt\) is the rate of disappearance/appearance of \(y\), \(t\) is the electrocoagulation time, \(k\) is the rate constant, and \(y_e\) is \(y\) at equilibrium.

Equation (2) is the analytical solution of the above ODE obtained upon separation of variables and integration, where \(y_0\) is \(y\) at \(t = 0\). It was firstly applied to reproduce the experimental kinetic data of concentration of aluminum

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Synthetic clomazone solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>7.9</td>
</tr>
<tr>
<td>Clomazone</td>
<td>mg L⁻¹</td>
<td>500</td>
</tr>
<tr>
<td>Aluminum compounds</td>
<td>mg L⁻¹</td>
<td>0</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>197</td>
</tr>
<tr>
<td>Apparent color</td>
<td>PtCo</td>
<td>319</td>
</tr>
<tr>
<td>COD</td>
<td>mg L⁻¹</td>
<td>1,392</td>
</tr>
<tr>
<td>TOC</td>
<td>mg L⁻¹</td>
<td>93</td>
</tr>
</tbody>
</table>
hydroxides shown in Figure 2(a). At such a condition y represents the concentration of aluminum compounds ([Al]). k (2.1 × 10⁻³ ± 0.5 × 10⁻³ s⁻¹) and yₑ (0.95 ± 0.04 mg L⁻¹) were simultaneously tuned on these experimental results by applying the optimization method of Levenberg-Marquardt and an objective function given by the sum of the squared differences between the experimental and calculated [Al] (StatSoft, Inc. 2005).

\[ y = yₑ + (y₀ - yₑ) \exp(-kt) \]  \hspace{1cm} (2)

As may be promptly observed, the model was able to describe correctly the increase of [Al] as the time of coagulation passes \((R^2 \approx 0.993)\). Because the pH shown in Figure 2(b) varied between approximately 7.9 to 8.8, it was inferred from early evidence reported in the literature that Al(OH)₃ was the dominant aluminum specie in the solution (Vepsalainen et al. 2002). It is well-accepted in the literature that in the pH range from 6 to 9 soluble Al³⁺ produced by the anodic reaction is converted to Al(OH)₃ according to Equation (3) (Gregory & Duan 2001; Brillas & Martínez-Huitle 2003). pH curves with lower and upper pH limits analogous to those currently observed were also obtained and explained properly by independent researchers that performed similar experiments (Kobya et al. 2006; Feng et al. 2007). It supports the reliability of the current results.

\[ \text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3/2\text{H}_2 \]  \hspace{1cm} (3)

Figure 2(b) also presents the kinetics of clomazone removal. A rapid decay of clomazone concentration is initially observed, but as time is increased the percentage of clomazone approaches a limit value close to zero. It confirms the efficiency of the electrocoagulation process for the purpose of clomazone removal. However, the most interesting result that emerges from such a plot is that the rate of consumption of clomazone and the rate of appearance of Al(OH)₃ are the same. In fact, Equation (2) with \(y₀\) equal to 100%, \(yₑ\) close to 2.3 ± 2.2% and the same \(k\) earlier used to describe the kinetics of formation of aluminum compounds (i.e., 2.1 × 10⁻³ ± 0.5 × 10⁻³ s⁻¹) reproduced the experimental decay of clomazone with time \((R^2 \approx 0.997)\). \(yₑ\) is now the single adjusted parameter of Equation (2) calculated by applying the same tuning procedure early reported, but now by involving those experimental data of clomazone concentration presented in Figure 2(b).

The kinetics of color and turbidity removal are shown in Figure 3(a). As may be noticed, it took only 600 s to have negligible experimental values of both these variables. Although the dependence of color and turbidity on the amount of metal hydroxides is well-established in the literature (Feng et al. 2007), for an unknown reason there is a residual disagreement (especially at \(t < 600\) s) between the experimental results and those calculated with Equation (2) using \(k\) based on the kinetics of formation of aluminum compounds (i.e.; 2.1 × 10⁻³ ± 0.5 × 10⁻³ s⁻¹) \((R^2 \approx 0.931)\). In this case, \(y₀\) in Equation (2) is obviously equal to unity, while \(yₑ\) (i.e., color and turbidity at equilibrium) tuned on experimental data in Figure 3(a) are approximately zero. Such an almost complete removal of color and turbidity in a slightly alkaline pH range (≈7–9) by electrocoagulation with aluminum electrodes is confirmed in the literature.
(Kobya et al. 2006; Merzouk et al. 2011; Ozyonar & Karagozoglu 2011; Borbón et al. 2014).

Figure 3(b) illustrates that COD was efficiently reduced over electrocoagulation time. In particular, it dropped sharply for about 1,000 s according to a rate identical to that for formation of Al(OH)₃. Ozyonar & Karagozoglu (2011) also observed a rapid decay of COD (i.e., 71–72% of removal) when a domestic wastewater was treated by electrocoagulation for only 600 s at an initial pH of 7.8, and a current density not different than that currently considered (100–150 A m⁻²). However, for t longer than approximately 1,000 s the rate of oxygen demand fell to approximately zero and the COD approached a constant value close to 169 ± 80 mg L⁻¹ at an α (level of significance) equal to 0.05. Such a result of COD at equilibrium is one that again minimized the sum of the squared residuals when applying Equation (2) to model the COD removal (StatSoft, Inc. 2005) ($R^2 \approx 0.958$). It means that the maximum COD reduction at the examined operating condition was between 82 and 94%, which is in agreement with the many previous studies of electrocoagulation with electrodes of aluminum (Bensadok et al. 2008; Merzouk et al. 2010; Ozyonar & Karagozoglu 2011; Saeedi & Khalvati-Fahlyani 2011).

The kinetics of TOC abatement is shown in Figure 4(a). The TOC values from the first-order semi-empirical kinetic model given by Equation (2) ($y_0 = 1; \ y_e = 0.7 \pm 0.1$ for 169 ± 80 mg L⁻¹ at an α (level of significance) equal to 0.05. Such a result of COD at equilibrium is one that again minimized the sum of the squared residuals when applying Equation (2) to model the COD removal (StatSoft, Inc. 2005) ($R^2 \approx 0.958$). It means that the maximum COD reduction at the examined operating condition was between 82 and 94%, which is in agreement with the many previous studies of electrocoagulation with electrodes of aluminum (Bensadok et al. 2008; Merzouk et al. 2010; Ozyonar & Karagozoglu 2011; Saeedi & Khalvati-Fahlyani 2011).

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\( \alpha = 0.05 \) or \( y_e = 0.7 \pm 0.2 \) for \( \alpha = 0.01 \); \( k = 2.1 \times 10^{-3} \pm 0.5 \times 10^{-3} \text{ s}^{-1} \) do not agree well with those experimentally determined. However, when one considers the uncertainty in \( y_e \), it is possible to state that at a probability higher than 99\% (\( \alpha < 0.01 \)) it describes the changes of TOC with time.

The only possible explanation for the limited TOC removal at equilibrium (10–50\% at a 0.99 probability level), a recurrent problem of electrocoagulation (GilPavas et al. 2009; Arslan-Alaton et al. 2010), is the presence of reaction by-products that were not completely oxidized or

**Figure 5** | Mass chromatograms, structural formula and mass spectra of clomazone (a), benzonitrile-2-chloro (b), and 2-chloro-hex-2,4-diene-1,6-dioic-acid (c).
removed by electrocoagulation/sedimentation. The identification of two clomazone by-products in the treated solution (benzonitrile-2-chloro with m/z 137 and 2-chlorohex-2,4-diene-1,6-dioic-acid with m/z 177) supports such an assumption. The area under peaks of these two formed species were monitored over the entire period of electrocoagulation. Because the data varied considerably from each other at different electrocoagulation time and no tendency was identified, the mean and standard deviations of the readings for both these species are presented (see Figure 4(b)).

The no clear influence of time on formation of benzonitrile-2-chloro and 2-chlorohex-2,4-diene-1,6-dioic-acid is evidence of the multiple mechanism of removal of pollutants by electrocoagulation. Besides the electrolysis, neutralization of charges on the dispersed/soluble compounds, coagulation and sedimentation, Figure 4(b) leads one to presume that clomazone abatement may be at least partially attributed to an additional oxidation reaction.

Among the oxidizing agents typically reported in the literature (Booking 2006), O₂ and H₂O₂ are the most probable candidates for the oxidation of clomazone at the current circumstances. The reason for this is that O₂ was available from the air injected to promote mixing, while H₂O₂ could be theoretically produced from a reaction between water-soluble O₂ and H⁺ according to Equation (4) (Oturan et al. 2012). In such a mechanism, the H⁺ supply is due to the electrolysis of water (Mollah et al. 2004; Mouedhen et al. 2008) (Equation (5)), which is believed to occur because the current applied voltage (≈24 V) was higher than the potential for such a reaction at 25°C (≈1.23 V) (Lide 2006).

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{4}
\]

\[
2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{5}
\]

The mass spectra and mass chromatogram of clomazone at the time of 120 s, as well as those of benzonitrile-2-chloro and 2-chlorohex-2,4-diene-1,6-dioic-acid at the time of 600 s are shown in Figure 5.

**CONCLUSIONS**

Electrocoagulation with aluminum electrodes at 20°C, 106 A m⁻² and pH 7.9–8.8 was carried out in a batch reactor. Except for an incomplete mineralization (TOC ≈10–50%) caused by the formation of by-products (benzonitrile-2-chloro and 2-chlorohex-2,4-diene-1,6-dioic-acid), the examined pollutant parameters were efficiently reduced, that is, at equilibrium clomazone removal was ≈95–100%, color and turbidity removal was 100% and COD removal was ≈82–94%. A first-order kinetic model with an identical rate constant tuned on the experimental data of Al(OH)₃ production was able to describe correctly the kinetics of clomazone, color, turbidity, COD and TOC abatement. From a practical point-of-view, the current results confirm that electrocoagulation may be applied as a treatment/pre-treatment technique for the removal of pesticides from contaminated water.

**REFERENCES**


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