

Electrochemical Degradation of Atrazine in Aqueous Solution at a Platinum Electrode

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Abstract

Atrazine is a highly used herbicide and it has been found in both deep and superficial waters. Its solubility in water is reduced and is relatively stable in humid environments, where it has a half-life of one hundred days. Atrazine can be degraded by oxidative photolysis or by microorganisms. It is moderately toxic in humans, animals and plants, because it can be absorbed by inhalation, ingestion or through the skin.

In this work, we study the degradation of atrazine in aqueous solution using current controlled electrolysis at a platinum electrode. The effects of pH, current magnitude and direction, and temperature, were evaluated. The atrazine decomposition was monitored during electrolysis by UV-Vis spectrophotometry; quantification of atrazine was done by GC/MS, and quantification of cyanuric acid was done by HPLC.

It was found that at 25 °C in acid media, atrazine is degraded partially to cyanuric acid with formation of persistent intermediate compounds, but at 60 °C atrazine is completely degraded to cyanuric acid. The TOC results indicate no electrochemical combustion and no mineralization was observed under the experimental conditions studied.

Keywords: atrazine, electrochemical degradation, cyanuric acid, TOC.

Introduction

The compound 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, or atrazine, is a highly used herbicide of pre- and post-emergency. Atrazine, which has been found in both deep and superficial waters, presents a low solubility in water (1.6×10^{-4} M at 20 °C) and it is relatively stable in aqueous environments and soils, where it has a half-life of one hundred days. Atrazine can be degraded by oxidative photolysis or microbial action. [1] Moderately toxic to humans and other animals, it can be absorbed through inhalation, oral route or the skin. The degradation of this herbicide has been studied by means of biological [1]

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(bacterial decomposition, metabolization in plants) and physicochemical methods [2,3] (adsorption on solid adsorbents and oxidative degradation with free radicals), visible or ultraviolet radiation, ultrasound and microwaves [4-9]. The final products detected after oxidative degradation are cyanuric acid as predominant compound and other substituted triazines.

Alternatively, electrochemical techniques can be used for atrazine degradation, where catalytic properties of several electrode materials for producing oxidative or reductive reactions are well known. These methods can readily be coupled with other chemical or biological methods. For example, by means of reductive electrolysis in aqueous acidic medium, or on mercury electrodes, where atrazine and other chlorinated triazines lose chlorine or an alkyl group. [4,10]

In this work, we study the electrochemical degradation of atrazine at a platinum electrode at different conditions of pH, temperature, anodic and cathodic current density, in the electrochemical cell.

Experimental

Reagents

Atrazine (CAS: 1912-24-9), 99% pure (Supelco), was used without further purification. Cyanuric acid, (CAS: 108-80-5), 98% pure (Fluka) was used as received. Sodium phosphates, 98% pure (Carlo-Erba), were used to adjust pH. Acetonitrile, dichloromethane, methanol and *n*-hexane (Mallinckrodt and Carlo-Erba, respectively), HPLC grade, were used for the chromatographic analyses. Potassium acid phthalate (CAS: 877-24-7), 99% pure was used in the TOC analyses. Deionized water (milliQ-millipore) was used in all experiments.

Electrochemical system

All electrolysis were performed in an two-compartment electrochemical cell (100 mL each), separated by a glass membrane (2 μm pore diameter). Two 2.15 cm^2 mesh platinum electrodes were used as anode and cathode and counter electrode, respectively. In the set of experiments where the working platinum electrode was used as a cathode, atrazine did not degrade.

The cell was driven by a 50-300 mA current source. The effect of pH, temperature and current density over the oxidative reaction of atrazine and cyanuric acid was studied. The pH was fixed between 0.8 and 11.5 by using phosphate buffer solutions. The reaction was performed at 25 and 60 $^{\circ}\text{C}$ and 0.023 and 0.12 Acm^{-2} . Constant stirring was used in all experiments. Aliquots of 3.0 mL were drawn from the cell at 0, 5, 15, 30, 60, 120 and 240 minutes of electrolysis for chromatographic and spectroscopic analyses.

UV-Vis spectrophotometry

UV-Vis spectra were taken with a Shimadzu, model UV-160A spectrophotometer. The spectra were recorded between 200-600 nm at a scan rate of 30 nm/s in a 1.0 cm quartz cell.

Atrazine quantification

Atrazine in aqueous solution was extracted from the electrolysis medium using methylene chloride as organic phase (73.2 % of recovery). The extracts were dried and reconstituted to 0.5 mL with *n*-hexane. These samples were analyzed with a Shimadzu GC/MS-QP2010 system with a Restek XTI-5 column (30 m x 0.3 mm x 0.25 μ m), helium as mobile phase, and the quadrupole detector operated in single ion monitoring mode, SIM. The GC column temperature was set at 80 °C for 1 minute, ramped to 180 °C at 30 °C/min then to 230 °C at 10 °C/min and kept at 230 °C for 6 minutes. For quantification, the peak at $m/z=215$ [molecular ion, $C_8H_{14}N_5Cl^+$] was used.

Cyanuric acid quantification

A HPLC Perkin-Elmer LC 100EI chromatograph with a Hypersil ODS column (length=125 mm, internal diameter=5 μ m) was used. A mixture of 2% methanol, 98% phosphate buffer solution (pH 6.94) was used in an isocratic mode with a constant flow of 0.7 mL/min. Detection was done with an UV Hewlett Packard unit at $\lambda=215$ nm [11].

Total organic carbon analysis

TOC of the atrazine electrolysis solution was determined in a TOC analyzer Shimadzu Model TOC-VWS, calibrated by using potassium acid phthalate. The detection and quantification limits were 1.0 and 3.0×10^{-2} mM, respectively.

Results and discussion

Experimental design

The experimental conditions of the electrolytic experiments are shown in Table 1.

Table1. Experimental conditions used for the electrolysis of atrazine 5.0×10^{-3} mM.

pH	Current density (Acm⁻²)	Working electrode	Temperature (°C)
6.9	0.02	Cathode	25
6.9	0.02	Anode	25
6.9	0.07	Anode	25
6.9	0.07	Cathode	25
6.9	0.12	Anode	25
3.5	0.07	Anode	25
3.5	0.07	Cathode	25
0.8	0.07	Cathode	25
0.8	0.07	Anode	25
0.8	0.07	Cathode	60
0.8	0.07	Anode	60
10.5	0.07	Anode	25
10.5	0.07	Cathode	25

Monitoring reaction by UV spectroscopy

The UV spectrum of atrazine in aqueous solution (natural pH) exhibits a main band centered at 222 nm and a band of minor intensity at 270 nm. Cyanuric acid (found as final predominant product) absorbs below 235 nm without reaching a maximum above 200 nm. However, at pH 10.0, cyanuric acid shows a band with a maximum at 235 nm. Since the molar absorptivities for cyanuric acid between 200 and 250 nm are very small compared to those of atrazine, it is possible to follow the decay of atrazine by monitoring the absorbance at 222 nm because at this wavelength, interference by cyanuric acid can be neglected.

Anodic electrolysis

The degradation rates of atrazine increase with anodic current density up to 0.12 Acm^{-2} as shown in Fig.1.

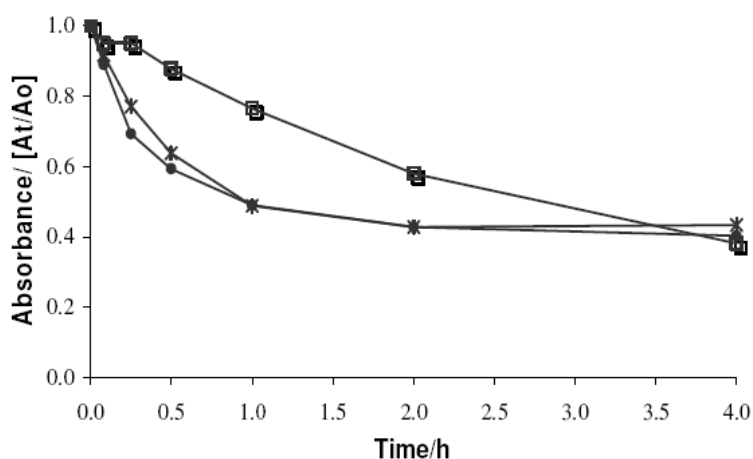


Figure 1. Normalized variation of absorbance at 222 nm, during oxidative electrolysis of atrazine at pH=6.9 and 25 °C. Current densities, in Acm^{-2} : 0.12 (asterisks), 0.07 (full circles), and 0.02 (white squares).

Higher current densities do not change the degradation rates, indicating that the reaction rate becomes limited by mass transfer towards the anode. In another set of experiments, in which the working platinum electrode was used as a cathode, atrazine did not degrade.

pH effect

As shown in Fig. 2, at pH 0.8 and 3.5, the absorbance decreases linearly at the beginning of the reaction, reaching steady state after ca. 2 hours. At pH 6.9, the absorbance changes slowly for 1.5 h and then decays faster. At pH 10.5, the absorbance decreases by only ca 10 % after 4 h of electrolysis, suggesting that atrazine follows different mechanisms of degradation with pH.

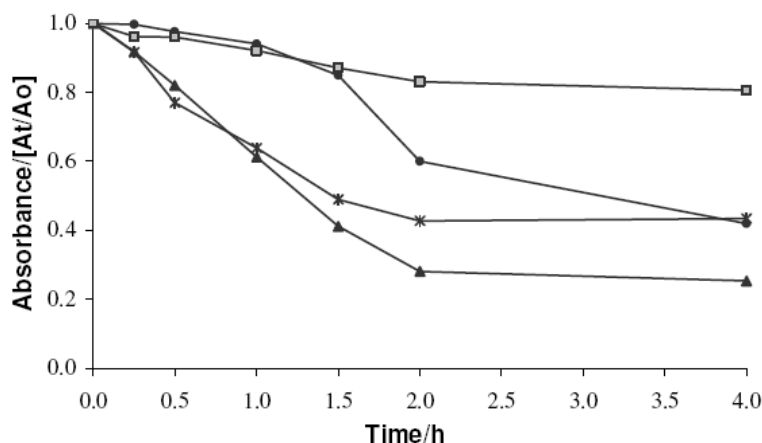


Figure 2. Normalized variation of atrazine absorbance at 222 nm during oxidative electrolysis at 0.007 A cm^{-2} and temperature of $25 \text{ }^\circ\text{C}$. Reaction pH, 0.8 (triangles), 3.5 (asterisks), 6.9 (circles), and 10.5 (white squares).

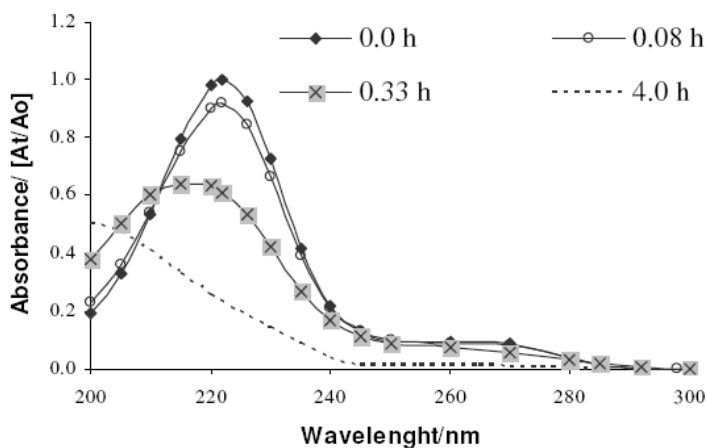


Figure 3. Variation of the UV spectrum during atrazine electrolysis at 0.07 A cm^{-2} , temperature of $25 \text{ }^\circ\text{C}$, and $\text{pH}=0.8$.

Fig. 3 shows the variation of atrazine spectra during the anodic electrolysis at 0.07 A cm^{-2} , temperature of $25 \text{ }^\circ\text{C}$, and $\text{pH} 0.8$. Under these conditions, atrazine is protonated and the spectrum registered after 4 hours of electrolysis shows the decrease of the main band at 220 nm, and residual absorption between 200 to 240 nm, indicating that the products of the reaction are aromatic. At $\text{pH} 0.8$, the absorbance at 222 nm decreases by 70% in 4.0 h. In basic medium, during the same time scale, the atrazine conversion is negligible. Several degradation routes of atrazine and similar compounds have been proposed. These routes involve free radicals [12-14]. The following reactions have been proposed:

- substitution of the chlorine atom by a hydroxyl group as initial step of degradation;
- reduction of the amine groups, with protonation preceding electron transfer;
- oxidation of alkyl groups of the amines to produce carbonyl or hydroxyl groups.

Fig. 4 shows two possible degradation products of atrazine. The acidity of the reaction medium has a marked influence in the degradation of atrazine since complete protonation affects the substitution at the ring and produces one or several dealkylated products. The susceptibility of electrophilic attack will be similar for the carbons of the ring bonded to the amines. The steric hindrance is probably bigger for the carbon next to the ethylamine group because it doesn't present chain ramifications and it is one carbon short with respect to the isopropylamine.

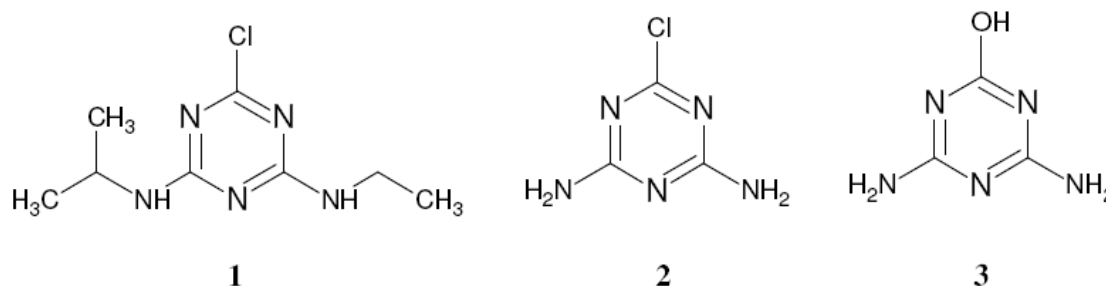


Figure 4. Atrazine (1) and two probable products of the degradation process. Simazine di-dealkylated (2) and ammeline (3).

The amino substituents in the deprotonated atrazine species shows low reactivity and the chlorine is likely to be replaced by a hydroxyl group. In spite of the electron donating characteristics of amines that activate the aromatic ring, the UV spectra suggest that an alkaline medium does not favor the electrochemical reaction. Under the experimental conditions studied, formation of cyanuric acid was observed at the end of electrolysis. Fig. 5 shows the structure of this compound.

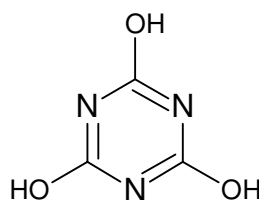


Figure 5. Structure of the cyanuric acid.

Spectroscopic monitoring of the reaction allowed selecting the best conditions for atrazine, as shown in Table 2.

Table 2. Experimental conditions selected for the quantification of atrazine electrolysis.

pH	Current density (Acm^{-2})	Electrode	T ($^{\circ}\text{C}$)
0.8	0.07	Anode	25
3.5	0.07	Anode	25
7.0	0.07	Anode	25
0.8	0.07	Anode	60

Fig. 6 shows the concentration variations of atrazine and cyanuric acid during electrolysis at different pH. Consistent with the UV spectra, low pH favors the degradation of atrazine, as observed in Table 3.

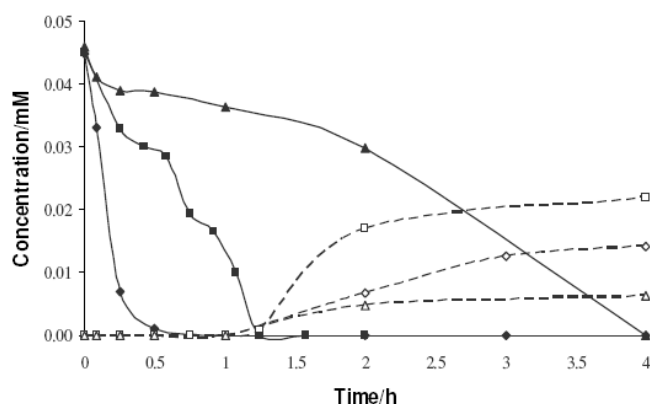


Figure 6. Variation of atrazine (continuous lines) and cyanuric acid (dashed lines) with time at pH: 0.8 (diamonds), 3.5 (squares) and 7.0 (triangles), current density of 0.07 Acm^{-2} and temperature of $25 \text{ }^\circ\text{C}$.

Table 3. Percentages of atrazine conversion after 0.5 h of electrolysis.

Atrazine conversion (%)	pH
97.5	0.8
36.5	3.5
13.9	7.0

Fig. 7 shows the effect of temperature on the degradation of atrazine: at $60 \text{ }^\circ\text{C}$, 93.3% of atrazine is converted to cyanuric acid, while at $25 \text{ }^\circ\text{C}$ only 31.3% are oxidized. The conversion from intermediates to cyanuric acid is faster and the final product appears after total degradation of atrazine at the higher temperature. The benefit to do the electrolysis at higher temperature is the elimination of side reactions and the obtaining of only one product. Finally, the TOC analyses do not show electrochemical combustion and no mineralization of the electrolytic media was observed.

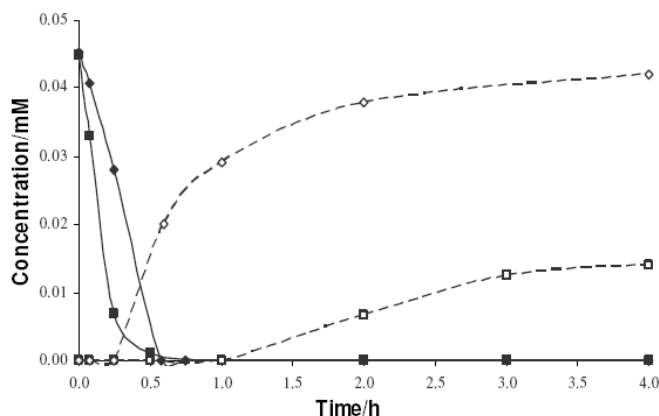


Figure 7. Variation of atrazine concentration (continuous line) and cyanuric acid (dotted line) at pH=0.8 and temperatures of $25 \text{ }^\circ\text{C}$ (squares) and $60 \text{ }^\circ\text{C}$ (diamonds).

Conclusions

In aqueous acidic media, atrazine is degraded at a platinum anode. At 60 °C, atrazine is degraded completely to cyanuric acid in 4 hours of electrolysis. At 25 °C atrazine is partially degraded and intermediates that persist after 4 hours of electrolysis. No mineralization of this heterocyclic compound was observed in any experiment.

Acknowledgments

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References

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