Photo-assisted electrochemical degradation of the commercial herbicide atrazine

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ABSTRACT

This paper presents a degradation study of the pesticide atrazine using photo-assisted electrochemical methods at a dimensionally stable anode (DSA) of nominal composition Ti/Ru0.3Ti0.7O2 in a prototype reactor. The effects of current density, electrolyte flow-rate, as well as the use of different atrazine concentrations are reported. The results indicate that the energy consumption is substantially reduced for the combined photochemical and electrochemical processes when compared to the isolated systems. It is observed that complete atrazine removal is achieved at low current densities when using the combined method, thus reducing the energy required to operate the electrochemical system. The results also include the investigation of the phytotoxicity of the treated solutions.

Key words | atrazine, electrochemical degradation, photo-assisted degradation, phytotoxicity

INTRODUCTION

Pesticide wastes can contain a wide range of chemical species that are not necessarily pesticides, but auxiliary components such as surfactants, emulsifiers, and (depending on the application method) engine oils (Felsot et al. 2003). This wide range of chemical substances can make efficient and safe disposal difficult (Felsot et al. 2003). It is suggested that incineration is probably the only applicable process for the wide variety of pesticide types and matrices encountered. However, incineration is an expensive procedure for small-scale users. As a result, there is the need to develop treatment systems that can be used by small-scale users or that can be shared between various users (e.g. a mobile system (Felsot et al. 2003)). Amongst the many pesticide species that have been studied aiming at developing alternative treatment systems, atrazine (Figure 1a) has received considerable attention. In aquatic environments, atrazine is highly toxic to invertebrates, making it necessary to control its release into the environment.

Many of the atrazine degradation processes use ultraviolet radiation at some point. The use of the photo-Fenton process to breakdown atrazine has been presented by various researchers. Lapertot et al. (2006) studied the solar light driven photo-Fenton degradation of atrazine and observed that the biodegradability of atrazine was significantly enhanced after 12 to 25-minute treatment times. In addition, Chan & Chu (2006) studied photolysis, Fenton, and photo-Fenton methods, observing an apparent synergistic effect and suggesting, based on mass balances, that the azine ring can be broken down. This is noteworthy
as many studies indicate that the final product of many degradation processes is cyanuric acid (Figure 1b), which is a species known to be resistant to certain advanced oxidation processes (Mineiro et al. 2000).

In recent years there has been a growing interest in applying electrochemical processes in the treatment of toxic and/or recalcitrant organic compounds (Chen 2004). Frequently, NaCl (> 3 g L⁻¹, (Chen 2004)) is added to the electrolyte mixture in order to both increase conductivity and improve the removal rate through the in situ formation of oxidizing agents (Cl₂ and OCl⁻). There are many advantages associated with electrochemical treatment processes. For example, the catalyst/electrode is immobilized (thus reducing the need to separate the catalyst from the reaction mixture), the variables (i.e. current and potential) are easily controlled, facilitating process automation and generally lowering equipment cost and, additionally, electrochemical processes are easily adapted for use in flow systems. The work of Vlyssides and co-workers (Arapoglou et al. 2003; Vlyssides et al. 2004a,b) is an example of the electrochemical degradation of pesticides.

It has been demonstrated that the pesticides atrazine (Malpass et al. 2006) and carbaryl (Miwa et al. 2006) can be electrochemically removed quickly in the presence of NaCl, but only slowly in the presence of other supporting electrolytes (e.g. Na₂SO₄), using dimensionally stable anodes (DSA®). In an important study, Polcaro et al. (2005) demonstrated that cyanuric acid can be electrochemically degraded at boron-doped diamond electrodes (BDD), promoting the cleavage of the azine ring.

It is known that the simultaneous application of an external anodic bias to an irradiated semiconductor catalyst can increase the rate of organic mineralization (Vinodgopal & Kamat 1996). The term photo-assisted electrochemical (PAEC) degradation has been used in studies involving the degradation of dyes (Catanho et al. 2006a,b), textile effluents (Alves et al. 2010) and pesticides (Malpass et al. 2007, 2009) demonstrating that DSA® electrodes of composition Ti/Ru₀.₃Ti₀.₇O₂ can be used in such degradation processes with increased efficiency in comparison to purely electrochemical systems. In a previous paper, we have demonstrated that the efficiency of atrazine removal is greatly increased when the electrochemical method is used simultaneously with UV radiation (Malpass et al. 2007).

The objective of the present paper is to investigate a photo-assisted electrochemical treatment system (simultaneous application of UV-Vis radiation and an electric current) for atrazine using a commercial DSA® electrode (Ti/Ru₀.₃Ti₀.₇O₂). The goal is to combine the electrochemical properties of the RuO₂ component with the photocatalytic properties of the TiO₂ component, in order to enhance the degradation rate. The effect of several experimental variables was investigated (current density, flow rate, and concentration) and, as indicated by IUPAC, the electrical energy per order (EEO/kWh m⁻³ order⁻¹, Bolton et al. (2001)) is used as the principal figure of merit, although the chemical oxygen demand (COD) removal is also presented. It should be noted that this paper is a continuation of the studies on electrochemical (Malpass et al. 2006) and photo-assisted electrochemical degradation (Malpass et al. 2007) of atrazine previously published by this laboratory. Whereas the previous studies have been based on bench-scale systems (maximum volume: 250 mL), in this paper we discuss the scale-up of the PAEC system to a pilot-scale reactor (volume: 22 L) in order to discuss the feasibility of potential field applications.

**EXPERIMENTAL**

The experimental apparatus consisted of a prototype electrochemical reactor, a hydraulic pump to recirculate the solution, a flow meter, and an electrolyte reservoir (maximum capacity: 25 L). The electrochemical reactor was a single compartment tubular flow reactor comprised of a 0.07 m internal diameter, 1.0 m long titanium tube (0.5 mm thick wall) with its inner surface (area = 0.18 m²)
coated with an oxide layer composed of (TiO$_2$)$_{0.7}$(RuO$_2$)$_{0.3}$. Readers are directed to Fukunaga et al. (2008) for more details about the reactor design. The coated titanium tube was supplied by De Nora (Brazil) and used as the anode (1,800 cm$^2$). Concentric to this tube, the cathode consisted of a 0.055 m diameter titanium tube to which an expanded Ti plate screen (mesh diagonals of 5 mm × 2 mm) was welded to increase the area and promote turbulence. The anode/cathode gap was 3 mm. A low-pressure UV-lamp (Philips, 36 W, irradiance of 50 mW cm$^{-2}$) was inserted in the centre of the reactor and extended the whole length of the reactor.

The experimental set-up was operated in batch recirculation mode, with an adjustable flow rate (1,000, 3,000, 4,500, and 6,000 L h$^{-1}$, which corresponds to fluxes of 0.243, 0.729, 1.094, and 1.406 m$^3$ m$^{-2}$ s$^{-1}$, respectively) depending on the experiment. The system was operated under a turbulent hydraulic flow regime. The electrolyte temperature was maintained constant (20 ± 1°C) by a refrigeration system, which was inserted into the electrolyte reservoir. All of the experimental runs were carried out using 22 L of solution, a sufficient volume to fill the reservoir and connecting pipes. In all runs, samples were taken at predetermined time intervals for subsequent analysis. The sampling point was at the base of the electrolyte reservoir and thus represents the average concentration of the system at a given time. The supporting electrolyte used was sodium sulphate (0.1 mol L$^{-1}$) and atrazine was obtained from a commercial solution (3,000 L h$^{-1}$) and this was subsequently diluted to starting COD values for 20 mg L$^{-1}$ solutions of atrazine was 115.3 mg L$^{-1}$.

Phytotoxicity assays were carried out based on ASTM (2000) methods using lettuce (Lactuca sativa) seeds as the test organism. The response variable was the Germination Index (%), shown in Equation 1, where: $G$ is the number of germinated seeds, $L$ is the roots average length, and subscripts S and C refer to sample and control experiments, respectively (Rossi & Beltrami 1998). Distilled water was used in the control experiments. Statistical analyses performed to determine the EC$_{50}$ parameter (concentration of the sample in which a 50% decrease is observed in the Germination Index) were based on the adjusted Spearman–Karber method (Hamilton et al. 1977).

$$GI(\%) = \frac{(G_S \times L_S) \times 100}{(G_C \times L_C)} \quad (1)$$

**RESULTS AND DISCUSSION**

**Effect of the Current Density**

The effect of increasing current density (10 to 80 mA cm$^{-2}$) on the atrazine removal rate was investigated for both the purely electrochemical (EC) and the photo-assisted (PAEC) systems. In Figure 2a, a typical concentration-time profile is presented for atrazine degradation at 60 mA cm$^{-2}$.

The profile of the photochemical (PC) degradation of atrazine is also presented in Figure 2a, where it can be observed that the extent of atrazine removal is greater for the PAEC method when compared to the individual methods themselves. This fact is further illustrated by considering the “theoretical combination”, which would be the sum of the removal for PC and EC methods separately (Malpass et al. 2007). This is represented by the solid line in Figure 2a, and it can be seen that there is a considerable increase in the removal rate for the PAEC method compared to the separate ones, indicating the possibility of a synergistic effect when the processes are applied simultaneously, as previously observed (Catanho et al. 2006a,b; Malpass et al. 2007). The increase in the level of degradation is probably due to the generation of hydroxyl...
radicals (HO\(^\cdot\)) at the TiO\(_2\) surface during interaction with the UV radiation. This occurs in conjunction with the electrochemical degradation mechanism that takes place at the RuO\(_2\) sites (Simond et al. 1997). It should also be noted that degradation in the bulk could also be achieved through direct atrazine photolysis. The results obtained here are in agreement with those previously obtained for atrazine (Malpass et al. 2007), which demonstrate that purely electrochemical removal is both limited and inefficient. As a result, the present study was continued using the photo-assisted degradation method only.

Figure 2b displays the extent of atrazine removal after 90 min of treatment at different current densities and it can be observed that there is an almost linear increase with the applied current. It is, however, possible to see that removal rates >90% are only possible at current densities >80 mA cm\(^{-2}\) in the 90 minutes of treatment herein used. Analysis of the results obtained indicates that the decrease in the concentration of atrazine obeys pseudo 1st order kinetics, in agreement with previous results obtained in static (Malpass et al. 2006) and flow reactors (Malpass et al. 2007). When the kinetics display 1st order dependence, it is possible to apply the Energy per Order (kWh m\(^{-3}\) order\(^{-1}\)) as the appropriate figure of merit (Bolton et al. 2001). In any energy-intensive oxidation process, a measure of the energy consumption is of vital importance. In the present study, the electrical energy per order for a batch process can be calculated by Equation 2, where \(P_{el}\) is the electrical power input in kW, \(t\) is the time in h, \(V\) is the solution volume in m\(^3\), and \(c_i\) and \(c_f\) are the initial and final concentrations, respectively, of the substance of interest.

\[
E_{EO} = \frac{(P_{el})(t)}{(V)(\log(c_i/c_f))}
\]

The appropriate values of the \(E_{EO}\) with increasing current density are given in Figure 3 and it is possible to observe that they increase almost linearly with increasing current density. When these results are compared with those obtained in a previous work (Figure 3, open circles, Malpass et al. 2007) it is apparent that the behaviour in the present study is not the same as previously observed. In the case of the lab-scale reactor, a maximum \(E_{EO}\) value of...
1.84 kWh m⁻³ order⁻¹ (5 mA cm⁻²) was obtained and this tended to remain constant with increasing current density. However, it is important to note that in the present study a commercial solution of atrazine was used and not pure atrazine as in Malpass et al. (2007) and that commercial solution contains an extra 600 mg L⁻¹ of auxiliary substances. In Malpass et al. (2007), the effect of using the commercial solution was studied at optimised conditions (10 mA cm⁻²) and a value of ∼3 kWh m⁻³ order⁻¹ was obtained. In the present study, an EEO value of approximately of ∼3.57 kWh m⁻³ order⁻¹ at 10 mA cm⁻² was obtained, which is sufficiently close, given the difference in the types of reactors.

Figure 4a presents the profile of the removal of the chemical oxygen demand (COD) as a function of electrolysis time for current densities of 10, 20, 40 and 60 mA cm⁻². It can be observed that approximately 95% COD removal is possible in 90 minutes of electrolysis. This might seem strange when considering the fact that atrazine is difficult to be completely removed, but it must be remembered that the COD values include the inert components in the pesticide formulation. Figure 4b presents the final levels of COD after 90 min of electrolysis and it is possible to observe that for current densities above 60 mA cm⁻² the increase in the current results in insignificant benefit in terms of COD removal. In the current region of 10 to 60 mA cm⁻², removal increases from 70 to 90%, whereas between 60 and 120 mA cm⁻² the increase is from 90 to 96%. Taking into consideration the aforementioned results, it was decided to investigate the removal of atrazine and COD at 60 mA cm⁻² whilst other parameters were varied. Although this current density did not present the best EEO (i.e. atrazine removal) it did present the best COD removal. The variables chosen at this stage were electrolyte flow rate through the reactor and the initial concentration of atrazine.

Effect of the flow rate

In this part of the study, the effect of varying the electrolyte flow rate (1,000–6,000 L h⁻¹) was studied using flow rates of 6,000, 4,500, 3,000, and 1,000 L h⁻¹. Figure 5 presents the dependence of the atrazine concentration as a function of electrolysis time. It can be seen that there are no appreciable differences in the rate of atrazine removal when the flow rate is increased. The EEO values for the different flow rates are given in Figure 5 (insert) and it can be observed that greater flow rates result in lower energy costs—from 46 to 26 kWh m⁻³ order⁻¹ at 1,000 and 6,000 L h⁻¹, respectively. This is partially due to the fact that the operating cell potential is approximately 600 mV lower at 6,000 L h⁻¹ than at 1,000 L h⁻¹. This indicates that the higher flow rate is more efficient at removing the gases (principally O₂) formed at the electrode surface, reducing
the electric resistance of the cell. As a result, the cell potential is reduced at higher flow rates, changing from 5.70 V at 6,000 L h\(^{-1}\) to 6.30 V at 1,000 L h\(^{-1}\). As the actual rate of atrazine removal differs little at high and low flow rates, it is probable that the removal process is controlled by electron transfer and/or formation of the active species at the electrode surface. These results do not agree with those previously obtained (Malpass et al. 2007), where a flow rate increase led to increased atrazine removal. However, it should be remembered that much greater flow rates were employed in this study (1,000–6,000 L h\(^{-1}\)) when compared to a maximum of 25 L h\(^{-1}\) before, indicating that in this study the system functions under purely electron transfer control. The COD removed during the treatment process is given in Figure 6 where it can be observed that COD removal increases from \(\sim 70\%\) at 1,000 L h\(^{-1}\) to \(\sim 95\%\) at 6,000 L h\(^{-1}\).

**Effect of the atrazine concentration**

The effect of varying the atrazine concentration at 5, 10, 20, and 30 mg L\(^{-1}\) was studied and the concentration-time profile for atrazine is given in Figure 7. As expected, atrazine is rapidly removed at the lower starting concentrations (5 and 10 mg L\(^{-1}\)). At the higher starting concentrations, the time required to reduce the concentration is greater; however, after 90 minutes it is possible to remove \(\sim 95\%\) of the atrazine present—even at 30 mg L\(^{-1}\). For all the concentrations studied, the rate constant is relatively constant at 2.50 \(\times\) 10\(^{-4}\) s\(^{-1}\), with a maximum variation of \(< 5\%\). The values for the \(E_{EO}\) and the extent of COD removal are given in Table 1 and it can be observed that the % of COD removal decreases with increasing initial concentration.

**Phytotoxicity investigations**

Before it can be applied, a new treatment process should be able to demonstrate that the treated effluent is less toxic than the starting one. This can be achieved by analytical detection of individual toxic substances, which requires time and sophisticated equipment, or by a general toxicity test. In the present study, the ecotoxicity of the effluent was evaluated by a phytotoxicity test that employs

![Figure 6](https://iwaponline.com/wst/article-pdf/62/12/2729/445769/2729.pdf)  
**Figure 6** | Removal of COD during PAEC degradation at different flow rates during electrolysis of atrazine (20 mg L\(^{-1}\)) in Na\(_2\)SO\(_4\) (0.1 mol L\(^{-1}\)) after 90 min. Current density: 60 mA cm\(^{-2}\).

![Figure 7](https://iwaponline.com/wst/article-pdf/62/12/2729/445769/2729.pdf)  
**Figure 7** | Concentration-time profile during electrolysis of different atrazine concentrations (0.1 mol L\(^{-1}\)): (●) 5; (○) 10; (□) 20; (□) 30 and (△) 40 mg L\(^{-1}\) atrazine. Current density: 60 mA cm\(^{-2}\). Flow-rate: 6,000 L h\(^{-1}\).

<table>
<thead>
<tr>
<th>[Atrazine] (mg L(^{-1}))</th>
<th>(E_{EO}) (kWh m(^{-2}) order(^{-1}))</th>
<th>COD removed (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>17.0</td>
<td>7.9 (97%)*</td>
</tr>
<tr>
<td>10</td>
<td>24.5</td>
<td>15.6 (95%)</td>
</tr>
<tr>
<td>20</td>
<td>26.0</td>
<td>31.1 (95%)</td>
</tr>
<tr>
<td>30</td>
<td>38.7</td>
<td>36.4 (75%)</td>
</tr>
<tr>
<td>40</td>
<td>46.1</td>
<td>37.5 (65%)</td>
</tr>
</tbody>
</table>

*Overall percentage of COD removed.
Lactuca sativa as the test organism (Standard Guide for Conducting Terrestrial Plant Toxicity Tests (ASTM 2000)). The optimized conditions (60 mA cm$^{-2}$, 20 mg L$^{-1}$ atrazine, flow rate of 6,000 L h$^{-1}$) were employed and the electrolysis was extended to 3 h in order to investigate the ecotoxicity over time. The results for the variation of the EC$_{50}$ over time are given in Figure 8. It can be observed that the purely electrochemical treatment actually increases the toxicity of the effluent, with the EC$_{50}$ going from $\sim$51 to $\sim$35%—hence indicating that the products formed are more toxic than the parent compounds. In the time interval studied, the photo-assisted method resulted in no significant difference in the degree of ecotoxicity of the effluent.

It should be noted that the ecotoxicity after the photo-assisted method is not significantly altered after treatment, even though up to 95% of COD and atrazine are removed. This is probably attributable to one of two factors (or a mixture of both): (1) Atrazine is only a part of the pesticide mixture and the auxiliary substances are an unknown quantity—these will result in the formation of unknown degradation products, which might be more or less toxic than the original solution or (2) One of the first steps in atrazine degradation is reported as being the cleavage of the Cl–C bond (Héquet et al. 2001) from the ring structure and the formation of chlorinated by-products is possible via the formation of Cl$_2$ at the anode and its subsequent reaction with organic material in solution. It is probable, as postulated in previous studies (Alves et al. 2010) that the photo-assisted process is capable of removing the quantity of chlorinated by-products formed at a faster rate.

**CONCLUSIONS**

The results demonstrate that it is technically possible to remove at least 95% of atrazine (concentrations up to 20 mg L$^{-1}$) from solution in less than 90 minutes with the photo-assisted electrochemical treatment and that COD removals of over 95% are also obtained. The results indicate the need for carefully optimising the system parameters. The phytotoxicity of the atrazine-containing solutions using Lactuca sativa remains unaltered after 3 h of PAEC treatment, but increases for the purely electrochemical treatment process.

The present study is important as it provides a link between purely bench-scale and large-scale studies and as such can be considered a continuation of previous papers published by this group. It is important to note that the results obtained in the present paper are analogous to the results (removal rate and energy efficiency) obtained in our previous studies. The principal problem is the need to refrigerate the system, which requires a further energy input as well as incrementing the amount of equipment required.

**ACKNOWLEDGEMENTS**

FAPESP (02/12017-0 and 04/09588-1).

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