

Oxidation of the pesticide atrazine at DSA[®] electrodes

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Abstract

This paper presents the study of the electrochemical oxidation of the pesticide atrazine at a Ti/Ru_{0.3}Ti_{0.7}O₂ dimensionally stable anodes (DSA[®]). The effect of using different supporting electrolytes (NaCl, NaOH, NaNO₃, NaClO₄, H₂SO₄ and Na₂SO₄) during the galvanostatic electrolysis of atrazine was investigated. It was observed that the removal of atrazine and total organic carbon (TOC) was only achieved at appreciable rates when NaCl was used as the supporting electrolyte, due to the oxidising species formed in this electrolyte (e.g. ClO⁻). Variation of the NaCl concentration demonstrated that, although only low concentrations of NaCl are necessary to result in the complete removal of atrazine in solution, TOC removal is almost linearly dependent on the quantity of NaCl in solution. Examination of the applied current density indicates that the efficiency of TOC removal reaches a maximum at 60 mA cm⁻². Testing of alternative electrode materials containing SnO₂ did not improve the efficiency of atrazine removal in Na₂SO₄, but in NaCl a small increase was observed. Overall there appears to be no great advantage in using SnO₂-containing electrodes over the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode.

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1. Introduction

The disposal of pesticide-containing waste is a problem of worldwide concern, with almost every stage of pesticide use involving the formation of wastes [1], which can contain substances that are strictly controlled by regulatory bodies. The presence of large stocks of pesticides that are unusable, either due to the fact that they are banned or have exceeded their self-life, is of great concern – especially in developing countries [2].

Methods for the disposal and degradation of pesticide waste have recently been well reviewed by Felsot and co-workers [1,3]. Various methods for pesticide treatment are available, according to the World Health Organisation these include high tempera-

ture incineration, chemical treatment or removal to specially engineered landfill sites [2]. However, it is possible that such methods may simply result in the “relocation” of the problem. In this context the development of clean methods of pesticide disposal is required. It is argued that there is a need for the development of treatment systems that can be used by small-scale users or at least as a mobile treatment system that can be shared between various users [1].

Amongst the possible methods of treatment of pesticides, ozonation [4], oxidation with Fenton’s reagent (with and without UV–vis radiation) [5], photodegradation in general [6] and photocatalysis [7] with TiO₂ have been investigated for a wide variety of pesticides.

A relatively unexplored treatment method for oxidation of pesticides is the electrochemical route. Since the 1990s, electrochemical methods have been widely studied for the removal of organic substances and a number of reviews are available in the literature [8–10]. The advantages of electrochemical treatment are various and well documented: the catalyst/electrode is immobilised (thus reducing the need to separate the catalyst from the reaction mixture), the variables (i.e. current and potential) are easily controlled and facilitate automation of a process and the cost of the equipment is generally not that high [10]. In addition,

Abbreviations: DSA[®], dimensionally stable anode; TOC, total organic carbon; BDD, boron doped diamond electrodes; RHE, reversible hydrogen electrode; OER, oxygen evolution reaction; Q^* , anodic charge in supporting electrolyte between 0.4 and 1.4 V versus RHE; Q_{SE} , anodic charge in supporting electrolyte between 0.4 and 1.6 V versus RHE; $Q_{SE+atra}$, anodic charge in supporting electrolyte + atrazine (20 mg L⁻¹) between 0.4 and 1.6 V versus RHE; % Q , percentage variation of $Q_{SE+atra}$ compared to Q_{SE} ($[Q_{SE+atra}/Q_{SE}] \times 100$); E_{EO} , energy per order (kW h m⁻³ order⁻¹)

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electrochemical processes are easily adapted for use in flow systems [10], a fact that is considered important for the feasibility of pesticide treatment systems [1]. Small-scale electrochemical treatment systems that are ideal for mobile applications are commercially available.

In recent studies Vlyssides and co-workers studied the electrooxidation of various organophosphorous pesticides – methylparation [11,12]; phosalone, azinphos-methyl, methidathion [13]; Demeton-S-methyl, metamidophos, fenthion, Diazinon [14]. The authors studied the oxidation of varying pesticides in brine solutions using Ti/Pt anodes. Good removal rates were observed and it is suggested that electrochemical methods can be used as a pre-treatment step in pesticide waste disposal [13,14]. However, from a cost and practical point of view, the use of Pt electrodes is not ideal, especially when oxidising organic waste where “poisoning” of the electrode can occur. Recently, Polcaro et al. [15] demonstrated that atrazine can be electrochemically oxidised at high potentials using boron doped diamond electrodes (BDD). The authors demonstrated that high levels of TOC can be removed and that the reaction is pH-dependent.

Amongst the possible electrode materials, the so-called dimensionally stable anodes (DSA[®]) have received considerable attention in recent years [16]. DSA[®] are promising materials for many electro-organic applications and have been classified as ‘active’ or ‘non-active’ [16,17], depending on the electrode material. Active electrodes mediate the oxidation of an organic species via the formation of higher oxides of the metal (MO_{x+1}), where there is a higher oxidation state available (e.g., RuO₂ or IrO₂). This leads to selective oxidation. Non-active electrodes present no higher oxidation state available and the organic species is directly oxidised by an adsorbed hydroxyl radical, giving complete combustion (e.g., SnO₂ or PbO₂). A wide variety of organic compounds have been studied with a view to possible waste treatment systems. Organic compounds that have been studied using DSA[®] type electrodes include formaldehyde [18], 4-chlorophenol [19], chloroanilic acid [20], Olive oil wastewater [21], tannery wastewater [22] and wastewater containing naphthalene- and anthraquinone-sulphonic acids [23], to mention some recent examples.

Atrazine (Fig. 1), a widely used triazine herbicide, was chosen as the target molecule for the present study. Atrazine is used on a wide spectrum of crops, including corn, sorghum, sugar-

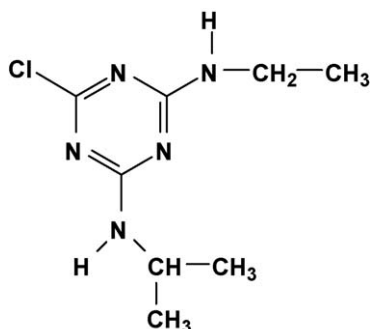


Fig. 1. Chemical structure of atrazine (2-chloro-4-ethylamino-1,3,5-triazine).

cane, Christmas trees and residential lawns [24]. The activity of atrazine is due to its ability to inhibit photosynthesis in plants [24] and, although it does not present a great risk to human health, in aquatic environments atrazine is highly acutely toxic to aquatic invertebrates. Such factors make it necessary to control the release of atrazine in to the environment.

This paper presents the study of a prospective electrochemical treatment system for atrazine using a commercial Ti/Ru_{0.3}Ti_{0.7}O₂ electrode. The effect of using different supporting electrolytes (NaCl, NaOH, NaNO₃, NaClO₄, H₂SO₄ and Na₂SO₄), varying the NaCl concentration (0.0125–0.10 mol L⁻¹) and current density (10–120 mA cm⁻²) upon the rate of atrazine and total organic carbon (TOC) removal are investigated. The results are also compared with those obtained for other, laboratory-made, electrodes that contain SnO₂ (Ti/Ir_{0.01}Sn_{0.99}O₂ Ti/Ir_{0.01}Ru_{0.01}Sn_{0.99}O₂).

2. Experimental

2.1. Cells and equipment

A single compartment electrochemical cell made of glass was employed using a typical three-electrode arrangement (Fig. 2). The working electrode was a DSA[®] disk ($\phi = 1$ cm) and the counter-electrodes were two platinum foils (1 cm × 1 cm) positioned parallel to the working electrode. All potentials are referred to the reversible hydrogen electrode (RHE).

All electrochemical measurements (cyclic voltammetry and galvanostatic electrolyses) were performed using a potentiostat/galvanostat (Autolab, model SPGSTAT30).

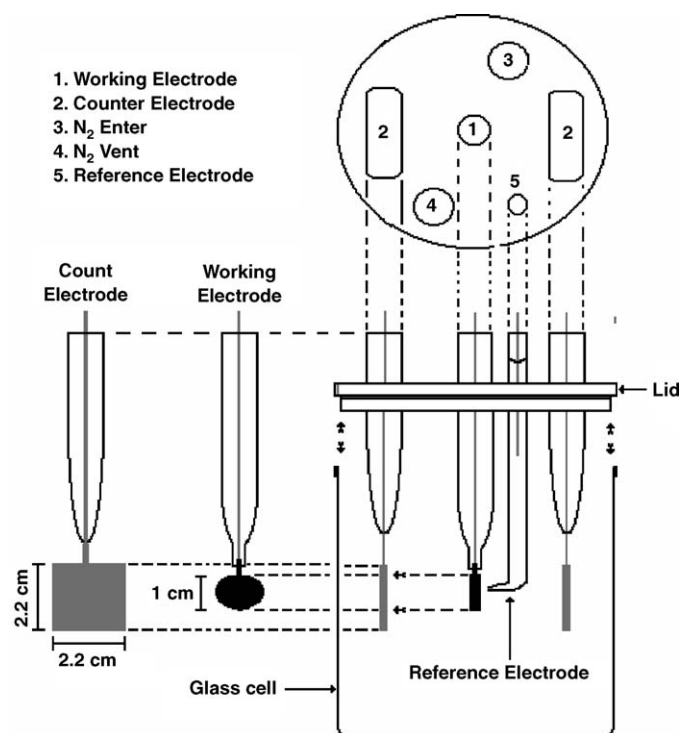


Fig. 2. Single compartment electrochemical cell used in the oxidation assays.

2.2. Analyses

Analyses of the reaction products were performed using HPLC (Shimadzu LC-10AD VP) with a reverse phase column (LC-18, Supelcol). The eluent was acetonitrile/water (1:1, v/v). The concentration of atrazine was monitored using an ultraviolet detector (SPD-10A VP) at $\lambda = 221$ nm [15]. The extent of organic removal was also studied by total organic carbon (TOC) analysis (TOC – V_{CPH}, Shimadzu).

2.3. Reagents

All the salts employed in this study (NaCl, NaOH, NaNO₃, NaClO₄, H₂SO₄ and Na₂SO₄) were obtained from Mallinckrodt and used without further purification. The sample of atrazine was obtained direct from the manufacturer (name withheld) and used without further purification.

All the concentrations of the different salts were adjusted so that the ionic strength remained constant in all experiments.

2.4. Procedure

In each galvanostatic electrolysis 75 cm³ of a solution of atrazine (20 mg L⁻¹) was transferred to the electrochemical cell. All experiments were performed at 25 ± 2 °C. The appropriate current density was applied and aliquots (1 cm³) of the reaction mixture were removed, at predetermined intervals during the experiment, and submitted for analysis.

3. Results and discussion

3.1. Cyclic voltammetry – effect of electrolyte

Prior to each galvanostatic oxidation assay, cyclic voltammetry investigations were performed in order to electrochemically characterise the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode. Cyclic voltammetry is a useful technique for probing the processes that occur at the electrode/solution interface [25]. The measurement of the current that results as the potential is varied can provide valuable insight into the reactions that occur at the electrode surface. It is widely accepted that cyclic voltammetry offers the most sensitive in situ characterisation of oxide materials [26]. In the case of the oxides used in this study, the voltammetric experiment is performed in the potential region where no permanent modification of the oxide surface occurs (0.4–1.4 V versus RHE). The anodic charge passed in this region (Q^* – measured in coulombs (C)) is generally considered to be a measure of the electrochemically active surface area [26]. However, in order for the oxidation of organic species to occur at oxide electrodes, potentials that enter the region of the oxygen evolution reaction (OER), i.e. >1.4 V, must be applied [27]. Authors have proven that the simultaneous O₂ evolution is the key in the organic oxidation process at such electrodes [27]. Fig. 3 presents the cyclic voltammetric profiles of the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode in two of the electrolytes studied (0.1 mol L⁻¹ NaCl and 0.033 mol L⁻¹ NaClO₄).

In both NaCl and NaClO₄ the Ti/Ru_{0.3}Ti_{0.7}O₂ anode presents features that are typical of this electrode in the supporting elec-

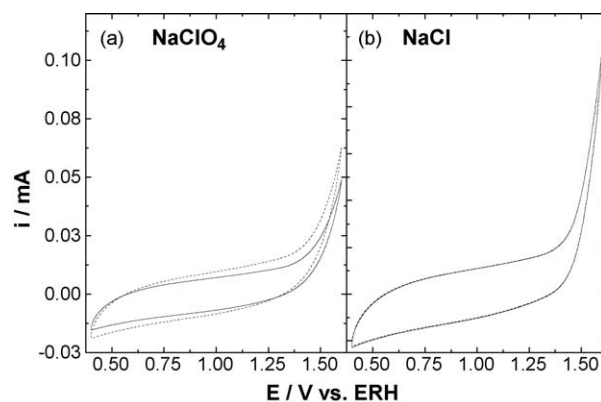


Fig. 3. Voltammetric profiles of the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode in (a) 0.1 mol L⁻¹ NaClO₄ and (b) 0.1 mol L⁻¹ NaCl, in the absence (solid line) and in the presence of 20 mg L⁻¹ atrazine. $v = 50$ mV s⁻¹.

trolytes employed. Between the potential limits of 0.4–1.4 V the voltammogram is featureless, at potentials above this the oxygen evolution reaction (OER), which is characterised by a rapid increase in the current, occurs. In this study the voltammetric charge used for comparison is that calculated between 0.4 and 1.6 V and is denoted as Q_{SE} and $Q_{SE+atra}$ in the absence and presence of atrazine, respectively. This was done in order to simulate electrolysis conditions (i.e. oxidation with simultaneous O₂ evolution [17]). In the presence of atrazine (20 mg L⁻¹) there is little or no apparent difference in the voltammetric profile (Fig. 3) in Na₂SO₄, H₂SO₄ and NaCl, all of which present a percentage variation in the voltammetric charge (% Q) of zero (Table 1). For 0.10 mol L⁻¹ NaOH, 0.10 mol L⁻¹ NaNO₃, and 0.10 mol L⁻¹ NaClO₄, an increase in the voltammetric charge can be observed (Fig. 3), indicating that there is a direct interaction between the electrode and the atrazine molecule in solution (Table 1).

3.2. Galvanostatic electrolysis

Galvanostatic electrolyses of atrazine solutions (20 mg L⁻¹) were performed for 2 h at 40 mA cm⁻², in the six different electrolytes mentioned. After each electrolysis, cyclic voltammetry was again performed in the electrolysed solution and two distinct forms of behaviour can be observed: in 0.033 M Na₂SO₄, 0.10 M NaClO₄, 0.10 M NaOH and 0.033 M H₂SO₄ the voltammetric profile presents almost no alteration. On the other hand, in

Table 1
Variation of the anodic charge in the absence (Q_{SE}) and presence ($Q_{SE+atra}$) of atrazine (20 mg L⁻¹)

Electrolyte	Charge (QC cm ⁻²)		
	Q_{SE} (0.4–1.6 V)	$Q_{SE+atra}$ (0.4–1.6 V)	% Q
0.033 M H ₂ SO ₄	0.535	0.535	~0
0.033 M Na ₂ SO ₄	0.034	0.034	~0
0.10 M NaClO ₄	0.022	0.026	15.5
0.10 M NaOH	0.436	0.465	6
0.10 M NaCl	0.033	0.034	~0
0.10 M NaNO ₃	0.032	0.035	8.5

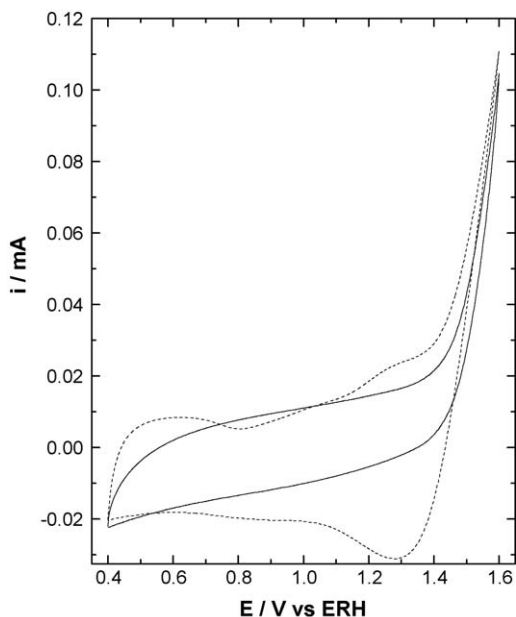


Fig. 4. Voltammetric profile of the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode in 0.1 mol L⁻¹ NaCl + 20 mg L⁻¹ atrazine, before (solid line) and after (dashed line) electrolysis at 40 mA cm⁻². $v = 50 \text{ mV s}^{-1}$.

0.10 mol L⁻¹ NaCl and 0.10 M NaNO₃ there is a distinct change in the voltammetric profile (Fig. 4). This fact indicates that the products of oxidation in NaCl and NaNO₃ are different from those formed in the other electrolytes and that the products interact with the electrode surface and thus alter the behaviour of the electrode.

Fig. 5 presents the variation of atrazine concentration with electrolysis time, for all the electrolytes studied. It can be observed that atrazine removal in electrolytes other than NaCl is only partial after 2 h of electrolysis, whereas in NaCl itself complete removal is achieved in under 1 h. The quantities of atrazine removed are given in Table 2 and it is apparent that removal is only partial for all the electrolytes with NaNO₃ presenting the highest extent of removal (19.2%).

For all electrolytes the decrease in the concentration of atrazine was observed to obey apparent 1st order kinetics (Fig. 6). The apparent 1st order constants ($k_{\text{ap}} \text{ s}^{-1}$), obtained from Fig. 6, are given in Table 2 and Fig. 7. From Fig. 7 it can be observed that, excluding NaCl, it is apparent that the rate of atrazine removal is faster at values of pH in the range of 5.5–7

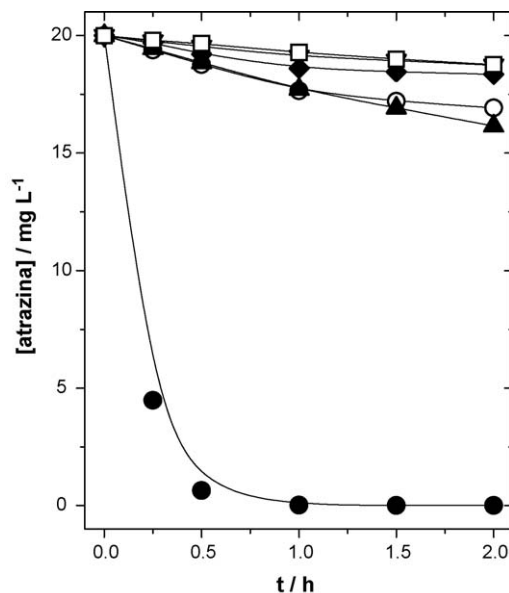


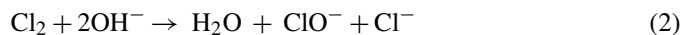
Fig. 5. Variation of atrazine concentration with time of electrolysis at 40 mA cm⁻². (●) 0.1 mol L⁻¹ NaCl, (○) 0.033 mol L⁻¹ Na₂SO₄, (▲) 0.1 mol L⁻¹ NaNO₃, (▽) 0.1 mol L⁻¹ NaOH, (◆) 0.1 mol L⁻¹ NaClO₄ and (□) 0.033 mol L⁻¹ H₂SO₄.

(NaNO₃, NaClO₄ and Na₂SO₄) and seems not to be favoured at extreme pH values (NaOH and H₂SO₄). This is in agreement with other oxidation studies [17] and also with field studies of atrazine degradation in soils [24].

As seen for the removal of atrazine, the highest TOC removal (33.2%) is achieved is when NaCl is used as the supporting electrolyte. All the other electrolytes studied present removals of between 6 and 9%. According to the literature, the increased rate of organic removal is due to the formation of chlorine gas (Cl₂) and hypochlorite (ClO⁻), which are both powerful oxidising agents. Chlorine gas is formed at the anode according to [28]:



The subsequent reaction of Cl₂ with HO⁻ formed at the cathode results in the formation of hypochlorite (ClO⁻):



Subsequently Cl₂ and ClO⁻ react to oxidise the organic in solution, resulting in an indirect oxidation mechanism. In the very initial stages of the experiment, it is probable that oxidation

Table 2

Data obtained during the galvanostatic oxidation of atrazine (20 mg L⁻¹) in different electrolytes

Electrolyte	E_{cell} (V)	Atrazine				TOC	
		Atrazine removal (mg L ⁻¹)	Atrazine removal (%)	k (10 ⁻⁵ s ⁻¹)	E_{EO} (kW h m ⁻³ order ⁻¹) ^a	TOC removal (%)	E_{EO} (kW h m ⁻³ order ⁻¹)
0.033 M H ₂ SO ₄	3.6	1.24	6.2	0.90	80.43	5.9	226.96
0.033 M Na ₂ SO ₄	4.4	3.08	15.4	2.40	97.62	6.7	243.24
0.10 M NaClO ₄	5.2	1.65	8.2	2.05	135.07	8.6	221.70
0.10 M NaOH	3.6	1.26	6.3	0.90	212.99	6.6	202.14
0.10 M NaCl	4.9	~20.00	~100.0	192.00	1.36	33.2	46.56
0.10 M NaNO ₃	5.9	3.85	19.2	3.00	104.72	8.9	242.67

^a Literature values [32]: 2.81 (UV ($\lambda = 253.7 \text{ nm}$)); 0.90 (O₃-UV); 1.67 (H₂O₂-UV); 0.102 (H₂O₂-O₃); 0.182 (O₃).

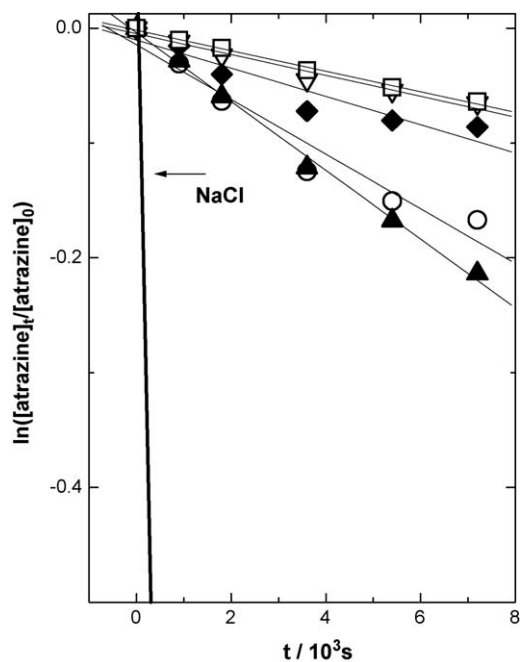


Fig. 6. Pseudo-first order plot for atrazine degradation at 40 mA cm^{-2} . (●) 0.1 mol L^{-1} NaCl, (○) 0.033 mol L^{-1} Na_2SO_4 , (▲) 0.1 mol L^{-1} NaNO_3 , (▽) 0.1 mol L^{-1} NaOH, (◆) 0.1 mol L^{-1} NaClO_4 and (□) 0.033 mol L^{-1} H_2SO_4 $[\text{atrazine}]_0$ and $[\text{atrazine}]_t$ denote concentration at start and at time t during electrolysis, respectively.

is due to Cl_2 dissolved in solution (e.g. hypochlorous acid – HOCl). However, as the electrolysis proceeds hypochlorite is rapidly produced [28] and, due to the greater solubility of ClO^- over Cl^- [29], it is probable that the predominant mechanism in aqueous media is via ClO^- . The chlorine evolution reaction is a reaction that occurs relatively easily at a wide spectrum of electrodes [26]. In this way relatively high organic removal rates are achieved when electrolysis is performed in the presence of NaCl.

On the other hand, in electrolytes other than NaCl, the reaction mechanism occurs via the formation of elevated oxida-

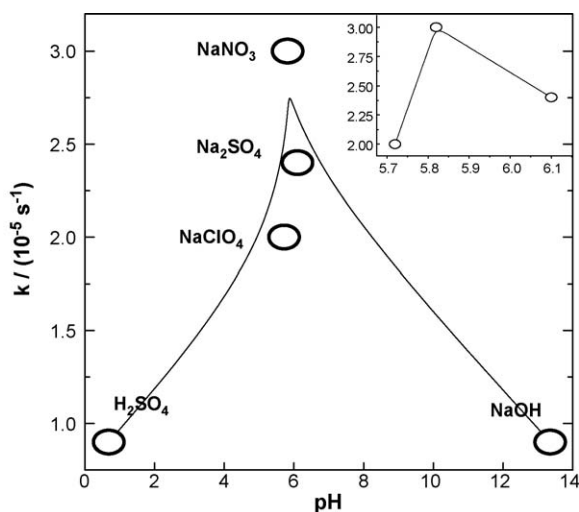


Fig. 7. Dependence of k_{ap} on the pH of the solution; inset: region of pH 5.6–6.2 expanded.

tion states [27]. The first step is the formation of an adsorbed hydroxyl radical ($\bullet\text{OH}$) on the oxide (MO_x) surface:



The next step is the formation of an elevated oxidation state (MO_{x+1}):



Subsequently MO_{x+1} can oxidise the organic in solution (R (Eq. (5))) or continue to form O_2 (Eq. (6)):



From the above reactions, it can be seen that the OER is a competing reaction that reduces the efficiency of organic oxidation. In fact, low coulombic current efficiencies for oxidation are generally observed at such electrodes (1–2% [30]). Moreover, the active species (MO_{x+1}) is only encountered at the electrode surface and does not diffuse in to the bulk of the solution. This means that oxidation relies on mass transport of the organic to the electrode surface, whereas Cl_2 and ClO^- can lead to oxidation in the bulk of the solution.

An important factor in the electrochemical treatment of organics is the energy necessary to remove the organic load. A parameter that has been used to determine the efficiency of atrazine removal is the energy per order ($E_{\text{EO}} \text{ kWh m}^{-3} \text{ order}^{-1}$) [31,32]. The E_{EO} is determined according to [32]:

$$\text{energy consumption} = \frac{38.4 P_{\text{el}}}{V k'_1} \quad (7)$$

where P_{el} is the rated power (kW), V the cell volume and k'_1 is the pseudo-first order rate constant.

As can be observed from Table 2, the E_{EO} in the presence of NaCl is by far the lowest, indicating a considerable energy saving over the other electrolytes. When compared to other advanced oxidation processes (AOP) presented in the literature [31], the electrochemical system is not as efficient as systems that employ O_3 (0.90 for O_3 -UV, 0.102 for H_2O_2 - O_3 and $0.182 \text{ kWh m}^{-3} \text{ order}^{-1}$ for O_3), but more efficient than other systems studied (1.67 for H_2O_2 -UV and $2.81 \text{ kWh m}^{-3} \text{ order}^{-1}$ for UV at $\lambda = 253.7 \text{ nm}$). The results indicate that the use of supporting electrolytes other than NaCl would not be as economically attractive for the removal of atrazine.

3.3. Effect of NaCl concentration

Considering the results presented above, it was decided to study the effect of NaCl concentration. This was done in order to investigate if the same extent of atrazine/TOC removal can be achieved using smaller additions of NaCl, thus reducing the cost of treatment. The concentration of NaCl was varied from 0.0125 to 0.1 mol L^{-1} and electrolyses at 40 mA cm^{-2} were performed for each different concentration.

The extent of atrazine removal as a function of NaCl concentration was observed to be the same ($\sim 100\%$) for all the

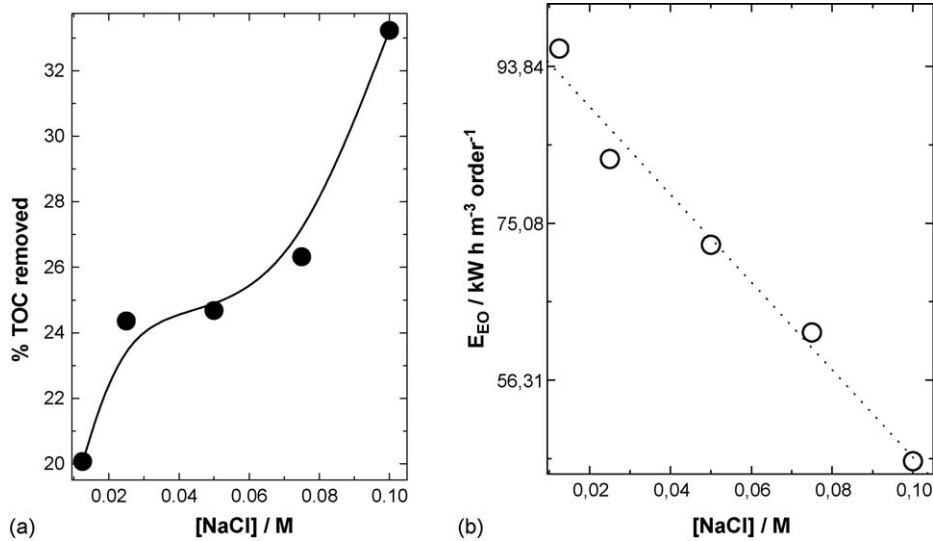


Fig. 8. Dependence of (a) TOC removal and (b) E_{EO} as a function of NaCl concentration.

concentrations studied. The apparent 1st order rate constant did not vary significantly for the different NaCl concentrations studied, being approximately $1.90 \times 10^{-3} \text{ s}^{-1}$ at all concentrations. This is interesting as it indicates that a smaller quantity of NaCl is required to obtain total removal of the pesticide. This result demonstrates that if the removal of atrazine were the sole objective of a treatment system, only low concentrations of NaCl would be required – thus reducing the cost of reagents.

Fig. 8a presents the extent of TOC removal as a function of NaCl concentration. From Fig. 8 it can be observed that the quantity of TOC removed is, in fact, dependent on the concentration of NaCl in solution – something which is not true for the removal of the pesticide in itself. In Fig. 8b it is possible to observe that E_{EO} value for TOC removal decreases linearly with NaCl concentration. This indicates that although the removal of atrazine itself can be achieved relatively easily, the rate of organic removal is more complex and is a function of the concentration of the species formed in Eqs. (1) and (2).

3.4. Effect of current density

If it is true that the rate of organic removal is function of the species formed in Eqs. (1) and (2), it is interesting to investigate the effect of electrochemically increasing the rate of their formation. This can be achieved by varying the applied current density. The current density was investigated from 10 to 120 mA cm^{-2} for oxidation of atrazine in 0.1 M NaCl , which is the concentration which gave the lowest energy consumption. As observed for different concentrations, the removal of atrazine is complete – even at 10 mA cm^{-2} . Again indicating the ease with which atrazine can be removed from solution in the presence of NaCl. Fig. 9a presents the extent of TOC removal as a function of applied potential and demonstrates that the removal of organic content increases linearly between 10 and 60 mA cm^{-2} . At 60 mA cm^{-2} the quantity of TOC removed passes through a maximum and then declines. As the current density increases, it is probable that there is increased competition between the

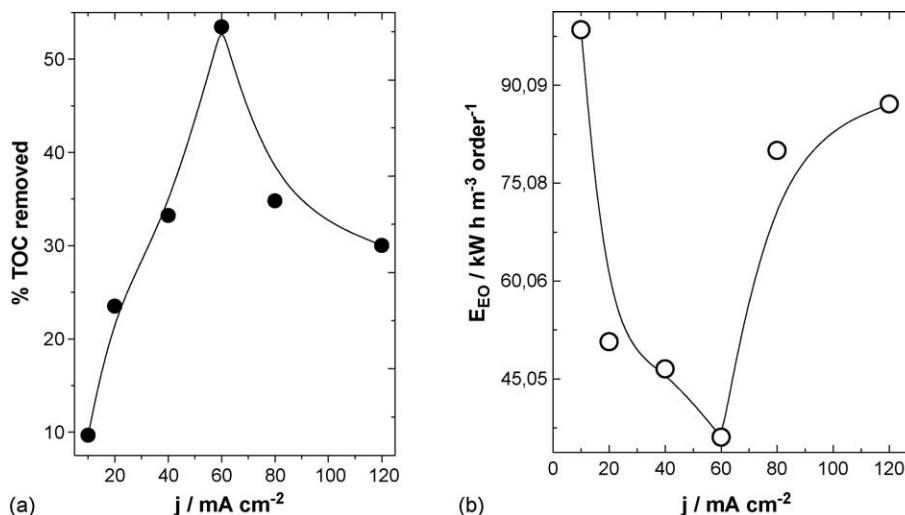


Fig. 9. Dependence of (a) TOC removal and (b) E_{EO} as a function of current density.

Table 3
Data obtained during the galvanostatic oxidation of atrazine (20 mg L⁻¹) at different electrodes

Electrode	<i>j</i> (mA cm ⁻²)	<i>E</i> _{cell} (V)	Atrazine		TOC	
			Atrazine removal (%)	<i>E</i> _{EO} (kW h m ⁻³ order ⁻¹)	TOC removal (%)	<i>E</i> _{EO} (kW h m ⁻³ order ⁻¹)
Ti/Ir _{0.01} Sn _{0.99} O ₂						
0.033 M Na ₂ SO ₄	40	6.0	16.69	125.97	4.24	498.96
0.10 M NaCl	40	4.5	100	1.25	30.94	51.04
0.10 M NaCl	60	5.9	100	1.64	35.15	58.70
Ti/Ir _{0.005} Ru _{0.005} Sn _{0.99} O ₂						
0.033 M Na ₂ SO ₄	40	6.0	24.63	81.47	5.25	401.01
0.10 M NaCl	40	4.8	100	1.33	30.83	54.62
0.10 M NaCl	60	6.1	100	1.72	46.35	45.80

formation of Cl₂ and O₂ with the latter being favoured at the potentials reached here. In actual fact, the available literature [26] suggests that an increase in the current density actually favours chlorine evolution. However, the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode presents a high internal surface area, to which rapid Cl⁻ diffusion from the bulk is difficult. This fact results in O₂ evolution occurring preferentially at the more difficult-to-reach areas of the electrode [26] – thus reducing the efficiency of Cl₂ formation.

A plot of *E*_{EO} as a function of the current density results in behaviour that is analogous to that shown in Fig. 9a. This demonstrates that the lowest value of *E*_{EO} is achieved at 60 mA cm⁻². At higher current densities the operating potential increases and leads to an increase in the energy consumption.

3.5. Effect of electrode material

According to the active/non-active mechanism proposed by Comninellis [16,17], varying the electrode material makes it possible to form different oxidising species and thus modify the oxidation pathway. Active electrodes mediate the oxidation of an organic species via the formation of higher oxides of the metal (MO_{x+1}), where there is a higher oxidation state available (e.g., RuO₂ or IrO₂). This leads to selective oxidation. Non-active electrodes present no higher oxidation state available and the organic species is directly oxidised by an adsorbed hydroxyl radical, giving complete combustion (e.g., SnO₂ or PbO₂).

In this study two electrodes that contained SnO₂ were tested in order to compare with the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode. The electrodes were of nominal composition Ti/Ir_{0.005}Ru_{0.005}Sn_{0.99}O₂ and Ti/Ru_{0.01}Sn_{0.99}O₂ and it was hoped that the presence of SnO₂ in the oxide layer would aid the complete combustion of atrazine to CO₂ [16,17]. Electrolyses were performed at 40 mA cm⁻² in 0.033 M Na₂SO₄ and at 40 and 60 mA cm⁻² in 0.1 M NaCl in order to be compared with the electrolyses previously performed with the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode.

Table 3 presents the data for the oxidation of atrazine at the SnO₂-containing electrodes. In both 0.033 M Na₂SO₄ and 0.1 M NaCl the behaviour of the electrodes is similar to that of the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode. In NaCl the removal of atrazine is complete at both current densities for both electrodes –

again indicating that the important reaction is the formation of Cl₂ and ClO⁻ whereas in Na₂SO₄ the removal of atrazine is incomplete. It is apparent that in the presence of Na₂SO₄ the Ti/Ir_{0.005}Ru_{0.005}Sn_{0.99}O₂ and Ti/Ir_{0.01}Sn_{0.99}O₂ electrodes present a more elevated level of atrazine removal compared to the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode. However, TOC removal is lower for the Ti/Ir_{0.01}Sn_{0.99}O₂ and Ti/Ir_{0.005}Ru_{0.005}Sn_{0.99}O₂ electrodes and, overall, there is little advantage in using SnO₂-containing electrodes over the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode.

4. Conclusions

The results demonstrate that the electrochemical removal of atrazine is pH-dependent in electrolytes where no species that results in oxidation in the bulk of the solution is formed. In such electrolytes, the removal of atrazine and TOC is limited. In the presence of NaCl atrazine and TOC are removed at much greater rates. The atrazine concentration is observed to rapidly reach completion, even at low NaCl concentrations. On the other hand, TOC removal is directly dependent on the quantity of NaCl and its electrochemically generated oxidising agents in solution, with 0.10 mol L⁻¹ NaCl (highest concentration used) giving the best results. The results indicate that increasing the current density results in a maximum TOC removal of ~46% at the Ti/Ir_{0.005}Ru_{0.005}Sn_{0.99}O₂ electrode, a value that is not attained by the SnO₂-containing electrodes used in this study.

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