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Electrochemical Degradation of Dimethyl Phthalate Ester on a DSA® Electrode

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O presente estudo objetiva a degradação eletroquímica do éster dimetilftalato (DMP) em uma célula em fluxo do tipo filtro-prensa, usando um ânodo dimensionalmente estável (DSA®). As melhores condições de eletrólise foram determinadas pela análise da natureza e concentração do eletrólito suporte, pH, densidade de corrente e temperatura. A remoção da concentração do DMP e do teor de carbono orgânico total (TOC) foram maiores na presença de NaCl, assim como os valores das constantes cinéticas de pseudo primeira ordem. Usando força iônica constante em 0,15 mol dm^{-3} pela adição de Na$_2$SO$_4$, a concentração de DMP diminuiu mais rapidamente a baixas concentrações de íons cloreto, enquanto que a remoção do teor de TOC após 1h de eletrólise aumentou com a adição de NaCl. A remoção do DMP foi similar para todas as densidades de corrente investigadas em solução ácida. A melhor opção operacional, considerando a eficiência energética, é de baixa densidade de corrente, já que o sistema eletroquímico encontra-se sob regime de transferência de massa.

The electrochemical degradation of dimethyl phthalate (DMP) using a one-compartment filter press flow cell and a commercial dimensionally stable anode (DSA®) is presented. The best electrolysis conditions were determined by the analysis of the influence of the nature and concentration of the support electrolyte, pH, current density and temperature. The abatement of DMP concentration and total organic carbon (TOC) removal were superior in the presence of NaCl, as well as the apparent first order kinetic constants. Using constant ionic strength at 0.15 mol dm^{-3} by adding Na$_2$SO$_4$, DMP concentration decreases faster at relative low NaCl concentrations while the TOC removal after 1 h of electrolysis increases with NaCl concentration. The DMP removal was very similar for all the current densities investigated at acidic solutions. When electric energy saving is considered, since the electrochemical system was under mass transport conditions, the best operational option is to use low current density values.

Keywords: endocrine disruptor, dimethyl phthalate, indirect oxidation, electrooxidation, mass-transport

Introduction

The contamination of aquatic ecosystems is among the most critical problems faced by the 21st century society as a consequence of the increasing waste production containing synthetic organic compounds, such as phthalates, dyes, antibiotics, hormones and personal care products. The phthalic acid esters (PAEs) are a class of organic compounds used as additives in plastic manufacture, namely polyvinylchloride (PVC), polyvinyl acetates, cellulose and polyurethanes.[1] The release of PAEs to the environment may occur through leaching promoted by water, as phthalates are physically bound to plastic structures,[2] such as those used in food packing, toys, blood transfusion bags and tubing. Consequently, contamination of the atmosphere, soil and water is likely to occur, as shown in many works in the literature.[3-5] Moreover, PAEs can affect the endocrine system[6] of animals and humans, leading to serious health problems,[7] even at low concentration levels (µg L^{-1} or ng L^{-1}) that are present in drinking water.[6] Consequently, effluents containing such synthetic organic compounds should be treated before their

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disposal to water bodies, since sustainability is part of many developing technologies or processes.[8]

The conventional treatment processes are inefficient to treat effluents containing PAEs or other endocrine disrupting compounds.[9] The hydrophobic nature of these compounds can also result in the production of contaminated sludge, which is detrimental to the soil. The electrochemical oxidation or electrooxidation processes could be a reasonable option to treat organic compounds, due to the implementation ease and high oxidation rates attained. The electrooxidation of pollutants can occur through:[10] i) direct process, in which the organic molecules are oxidized after adsorption on the electrode surface or ii) indirect process, in which the oxidation of organic contents carried out by electrogenerated oxidants. The most common electrogenerated oxidants are the hydroxyl radicals (•OH), originated from the oxidation of water and active chlorine (Cl_2, HClO and OCl^-), when chloride containing solutions are electrolyzed. As these species differ in the oxidation potential, the organic pollutants are susceptible to different attacks in their chemical bonds, leading to different reaction mechanisms,[11] as shown in the literature for PAEs.[12] Moreover, the presence of different alkyl groups in PAEs can lead to the generation of specific intermediates[13] due to the variation of their hydrophobic nature.[12]

The dimensionally stable anode (DSA®) is an interesting option for the degradation of organic compounds, such as atrazine,[14-16] carbaryl,[17] and dyes,[18,19] due to its versatile electrocatalytic property of active chlorine electrogeneration, electrochemical stability, and long lifetime.[20] Motheo and Pinhedo,[21] using dimensionally stable type anodes with different compositions in chlorine medium, studied the degradation of humic acid achieving the elimination of most of the electro-oxidation products after approximately 2 h of electrolysis at 40 mA cm^{-2}. Radjenovic *et al.*[22] reported that RuO_2/IrO_2 coated Ti anodes are capable of oxidizing 28 pharmaceuticals and pesticides present in the effluents of a wastewater treatment plant; however, an increase was noticed in the toxicity of the byproducts. On the other hand, Chatzisymeon *et al.*[23] reported that the electrooxidation of an olive mill wastewater, using DSA® anode in the presence of chloride ions, led to complete color and phenol removals, eliminating ecotoxicity. An advantage of DSA® is its semiconducting characteristics because, when UV radiation is associated to the electrochemical treatment, the energy consumption is substantially reduced by the use of low current densities.[16-17] In addition, Malpass *et al.*[24] showed that the photo-assisted electrochemical oxidation of atrazine resulted in toxicity reduction, when chloride-containing solutions are electrolyzed.

Thus, the aim of the present work is to study the electrochemical oxidation of dimethyl phthalate (DMP) using DSA® as the electrode material in the presence of chloride ions. These conditions are expected to improve the electrochemical oxidation of DMP, especially in acidic solutions. The optimization of the current density is important when the relationship between maximum pollutant removal and energy saving is considered.

Experimental

Electrochemical cell and equipment

The electrochemical experiments were carried out in a one-compartment filter-press reactor composed of the DSA® (nominal composition Ti/$Ru_{0.3}Ti_{0.7}O_2$, De Nora Brazil Ltda.) and Ti plates, as anode and cathode, respectively. The exposed area of both electrodes was 14 cm^2. The distance between the electrodes was kept at 0.9 cm by positioning Viton and Teflon® spacers of 1 and 2 mm thickness, respectively. A reversible hydrogen electrode (RHE: 0.5 mol dm^{-3} H_2SO_4) was used as the reference and positioned outside of the cell reactor. The electric contact was made through a cationic membrane strip (IONAC), in which one end was placed among the spacers and the other was positioned in an electrolytic bath filled with 0.5 mol dm^{-3} H_2SO_4. The cell reactor was connected to a peristaltic pump and to a reservoir through silicon tubes. More details about the electrochemical system and cell configuration are described elsewhere.[14,18,19]

Cyclic voltammetry measurements (10 cycles at 20 mV s^{-1}) were carried in a conventional electrochemical cell composed of the DSA® (0.88 cm^2), two Pt foils as cathode, and RHE as reference electrode. Prior to the measurements, a pre-treatment of the DSA® electrode was performed in 0.5 mol dm^{-3} H_2SO_4 solution. It consisted of 50 voltammetric cycles from 0 to 2.0 V_{RHE} at scan rate of 200 mV s^{-1}.

All electrochemical measurements (cyclic voltammetry and galvanostatic electrolyzes) were performed using a potentiostat/galvanostat coupled to a SPGSTAT30 Booster (Amplifier), both from AUTOLAB Eco Chemie. All glassware and components of the electrochemical cells were cleaned to remove all organic contamination. The method used was the acid-permanganate procedure followed by washing in an acidic H_2O_2 solution followed by heating in deionized water and subsequent abundant rinsing with deionized water.

Reagents

All chemicals, including DMP (a.r., Sigma-Aldrich), Na_2SO_4 (a.r., Qhemis), NaCl (a.r., Synth, Brazil), Ag_2SO_4

(a.r., JT Baker, Mexico), $HgSO_4$ (a.r., JT Baker, Mexico), H_2SO_4 (98%, Mallinckrodt), NaOH (a.r., Qhemis, Brazil), oxalic acid (a.r., Synth, Brazil) and acetonitrile (HPLC grade, JT Baker, Mexico) were used as received. Double deionized water (Millipore Milli-Q system, resistivity of 18.2 MΩ cm at 25 ºC) was used to prepare all solutions.

Electrochemical degradation experiments

The electrooxidations were carried out galvanostatically using 0.35 dm^3 of a solution containing 161.8 mg dm^{-3} DMP, which corresponds to an organic carbon content equal to 100 mg dm^{-3}. The investigated variables in the electrochemical degradation of the DMP compound were: *i*) the nature and concentration of the support electrolyte (NaCl and Na_2SO_4) by keeping the ionic strength at 0.15 mol dm^{-3}; *ii*) the initial pH (2-10); *iii*) the applied current density (20-120 mA cm^{-2}); and *iv*) the temperature (10-50 ºC). The flow rate was kept constant at 300 cm^3 min^{-1} using a centrifugal pump. The initial electrolysis time was set for 1 h, in order to assess the levels of the investigated variables on the degradation and mineralization of the DMP solution. After optimizing the variable system, a prolonged electrolysis was conducted for 5 h.

Analysis

The performance of the electrochemical degradation experiments were analyzed through high performance liquid chromatography (HPLC), chemical oxygen demand (COD) and total organic carbon (TOC) removals. The DMP concentration decay was monitored by HPLC (Shimadzu, LC-10ADVP) assays under reversed phase using a C18 column (150 mm × 4.6 mm, 5 µm). The mobile phase consisted of 50% acetonitrile and 50% water with a flow rate of 1 cm^3 min^{-1}. The temperature of the oven was maintained at 40 ºC and the DMP concentration was monitored at 274 nm (Shimadzu, SPD-10AVP). The area of the peak corresponding to the DMP molecule was compared to the one from a calibration curve that was previously obtained in the range of 1 to 200 mg dm^{-3}. COD measurements were taken at the beginning and after 1 h of electrolysis, by sampling 2.5 cm^3 of the electrolyzed solution. Then, aliquots of an acidic solution (1.5 cm^3) containing $K_2Cr_2O_7$ and $HgSO_4$ were added to the electrolyzed samples followed by the addition (3.5 cm^3) of concentrated H_2SO_4 containing $AgSO_4$. These solutions were oxidized by digestion for 2 h at 150 ⁰C in a COD block reactor, according to the methodology described in the literature.[25] Then, after the ambient temperature was reached, the absorbance of the samples was read at 600 nm

in a spectrophotometer (Hach DR 2800). The resulting COD values were compared to the ones from a calibration curve. TOC measurements (Shimadzu, VCPH) were carried out at every 15 min by sampling 9.0 cm^3 of the electrolyzed solution up to 1 h. The TOC values were obtained by subtracting the total carbon minus the inorganic carbon.

The current efficiency (CE) for the electrochemical degradation of the DMP compound was calculated as proposed by Comninellis and Pulgarin[26] and considering the relation between COD and TOC reported by Gray and Becker:[27]

$$CE = \frac{2.67\left[(TOC)_t - (TOC)_{t+\Delta t}\right]FV}{8I\Delta t} \qquad (1)$$

where TOC_t and $TOC_{t+\Delta t}$ correspond to the organic load (g dm^{-3}) at a certain time *t* (s) and *t*+Δ*t*, *F* is the Faraday constant (96,485 C mol^{-1}), *V* (dm^3) is the volume of the electrolyzed solution, and *I* (A) is the applied electric current. On the other hand, the electric energy consumption per unit volume of electrolyzed solution (*w*) was calculated as:
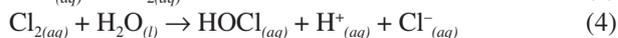
$$w = \frac{UIt}{V} \qquad (2)$$

where *U* is the cell potential (V).

Results and discussion

Effect of the support electrolyte

The effect of the salt nature is shown in Figure 1 for the DMP and TOC decay as a function of the electrolysis time in the presence of NaCl 0.15 mol dm^{-3} and Na_2SO_4 0.05 mol dm^{-3}. These concentration values were used to keep the ionic strength at 0.15 mol dm^{-3}. The DMP and TOC removals were superior in the presence of NaCl, as well as the apparent first order kinetic constants (Table 1), due to the electrogeneration of the chlorine oxidative species. Among these species, the Cl_2 and HClO are predominant in the acidic solutions (equations 3 and 4):[28]

$$2Cl^-_{(aq)} \rightarrow Cl_{2(aq)} + 2e^- \qquad (3)$$
$$Cl_{2(aq)} + H_2O_{(l)} \rightarrow HOCl_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \qquad (4)$$

Moreover, they also have the highest oxidation potentials in comparison to the OCl^- species. The electrochemical oxidation of organics, using DSA® in the presence of chloride ions, is responsible for high rates of pollutant removal due to the electrocatalytic evolution of Cl_2, as reported in the literature.[20,29] In the presence of sulfate ions, the electrooxidation is mainly due to the
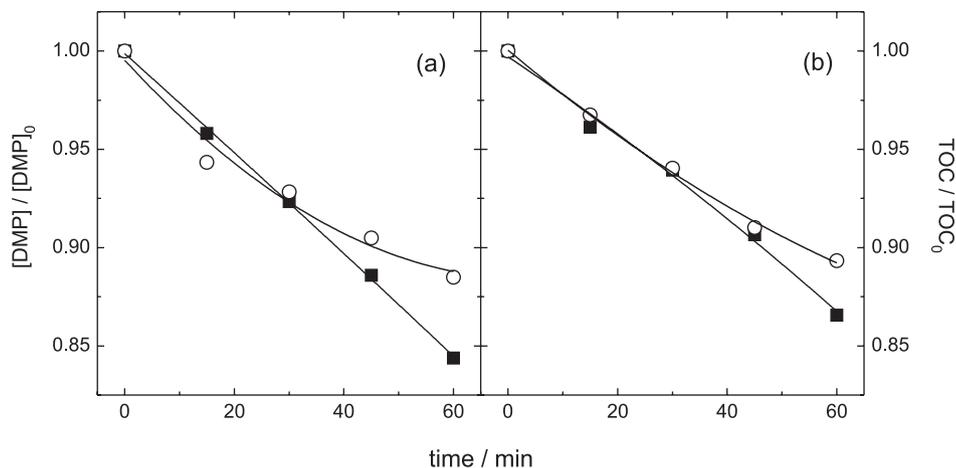
Figure 1. Relative DMP concentration and TOC decay as a function of the electrolysis time for different salt concentrations: 0.15 mol dm^{-3} NaCl (■) and 0.05 mol dm^{-3} Na$_2$SO$_4$ (○). Conditions: 20 mA cm^{-2}, 30 °C, and pH 2. Ionic strength of 0.15 mol dm^{-3}.

Table 1. Apparent first order kinetic constants (k_{ap}) obtained for the TOC and DMP concentration removal conditions after 1 h of electrolysis considering different variables and the corresponding extent of total removal or complete combustion (ϕ at equation 9) and current efficiencies (CE at equation 1)

Variables	Range	TOC removal			DMP abatement		
		k_{ap} / (10^{-3} min^{-1})	R^2	CE / %	k_{ap} / (10^{-3} min^{-1})	R^2	ϕ
Supporting electrolyte	NaCl	2.31	0.98	14.97	2.79	0.99	0.86
	Na$_2$SO$_4$	1.91	0.99	11.45	1.91	0.92	0.93
[NaCl] / (mmol dm^{-3})	7.04	2,54	0.97	15.17	4.06	0.96	0.70
	35.2	2.03	0.95	11.16	2.86	0.96	0.72
	70.4	2.07	0.94	11.99	2.68	0.96	0.81
Initial pH[a]	2.0 (2.0)	2.31	0.98	14.97	2.70	0.99	0.88
	6.0 (6.1)	0.99	0.97	6.45	2.01	0.99	0.53
	10.0 (5.3)	0.90	0.95	6.48	1.32	0.88	0.69
i / (mA cm^{-2})	20	3.09	0.99	18.20	3.01	0.84	0.95
	60	1.56	0.96	2.91	3.36	0.96	0.47
	120	1.08	0.96	0.42	3.47	0.95	0.14
T / °C	10	2.52	0.99	15.18	2.83	0.94	0.86
	30	3.37	0.92	19.78	3.84	0.97	0.88
	50	3.71	0.92	20.56	5.00	0.97	0.73

[a]The values in parenthesis refer to the pH values after the electrochemical degradation experiments.

direct process through the formation of the redox couple MO/MO$_{X+1}$ (active electrodes) at elevated oxidation states (equations 5 and 6):[14]

$$MO_x + H_2O \rightarrow MO_x(\bullet OH) + H^+ \qquad (5)$$
$$MO_x(\bullet OH) \rightarrow MO_{x+1} + H^+ \qquad (6)$$
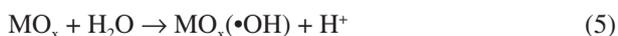
Then, the MO$_{X+1}$ species can oxidize the organic compound in the solution, through a mass transport mediated process, or it can lead to the concomitant occurrence of the parasitic reaction of O$_2$ evolution:

$$MO_{x+1} \rightarrow MO_x + \frac{1}{2}O_2 \qquad (7)$$

The possible formation of persulfate ions was also reported by Goldin *et al.*[30] using an anode covered with a mixture of oxides composed of IrO$_2$, RuO$_2$ and SnO$_2$; however, the concentration of these ions remained very low. The role of NaCl in the electrooxidation of organic compunds is well documented in the literature[14,15,19,31,32] using DSA® electrodes. Thus, hereafter the experiments will be carried out in the presence of NaCl.

To verify the anodic behavior of the Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrode, cyclic voltammetric analyses were performed using both supporting electrolytes in the presence and absence of DMP (Figure 2). As discussed by Malpass *et al.*,[14] these measurements are important to
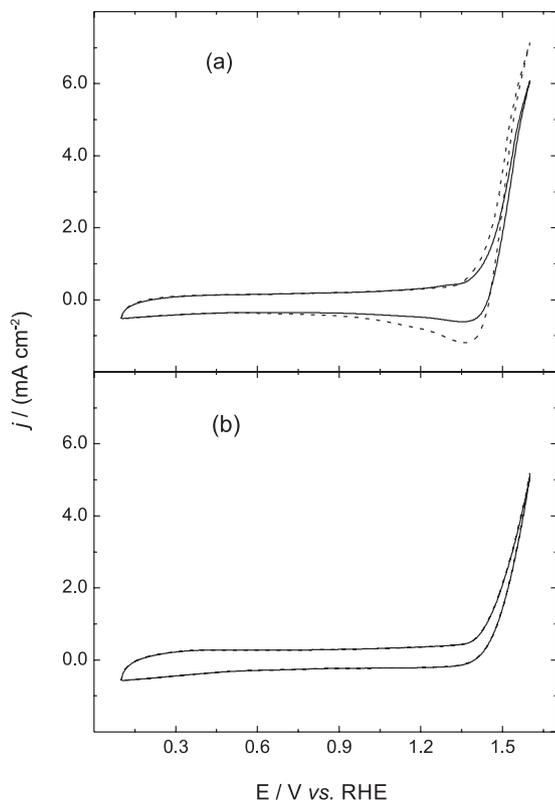
Figure 2. Cyclic voltammograms (10th cycle) of the commercial Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrode at (a) 0.15 mol dm^{-3} NaCl and (b) 0.05 mol dm^{-3} Na$_2$SO$_4$, in the presence (dashed line) and absence (solid line) of DMP. v = 20 mV s^{-1}. Ionic strength of 0.15 mol dm^{-3}.

study the behavior of the electrode surface under specific conditions. In both NaCl and Na$_2$SO$_4$, it can be observed from the cyclic voltammetric curves, that there is no oxidation peak until 1.4 V$_{RHE}$ and the oxygen evolution reaction occurs at potentials above this value. When using NaCl, the curve in the presence of DMP exhibited a slightly higher anodic current density (ca. 1.4 V$_{RHE}$), attributed to the reaction between DMP and Cl$_2$, with the consequent generation of oxidized byproducts in the electrode surface (Figure 2a), which leads to an increase of the cathodic current density. On the other hand, the voltammetric curves using Na$_2$SO$_4$, with and without DMP addition, exhibited no significant difference. The DMP molecule did not oxidize at this potential range and did not undergo any structural change from oxidizing agents that may have led to oxidized byproducts at the electrode surface.

Effect of the NaCl concentration

Figure 3 shows the DMP and TOC evolution as a function of the electrolysis time for different NaCl concentrations in acidic solutions. It is important to highlight that the ionic strength was kept at 0.15 mol dm^{-3} through the addition of Na$_2$SO$_4$. An interesting behavior is

the increase of the DMP removal, as well as the apparent first order kinetic constants (Table 1), at low chloride concentrations. It was expected to attain high DMP removal rates at high chloride concentrations, due to the increase in the production of oxidizing chlorine species, mainly HOCl, if the electrochemical system is under mass transport control with respect to Cl$_2$ evolution. Thus, it is interesting to estimate the limiting current density for Cl$_2$ evolution,[33] as shown below:

$$j_L = n \, F \, k_m \, C_{Cl^-} \qquad (8)$$

where n is the number of electrons involved in the Cl$^-$ oxidation (n = 1), F is the Faraday constant, k_m is the mass transfer coefficient (m s^{-1}), and C_{Cl^-} is the Cl$^-$ concentration (in mol m^{-3}). The k_m value was estimated by a standard limiting current test[34] and its value is 2.68×10^{-6} m s^{-1}, taking into account the hydrodynamic conditions of the electrochemical system. Considering that the Cl$^-$ concentration ranged from 7.0 to 70.4 mmol dm^{-3}, the anodic limiting current density for Cl$_2$ evolution remained between 0.18 and 1.82 mA cm^{-2}. These values are much lower than the investigated current density range (20 to 120 mA cm^{-2}). Consequently, the electrochemical system is under mass transport control with respect to Cl$_2$ evolution. Furthermore, the observed decrease of the DMP removal rate at high NaCl concentrations could be a consequence of parasitic reactions of chlorine consumption.[28]

The chlorine oxidative species can react in three different ways with the organic compounds:[35] *i*) substitution reactions; *ii*) addition reactions to unsaturated chemical bonds; and *iii*) oxidation reactions. Any of these reactions can lead to the formation of organochloride compounds, which can be more recalcitrant than the original DMP molecule. Consequently, lower levels of mineralization are expected as the chloride concentration is increased, as already observed in Figure 3, despite the similar values of the apparent first order kinetic constants (Table 1). An increase in the concentration of organochloride compounds, measured with the AOX technique, as a function of NaCl concentration, during the electrooxidation of glyphosate using a DSA® electrode was already reported.[36] Moreover, the highest removal of the herbicide and COD contents were attained at high NaCl concentrations. A similar behavior with respect to NaCl concentration was obtained during the electrooxidation of real textile waste using a DSA®.[37]

Malpass *et al*.[14] also observed an increase in the removal of the atrazine herbicide and in the TOC content as a function of NaCl concentration. The COD removal increases after 1 h of electrolysis with the NaCl concentration in solution, as shown in Table 2. This behavior indicates that the DMP
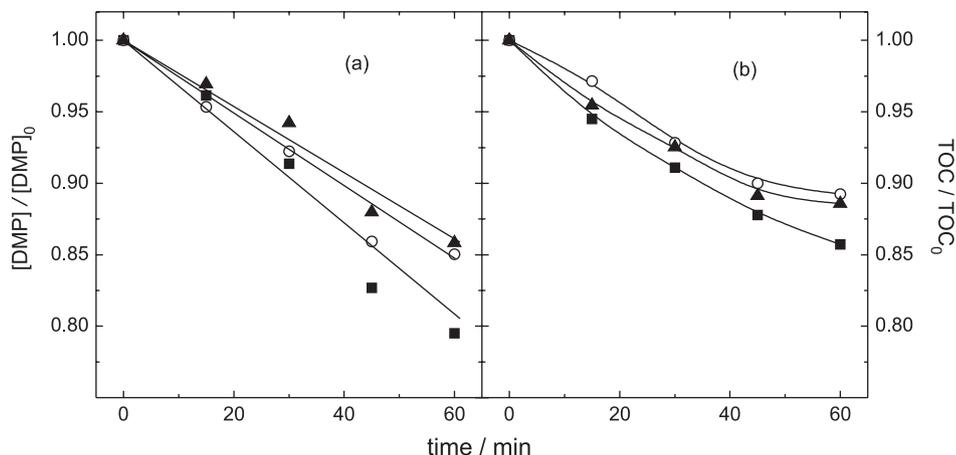
Figure 3. Relative DMP concentration and TOC decay as a function of the electrolysis time for different concentrations of NaCl: (■) 7, (○) 35, and (▲) 70 mmol dm⁻³ NaCl. Conditions: 20 mA cm⁻², 30 °C, and pH 2. Ionic strength of 0.15 mol dm⁻³ through addition of Na₂SO₄.

molecule is being oxidized by the chlorine oxidative species, followed by the generation of intermediate compounds that are more recalcitrant to mineralization during electrooxidation (no TOC abatement) or because the organic compounds are no longer oxidized by dichromate ions due to the formation of chlorinated compounds. The organochlorine compounds exhibited deviations from the theoretical and experimental COD values, as shown by Baker *et al..*[38] During the electrooxidation of an olive mill wastewater using a DSA® electrode, the NaCl addition did not contribute to an increase in the COD removal,[23] which can be associated to the recalcitrant organic species produced or to the low chlorine oxidative species concentration.

Table 2. COD obtained for the DMP removal considering different experimental parameters after 1 h of electrolysis

Variable	Range	COD removal / %
Supporting electrolyte	NaCl	66.4
	Na₂SO₄	61.8
[NaCl] / (mmol dm⁻³)	7.04	38.5
	35.2	44.0
	70.4	61.3
Initial pH	2	36.2
	6	10.2
	10	7.8
i / (mA cm⁻²)	20	29.7 (37.1)ᵃ
	60	45.6 (19.0)ᵃ
	120	61.0 (12.7)ᵃ
T / °C	10	62.0
	30	67.8
	50	68.8

ᵃThe values in parenthesis refer to the ratio between COD removal and Q_{ap} (kA h m⁻³) after 1 h of electrolysis.

In the present conditions, the COD removal increasing as a function of NaCl concentration was unexpected, since the Cl_2 evolution is under mass transport conditions. One possible explanation might be the Cl^- ions oxidation promoted by $Cr_2O_7^{2-}$ at high NaCl concentrations (70 mmol dm⁻³). As a consequence, erroneous COD measurements were obtained for this specific condition.

Effect of the initial pH

Figure 4 shows the DMP and TOC decay as a function of the electrolysis time for different initial pH values of the solution. Acidic solutions resulted in the best removal rates attained for the DMP and TOC, as well as the highest apparent first order kinetic constants (Table 1), as a consequence of the electrogeneration of the HOCl and Cl_2 species. In alkaline medium, OCl^- ions are probably present in higher concentration than other chlorine oxidative species; however, the removal of the organic compound decreases because of the low oxidation potential of the OCl^- species compared with Cl_2 and HOCl. The stability of the different chlorine oxidative species at a certain pH value is well described in the literature.[28,35] Moreover, these oxidants are sufficiently stable to oxidize organics in the bulk of the solution, after being electrogenerated at the electrode surface and diffused away from it.[31] According to Prasad and Srivastava,[39] an increase in the initial pH of the solution for the electrooxidation of a distillery wastewater on a ruthenium oxide coated Ti decreases the color removal. The authors suggested that at higher pH values the hypochlorous acid will be converted to ClO_3^- and ClO_4^- species and, as consequence, the decolorization is reduced. The generation of ClO_3^- and ClO_4^- species is likely to occur during the electrooxidation using DSA® electrodes, but their low concentration might be due to the competition between

the reactions of oxygen evolution and chloride oxidation, as discussed by Polcaro *et al.*.[40] On the other hand, Rajkumar and Kim[41] obtained similar removal rates for a mixture of dyes during the electrooxidation using a DSA® electrode at different pH conditions. Yining *et al.*[42] also reported a pH independent behavior with respect to the TOC removal of a solution containing 50 mg dm⁻³ of DMP, during the anodic oxidation using the boron-doped diamond (BDD) electrode, as a consequence of the electrode's high ability to electrogenerate hydroxyl radicals. Table 2 shows that the highest COD removal values were obtained at acidic conditions, as a consequence of the highest oxidation power of the Cl_2 and HClO; however, Zhou *et al.*[43] found similar COD removal values in the pH range of 2 to 8.3, during the electrochemical treatment of a high salinity solution containing alkanes using a Ti/IrO_2-RuO_2 electrode. In addition, COD removal values were superior in comparison to the ones attained for TOC removal, which indicates that the mediated oxidation is carried out through the formation of intermediate compounds. Thus, the remaining experiments were carried at pH 2.
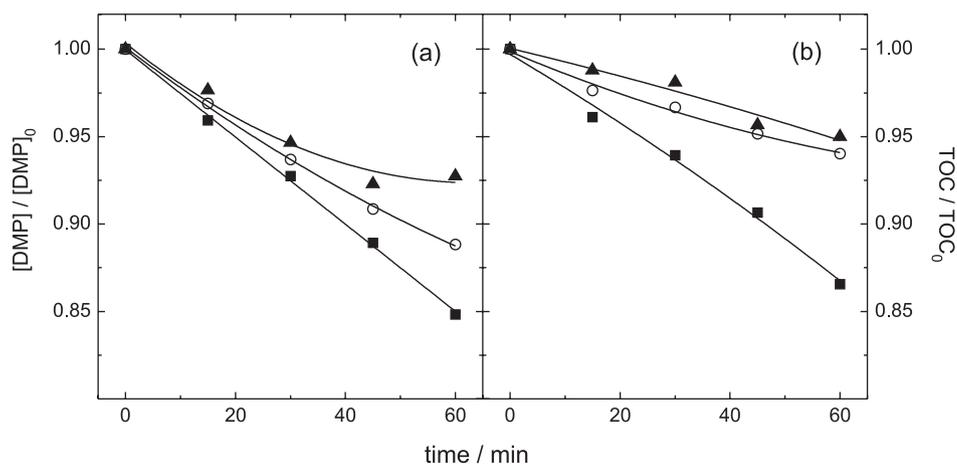
Effect of the current density

Figure 5 shows the DMP and TOC decay as a function of the charge applied *per* unit volume of electrolyzed solution (Q_{ap}) for different values of current densities. Although it can be observed that the DMP removal was very similar for all the current densities investigated (see also the apparent first order kinetic constants in Table 1), low current densities (low Q_{ap}) could be the option if energy saving is considered. On the other hand, the TOC removal levels decreased from 20 to 120 mA cm⁻². These behaviors indicate that the indirect oxidation mediated by the chlorine oxidative species is occurring followed

by the generation of intermediates. As discussed above, the generation of intermediates is responsible for the reduction of the DMP and COD contents, but without significant mineralization rates. Moreover, the TOC removal can only be accomplished with high oxidizing agents such as the hydroxyl or chlorine radicals. Thus, at high current densities the side reaction of oxygen evolution becomes the main electrode reaction and consequently, the production of high oxidizing agents diminishes, as can be confirmed by the lowest values of current efficiency. Moreover, the values of the apparent first order kinetic constants (Table 1) obtained for the DMP electrooxidation are much lower than the ones obtained by Yining *et al.*[42] using the BDD electrode, due to the greater oxidation power of this anode compared to the one of the DSA® electrode.

At this point, it is interesting to compare the extent of total removal or complete combustion of an organic pollutant, based on a ratio between the percentages of TOC and DMP removals (ϕ), as discussed by Miwa *et al.*.[31]

$$\varphi = \frac{\%[\mathrm{TOC}]_{removed}}{\%[\mathrm{DMP}]_{removed}} \tag{9}$$

Table 1 shows the ϕ values. Clearly, high current densities led to low levels of ϕ, indicating poor mineralization efficiency. The COD removal increased with the applied current density, as observed in Table 2; however, when the ratio between the COD removal and the Q_{ap} is considered, the COD removal at low current densities is the highest one. That behavior is due to the continuous evolution of O_2 at high current densities, leading to low current efficiencies. Thus, the electrochemical system can be operated using low current densities, which leads to higher removal rates of DMP, TOC and COD, hence the improvement in the

Figure 4. Relative DMP concentration and TOC decay as a function of the electrolysis time for different initial pH values: (■) pH 2, (○) pH 6, and (▲) pH 10. Conditions: 20 mA cm⁻², 30 °C, and 7.04 mmol dm⁻³ NaCl. Ionic strength of 0.15 mol dm⁻³ through addition of Na_2SO_4.
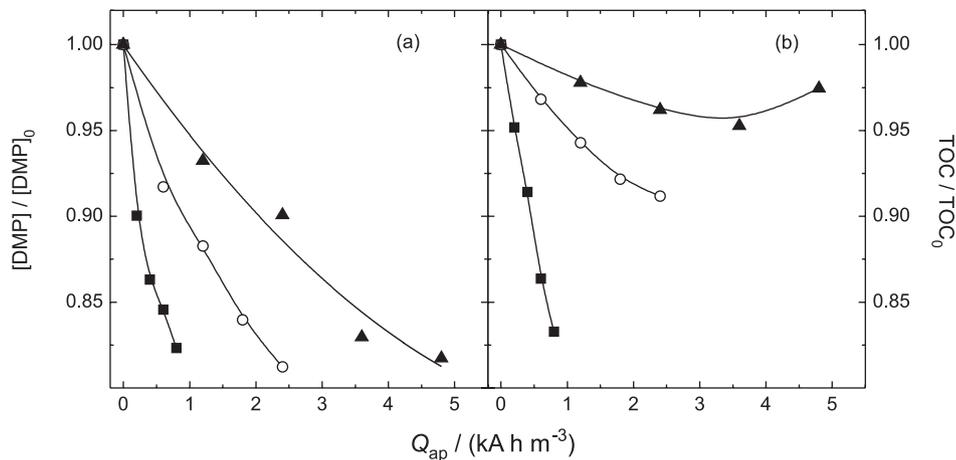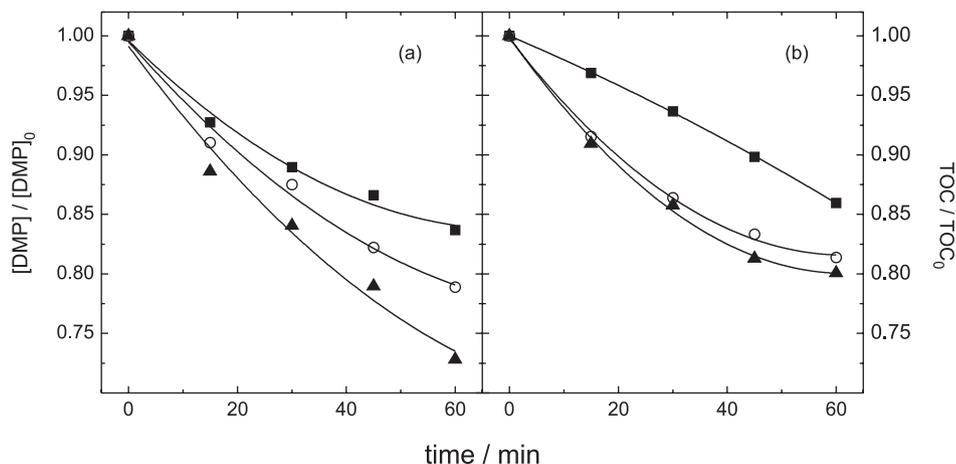
Figure 5. Relative DMP concentration and TOC decay as a function of the charge applied per unit volume of electrolyzed solution (Q_{ap}) for different values of current densities: (■) 20, (○) 60, and (▲) 120 mA cm^{-2}. Conditions: pH 2, 30 °C, and 7.04 mmol dm^{-3} NaCl. The ionic strength was kept constant at 0.15 mol dm^{-3} by addition of Na$_2$SO$_4$.

complete oxidation range. The choice of an adequate current density also depends on the flow regime of the electrochemical system under investigation, as interestingly discussed by Scialdone *et al.*.[32] If the electrochemical system is under mass transfer conditions, one can expect high removal efficiencies at high flow rates. The expected improvement in the mass transfer coefficient at high current densities,[44] as a consequence of the turbulence generated close to the anode, did not affect the removal rates attained. A similar behavior of increased COD removal as a function of current density was observed by Prasad and Srivastava;[39] however, maximum color removal was not observed at high current densities. Panakoulias *et al.*[45] observed that the COD removal for solutions containing the reactive red 120, using the Ti/IrO$_2$-RuO$_2$ anode, was not dependent on the current density, but increased with the applied charge. Thus, low current densities may be applied to the detriment of long treatment time.

Effect of the temperature

Figure 6 shows the DMP and TOC evolution as a function of the electrolysis time for different investigated temperatures. An improvement in the DMP and TOC removals at high temperatures (see the apparent first order kinetic constants at Table 1) is observed due to the increased oxidation power of the chlorine oxidative species (HClO and Cl$_2$). On the other hand, the expected decrease in the concentration of these chlorine species, essentially gaseous at acidic solutions, does not seem to influence the DMP or TOC removals. Moreover, a temperature increase can result in a similar improvement in the diffusivity coefficients of the species in solution, leading to high removal rates, since the electrochemical system is under mass transport regime. The higher DMP removal values in comparison to the TOC ones indicate that the electrooxidation is performed by the formation of intermediate compounds, as discussed above.

Figure 6. Relative DMP concentration and TOC decay as a function of the electrolysis time for different temperature values: (■) 10, (○) 30, and (▲) 50 °C. Conditions: 20 mA cm^{-2}, pH 2, and 7.04 mmol dm^{-3} NaCl. Ionic strength of 0.15 mol dm^{-3} through addition of Na$_2$SO$_4$.

Furthermore, the higher COD removal values (Table 2) in comparison to the DMP and TOC ones, could suggest the formation of recalcitrant intermediates. Scialdone *et al.*[32] also obtained high removal rates at temperatures of 50 and 70 °C during the electrooxidation of oxalic acid using a DSA® electrode ($Ti/IrO_2-Ta_2O_5$). This behavior was a consequence of the attenuation of water oxidation. A similar behavior was noticed by Chatzisymeon *et al.*[46] who attained high phenol removal rates at high temperatures (60-80 °C) using a Ti/IrO_2 anode.

After optimizing the investigated variables, a prolonged electrolysis (300 min) was carried out. Figure 7 shows the DMP concentration and TOC decay as a function of the electrolysis time for the optimized conditions for 5 h of electrolysis. The DMP electrooxidation was carried out with the concomitant mineralization ($\phi = 0.98$ after 300 min of electrolysis) thus, the possible formation of recalcitrant intermediates might have been suppressed. The instantaneous current efficiency (ε_{inst}) decreases when the Q_{ap} increases as a consequence of the organic load abatement and the consequent increase of the O_2 evolution reaction. The relative decay of DMP concentration and TOC as a function of the electric energy consumption (*w*) for 5 h of electrolysis shows that the *w* required to attain 40% of DMP concentration and TOC removals is ca. 23 kW h m^{-3}.
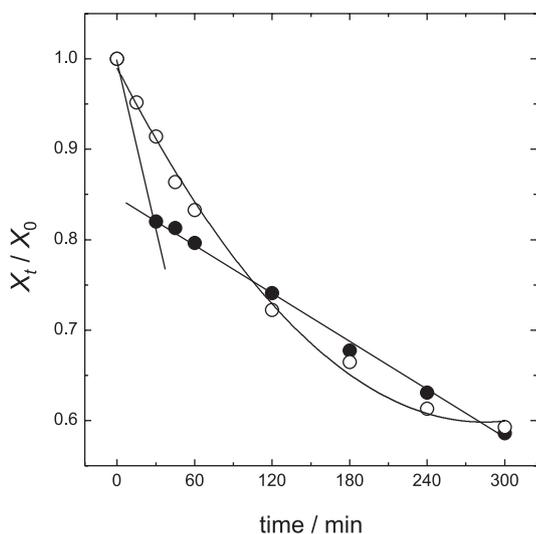
Figure 7. Relative (●) DMP concentration and (○) TOC decay as a function of the electrolysis time for the optimized conditions: 20 mA cm^{-2}, 30 °C, pH 2, and 7.04 mmol dm^{-3} NaCl. Constant ionic strength of 0.15 mol dm^{-3} with the addition of Na_2SO_4.

Conclusions

The electrochemical degradation of the DMP compound using the DSA® electrode exhibited low removal levels when compared to those using the BDD anode; however, it was interesting to observe that a considerable range of complete combustion was attained, which could indicate the decreased formation of intermediate compounds, when using low current densities. The electrolysis in the presence of low NaCl concentration exhibited the highest apparent first order kinetic constants for the DMP and TOC removals, possibly due to the low formation of recalcitrant organochlorine compounds. Furthermore, acidic conditions at high temperatures also yielded the best DMP and TOC removal rates, attributed to an increase in the oxidation power of the chlorine oxidative species, particularly Cl_2 and HOCl. Since the electrochemical system was under mass transport conditions, low current densities led to the highest levels of complete combustion and current efficiencies, as a consequence of diminished oxygen evolution reaction. Finally, the best conditions for the relation between maximum pollutant removal and energy saving can be attained at 20 mA cm^{-2}. The use of DSA® electrode could be an interesting option to treat effluents containing phthalates in the presence of chloride ions, as a consequence of its electrochemical stability, commercial availability and high extent of complete combustion; however, the need for acidic media to attain high removal rates could be the main drawback.

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