**Effect of the electrolyte on the electrolysis and photoelectrolysis of
synthetic methyl paraben polluted wastewater**

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Abstract

In this work, the electrochemical oxidation of methyl paraben (MeP) with diamond electrodes is studied. Results point out that this preservative can be easily removed from wastewater, either in sulfate or chloride media. Pollutant removal is faster in chloride media due to the chlorination of the molecule. However, mineralization is faster in sulfate media. Current density does not have a clear influence on the efficiency, explained by a mediated oxidation control of the process. Irradiation by UV light produces a synergistic effect on the process, which is greater in sulfate than in chloride media, a behavior that could be initially understood in terms of the formation of sulfate and chloride radicals. However, chemical tests showed that persulfate is not active for the oxidation of MeP neither in dark conditions nor under UV irradiation and that hypochlorite is active in the chlorination of the MeP molecule but not in the mineralization. Consequently, these results can be better explained considering the oxidizing effect of ozone and hydrogen peroxide, which are produced during the electrolysis on the surface of diamond, and that within the reaction conditions undertaken, are unstable and decompose to hydroxyl radicals. Regarding electrolysis in chloride media, although chlorates or perchlorates are produced, UV light significantly delays the appearance of both species.

Keywords

Methyl-paraben, diamond anodes, electrolysis, photoelectrolysis, synergism

Introduction

Parabens are esters of the *p*-hydroxybenzoic acid widely used as preservatives in food, pharmaceutical and cosmetic industry. Among them, methyl- and propyl-parabens are the most commonly used, frequently associated with other types of preservatives [1, 2]. Their large applicability is linked to a broad spectrum of antimicrobial activity, high stability (regarding thermal and pH variation) and low production cost, which results in a huge benefit-cost ratio [3]. However, several studies reported the action of parabens as endocrine disruptors [1-4] and related their uses with human breast cancer[5]. For this reason, some industries decided to replace those compounds for other preservatives, releasing the so-called “paraben-free” products. Nevertheless, the use of parabens is still controversial and is being regulated to low concentrations in several countries [6].

As a result of their widespread use, parabens have been detected in several environmental matrices, leading to high levels of human exposure [4]. Industrial wastewater discharges are considered the main source of releasing those compounds into water resource, due to a low efficiency of the treatments conventionally applied.

According to this necessity of removal of parabens from wastewater, several studies have been published in the recent years. They focus on different Advanced Oxidation Processes (AOPs), such as photocatalysis [6-10], sonochemical [11, 12] and oxidation by activated persulfate [13, 14]. In addition, there are other works focusing on the assessment of coupled technologies such as photo-biochemical process and ozonation coupled to corona plasma or to photocatalysis [15-18]. Anyhow, the main conclusions of these studies pointed out that parabens can be efficiently removed from the water, with removals close to 100%.

However, the mineralization of organic matter is more difficult to achieve, with results ranging from 15% to 66% of total organic carbon (TOC) removal. The efficiencies of the processes were found to be strongly dependent on the matrix composition and, hence, the higher is the complexity, the lower is the efficiency reached. In that context, coupled technologies have been demonstrated to be good alternatives to improve parabens mineralization.

Among the AOPs, electrochemical technologies have seem to exhibit good characteristics, either alone in anodic oxidation processes [19-21] or in combination with other techniques, such as sonoelectrochemical and photoelectrochemical processes [15-18, 22-24]. The complete removal of parabens and the mineralization of the organic load are generally attained [22-24], although efficiencies strongly depend on the nature of the electrode used [25]. However, there

is still room for more research in the topic and more information about the kinetics of the processes and about how to improve the efficiency is needed in order to design processes that can be widely applied. At this point, combination of electrolytic and photolytic processes can be seen as a good option. Electrolysis with diamond anodes is known to produce large amounts of oxidants from the interaction of the hydroxyl radicals formed on the surface of the anode with the different species contained in the water. In particular, interaction with anions of salts is very interesting from the viewpoint of the process efficiency, because of the formation of chlorine and perchlorate from chloride ions and peroxyanions from sulfate, carbonate, nitrate and phosphate anions [26-28]. All these oxidant species need to be activated in order to efficiently oxidize the organic matter contained in the waste and UV light irradiation seems to be one of the best ways to produce highly reactive radicals from them [29-32]. Meanwhile, the interaction of these radical species with organic matter depends on the functional groups of the pollutant molecules and, hence, there are cases in which a clear synergistic effect is observed while there are others in which the effect of light irradiation is nil or even antagonistic. For example, Martín de Vidales et al. [33, 34] observed that the UV light enhanced the electrochemical oxidation of progesterone solutions (both, in terms of pollutant removal and mineralization), while nil effects were observed in the case of sulfamethoxazole polluted wastewater. In the case of metoprolol and caffeine solutions, a synergetic effect was only observed in the removal of pollutant, but not of organic matter [35].

At this point, in this work we are focusing on the effects of this light irradiation during the oxidation of methyl-paraben (MeP), within a project in which we finally aim to know the reactivity of this species in complex matrixes where it can be found in actual cases. To do this, results obtained during the electrolysis and photoelectrolysis of synthetic wastewater polluted with MeP in chloride and sulfate media are going to be discussed and compared to those obtained in chemical oxidation test. It is aimed to shed light on the mechanisms of the anodic oxidation of this pollutant.

Materials and methods

Chemicals. Methyl paraben was obtained from Sigma-Aldrich. Na₂SO₄, NaCl and H₂SO₄ (all purchased from PanReac) were used as supporting electrolyte and for pH adjustment. Starch solution (1%), KI, Na₂S₂O₃, NaOH and As₂O₃, used for determination of oxidants, were supplied by Sigma-Aldrich. Acetonitrile, HPLC grade was obtained from VWR Chemicals.

High-purity water obtained from a Millipore Milli-Q system (resistivity >18M cm at 25 °C) was used for the preparation of all solutions. All reactants were used as received.

Experimental set-up. Experiments were carried out in a bench scale flow system described elsewhere [36]. A single compartment electrochemical cell with a plate of boron doped diamond (BDD) as anode and a plate of stainless steel as cathode (both with surface area of 75 cm²) was used for electrolysis. A HQ-Power PS3010 power supply (0-30 V, 0-10 A) provided the applied current density. For photochemical experiments, a low-pressure Hg vapor lamp (Vilber Lourmat model VL-215.MC, $\lambda = 254$ nm, 15 W) was coupled to the reservoir, directly irradiating the working solution. The system operates in a discontinuous mode in which the electrochemical cell is coupled to a peristaltic pump (PERCOM-I, JP Selecta, Barcelona, Spain) and to a glass tank, used to store 1 L of solution. A thermostatic bath (Digiterm 100, JP Selecta) was used to maintain the solution temperature at 25 °C.

Analytical techniques. Concentration of methyl paraben was monitored by high performance liquid chromatography (HPLC) in an Agilent Technologies 1260 chromatographer, equipped with an Eclipse Plus C18 (3.5 μ m 4.6 x 100 mm) and UV detector set in 280 nm. Acetonitrile and water (60:40 v/v) was used as mobile phase, at 25 °C and flow rate of 1 mL min⁻¹. Total organic carbon (TOC) was determined in a Multi N/C 3100 Analytik Jena analyzer. A GLP22 CRISON and GLP 31 CRISON were used for measurements of pH and conductivity, respectively. Inorganic anions (Cl⁻, ClO₃⁻ and ClO₄⁻) were measured by ion chromatography using a Shimadzu LC-20A system [37]. Since those compounds interfere in the hypochlorite peak, its measurement was carried out by titration, with a solution of As₂O₃ in 2.0 M NaOH. Oxidizing power of the solution was determined by iodometric titration.

Synergistic index. The synergy index (SI) is used to evaluate the effect of the coupling of different processes and it is calculated according to **Eq. 1**, where k_{p1-p2} , k_{p1} and k_{p2} are the kinetic constants for the coupled process and the individual processes 1 and 2, respectively.

$$SI = \frac{k_{p1-p2}}{k_{p1} + k_{p2}} \quad (1.)$$

Results and discussion

Fig. 1 shows the oxidation of methyl paraben (MeP) as function of time and current charge passed (inset) for electrolysis carried out at current densities (j_{app}) ranging from 15 to 60 mA cm⁻². MeP is completely oxidized in the three tests carried out and, as expected, the higher the

current density applied, the faster is the oxidation of MeP. Complete removal of the compound is achieved at 300 and 180 min for 30 and 60 mA cm⁻², respectively. Conversely, in the electrolysis carried out at 15 mA cm⁻², the total oxidation of the pollutant is not attained within the duration of the test (8 hours), although the trend clearly indicates that this complete oxidation can be attained by extending the electrolysis for a longer period.

The inset of **Fig. 1** shows that results are almost overlapped when the MeP decay is plotted against the specific current charge passed. That is, for the same electric current charge passed, the same oxidation degree of MeP is attained. In fact, only a very small improvement is observed by lowering the current density. This result indicates that the process is limited by mass transport, which is the expected response for diffusion-controlled systems, well-described in the literature [38-40]. However, results obtained here point out that mediated oxidation should be playing an important role, even much more important than the oxidation carried out on the surface of the anode and in the nearness of it (direct-like oxidation processes). At this point, it is worth to remind that the synthetic wastewater that undergo the three electrolysis tests is a solution containing high concentrations of sulfate. As it is known sulfate is transformed into peroxosulfates during electrolysis with diamond anodes [41]. This powerful oxidant is expected to combine with other oxidants formed in the reaction media and hence, to extend the oxidation reactions to the bulk of the wastewater promoting the formation •OH and SO₄• in the whole volume of treated wastewater.

Removal of total organic carbon (TOC) is presented in **Fig. 2**. The inset shows that almost total mineralization is achieved at 480, 240 and 180 min during the electrolysis carried out at 15, 30 and 60 mA cm⁻², respectively. Results are also plotted in semi-log and hence, the linear trend observed indicates that the electrolysis fits a first order kinetics [42]. However, it is possible to observe not only one but two regions of *pseudo*-first order kinetics, suggesting a change in the oxidation mechanism of organic matter during the electrolysis test. The values k_1 and k_2 , presented in **Tab. 1**, are the respective kinetic constants calculated for each region. The transition of kinetics occurs when approximately 80% of the MeP is converted to organic intermediates. At this point, it is expected the significant presence of low molecular carboxylic acids, such as malic, malonic, tartaric and oxalic acids, which have very different oxidation behavior respect to the MeP [43, 44]. The oxidation of these compounds seems to may be favored in the presence of sulfate radical anions formed [45, 46] during the electrolysis with diamond anode and this may explains the increase observed in the kinetics constants (**Tab. 1**)

which are more than doubled than those obtained by fitting experimental results to the first kinetic zone.

Once clarified the feasibility of the electrolysis with diamond anodes to mineralize MeP, and clarified that the current density has almost no effect on the efficiency of process, in the search of better efficiencies, wastewater undergoing the electrochemical process was irradiated with 254 nm UV light (photoelectrolysis). In addition, the effect of supporting electrolyte was also evaluated, by comparing results obtained in the electrolysis of wastewater containing chloride and sulfate salts. As it is known, in the first case hypochlorite is the main expected mediator [47], while in the second, the main mediator expected is peroxosulfate [30]. Hence, great differences are expected. In addition, both species can be activated in a different way with UV light and, hence, light irradiation can be expected to influence on results in a very different way. **Fig. 3** shows the removals of MeP and TOC as function of time in sulfate and chloride medium during electrolysis (ECh) and photoelectrolysis (PECh) test carried out at 30 mA cm⁻². For comparison purpose, results obtained during photochemical (PCh) process are also shown.

Photolysis process did not show significant removal of MeP or TOC. Just small changes that indicates a minor transformation of the raw molecule and that are reflected on the TOC values (which are even higher than the initial values, perhaps because of the different response of the TOC equipment to this molecule). On the other hand, both the electrochemical process irradiated and non-irradiated, were capable to completely removed MeP in both studied media.

In chloride medium, 100% of MeP removal was achieved within less than 20 min of electrochemical and photoelectrochemical treatment. It is well-known that for electrochemical wastewater treatments in this medium, the ClO⁻ generated rapidly converts the pollutants in organochlorinated compounds[48, 49]. Thus, it is expected high conversion of MeP by the chlorination of the aromatic ring, as the first step of the degradation mechanism. This is in accordance with the observed removal of TOC, which shows slower rate of organic matter removal, justified by the high chemical stability of organochlorinated molecules (**Fig. 3a**). On the other hand, in the presence of sulfate, complete removal of MeP is obtained between 240 and 300 min of the applied electrochemical process (electrolysis and photoelectrolysis). The main oxidizing agent in this medium is SO₄^{-•} species, which promotes the breakdown of MeP by attacking C-C bonds. As a result, the removal of pollutant and organic matter are practically concomitant as **Fig. 3b** shows. Higher efficiency can be observed for the TOC removal with

the irradiated process, indicating that UV light activates persulfate anions, increasing the formation of $\text{SO}_4^{\bullet-}$ species which are more reactive than the peroxosulfate anion [50].

Kinetics of mineralization and the respective kinetics constants are presented in **Fig. 4** and **Tab. 2**. Although photochemical process showed small oxidation of MeP, about 17% and 5% in Cl^- and SO_4^{2-} media (**Fig. 3**), the values of kinetic constant calculated for PCh process are very close to zero, indicating that no TOC removal was achieved in those conditions. Additionally, the negative values observed can be explained by the dispersion of the points.

For the other processes, it is possible to observe two kinetic regions, being faster the degradation at the end of the electrolysis test, just in the moment in which carboxylic acids intermediates are the key species in the water treated. Complete mineralization was achieved for the electrochemical processes irradiated and non-irradiated with UV light, but higher kinetic constants were obtained for the coupled process.

This has an important effect on the treatment results that it is higher than that which can be expected with the addition of the two single processes. Thus, a SI of 1.66 is observed for the photoelectrolysis in sulfate media and this value is still high, although slightly lower, in the case of the chloride media (1.40). As it is known, SI values above 1.0 indicate a synergism between processes (the higher the value, the higher the effect). Thus, in both cases the irradiation of UV light improves the results and as discussed before, UV irradiation can contribute to the activation of persulfate anions, but also, hypochlorite, generating $\text{SO}_4^{\bullet-}$ and $\text{Cl}^{\bullet}$ species, which are responsible for the improvement observed in the coupled process. Thus, radical species are expected to be produced by light decomposition of peroxosulfates (**Eq. 2**) [51, 52] and hypochlorite (**Eq. 3** and **4**) [53]. In this later case, it has been demonstrated that under non-extreme pH condition, chlorine radicals (**Eq. 3**) and hydroxyl (**Eq. 4**) are the main products resulting from the light assisted degradation of hypochlorite.

Both radicals have a high redox potential, higher in the case of $\text{SO}_4^{\bullet-}$ (2.5 – 3.1 V) compared to $\text{Cl}^{\bullet}$ (2.2 – 2.6 V) that can help to explain the higher synergistic effect observed. **Fig. 5** shows the changes in the oxidants measured in solution and the changes in the speciation of chlorine during the electrolysis and photoelectrolysis. It is important to see how the amount of oxidants available are much higher during the electrolysis carried out to solutions containing chloride

(more than one log-unit) and how irradiation of light seems to have a positive effect on this concentration. This does not correspond to the more efficient mineralization observed in sulfate medium and points out the discrepancies between the oxidants measured (those that do not react) and the oxidation observed. Thus, this oxidation is more important in the case of the sulfate media, although concentration of oxidants measured is much lower. This is not a contradiction though; it only suggests that oxidants formed are rapidly used for oxidation of other compounds once formed.

Regarding the speciation of chlorine, both electrolysis and photoelectrolysis promote the formation of chlorates and perchlorates and the only effect of light irradiation is a small delay in the production of these two species that match with the higher concentration of oxidants observed in this case. As it is known, chlorates and perchlorates are not efficient in the oxidation of organic compounds at the operation conditions studied. This means that the formation of these species has a negative impact on the efficiency of the process.

Hence, there are important differences between the oxidation of MeP in sulfate and chloride media, and in both cases light improves the efficiency of the process, although in a more important way in the electrolysis of the MeP wastewater that contained sulfate. In order to clarify the role of mediated oxidation and of the main species involved in the degradation of MeP, four sequences of chemical oxidation tests have been carried out: ClO^- oxidation in presence and absence of UV light and $\text{S}_2\text{O}_8^{2-}$ oxidation in presence and absence of UV light. To do this, a given amount of hypochlorite (to attain a concentration of 0, 0.01, 0.24 and 0.60 g L^{-1}) and peroxodisulfate (to attain a concentration of 0, 1.3, 4.9 and 8.8 g L^{-1}) was added to 60 mL of MeP solution and the system was kept under UV irradiation (254 nm) or dark conditions over 4 hours, moment in which remaining oxidants, MeP and TOC were measured. **Fig. 6** shows the results obtained in terms of MeP removal and oxidants remaining after the treatment.

As expected, hypochlorite and peroxodisulfate reactivity is quite different: hypochlorite rapidly reacts with MeP and this disappears immediately by chlorination of the aromatic ring (as observed also during electrolysis), while peroxodisulfate does not seem to attack to MeP molecule. In both cases, TOC remains almost constant after the 4 h of chemical oxidation test. Similar results are obtained in UV-irradiated tests. On contrary of that expected, UV-light does not seem to promote the activation of the hypochlorite and peroxodisulfate, and thus the effect of UV-light irradiation is almost nil. This fact indicates that the synergetic effects observed during photoelectrolysis technology may not only be related to the light-activation of these

species. Thus, other activation mechanisms, such as chemical activation by interaction with other oxidants electrogenerated in the electrolyte, must be promoted in the electrochemical cell. In addition, the effect of other oxidants has to be considered in order to explain the experimental evidence.

At this point, it is worth to mention that during electrolysis a cocktail of oxidants are known to be formed and that they coexist (in significant concentration) in the nearness of the electrode surface, being the interaction between them very important. Thus, it is reported the formation of hydrogen peroxide by coupling hydroxyl radicals (**Eq. 5**) or the ozone formed by oxidation of oxygen (**Eqs. 6 and 7**) [54]. These reactions develop in the very nearness of the electrode surface but the stability of these species is larger than that of hydroxyl radicals and it allows their transport to the bulk improving the electrolytic efficiency.

However, despite being less active than hydroxyl radicals, these oxidants do have a very important chemical reactivity and this reflects in the fact that despite they can be measured, it is plausible that their production would be much higher than the concentrations measured. Thus, they can combine to form hydroxyl radicals (**Eq. 8**) [55] or they can undergo light decomposition by reactions proposed in **Eq. 9 and 10** [56, 57], reintroducing again the hydroxyl radicals not in the nearness of the electrode surface but in the bulk of the wastewater.

Moreover, these two species can also react with peroxosalts leading to the formation of radicals of the precursor peroxosalts and/or to hydroxyl radicals. Hence, according to the results obtained and the differences observed between irradiated chemical oxidation tests and photoelectrolysis essays, the role of hydrogen peroxide and ozone in the mediated oxidation during electrochemical processes should be even higher than that expected, as they seem to act as radical precursors.

Conclusions

From this work, the following conclusions can be drawn:

- Methyl paraben can be fully mineralized by electrolysis with diamond anodes in synthetic wastewater containing chloride and sulfate salts. Although removal of the pollutant is faster in chloride media, its mineralization is more efficient in sulfate media.
- From the kinetic point of view, the electrolysis and photoelectrolysis of MeP solutions fits well to first order kinetics although two zones can be clearly distinguished. The kinetic constants calculated in the second zone are more than double of the calculated in the first zone, indicating the high reactivity of intermediates formed.
- Irradiation of UV light has a synergistic effect on the electrolysis of MeP in sulfate and chloride media. The SI is higher in the case of sulfate and this can be explained in terms of the harsher oxidation conditions produced in this media.
- Electrolytic results do not match with the results of chemical test in which the reactivity of hypochlorite and persulfate are studied. This suggests that other oxidants formed in the reaction media (in particular hydrogen peroxide and ozone) can play a very important role in the mediated oxidation observed during the electrolysis of wastewater.

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Table caption

Tab. 1 Observed kinetics constants for the removal of TOC by electrochemical process in 3 g L⁻¹ of Na₂SO₄

Tab. 2 Observed kinetics constants for TOC removal by electrochemical processes irradiated and non-irradiated by UV, in 3.0 g L⁻¹ of Na₂SO₄ and 3.7 g L⁻¹ of NaCl

TABLE 1

j_{app} (mA cm⁻²)	k₁ (min⁻¹)	k₂ (min⁻¹)
15	0.0024	0.0056
30	0.0074	0.0150
60	0.0116	0.0366

TABLE 2

Medium	Process	k₁ (min⁻¹)	k₂ (min⁻¹)
SO₄⁻²	ECh	0.0074	0.015
	PCh	-0.00007	
	PECh	0.0122	0.0311
Cl⁻	ECh	0.0039	0.0179
	PCh	-0.00005	
	PECh	0.0054	0.021