Competitive anodic oxidation of methyl paraben and propylene glycol: keys to understand the process

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Abstract

This work focuses on the competitive oxidation of two very different molecules, when they underwent electrochemical oxidation with diamond electrodes. To shed light on the mechanisms of this competitive oxidation, solutions containing methyl paraben and propylene glycol at different ratios are electrolyzed (using sulfate or chloride supporting electrolytes). Results obtained pointed out that removal of both species can be easily attained by the electrochemical process, being promoted the mineralization by the action of the sulfate derivative products and the formation of chlorinated hydrocarbons by the action of chlorine oxidants, although the mechanisms of the oxidation do not depend on the primary anion contained in the waste. The higher the concentration of species to be oxidized, the higher is the amount of intermediates and the slower is the mineralization the ratio influences. An important outcome is that there is a limit concentration in each one organic compound interferes on the degradation of a pollutant. Thus, the interference effect of PG on MeP oxidation was only observed for low MeP/PG ratios.

Highlights

- Methyl paraben and propylene glycol can be completely exhausted from wastewater by anodic oxidation.
- Chloride ions promote fast oxidation of pollutants and sulfate faster mineralization.
- There is a limit concentration for the interference of organics.
- The interference effect of PG on MeP oxidation was only observed for low MeP/PG ratios.
- Higher concentrations of organic matter promoted faster abatement of initial pollutants but hinders the mineralization process.

Introduction

Over the last years, hundreds of papers have been published regarding the electrochemical oxidation of wastewater, using either single anodic oxidation or more complex processes, such as those which integrate Fenton and/or UV or US irradiation in the same electrochemical cell [1-6].

Nowadays, operating conditions to attain mineralization are well-known, but there is still slot for research, in particular when wastewater to be degraded consists of a complex matrix of components. In this context, competitive oxidation is one of the most interesting points to be clarified [7-9]. This is because the concentration of pollutants has a critical influence on the performance of electrochemical treatment technologies, as most of them operate typically under diffusion control. Many efforts are being carried out in the recent years in order to deal with this limitation, including the combination of electrochemical technologies with concentration operations [10-13].

However, this is a novel approach to solve the problem and, traditionally, the improvement in the efficiency has been faced by promoting the formation of highly-effective oxidants in the electrolyte during the electrolysis of wastewater. This approach has two bottlenecks:

- the electrodic formation of the oxidants, which is strongly related to the electrode material used, and
- the activation of the oxidants electrogenerated, which can be carried out chemically or by irradiation of UV light and ultrasound.

Formation of oxidants lead to the development of many competitive oxidation processes. In the case of the oxidation with diamond anodes, because of the generation of many different oxidants during the electrolysis, this competitive oxidation has to be well-understood in order to get more efficient processes than those that are being studied nowadays.

Thus, it is well-known that during the electrochemical oxidation with diamond anodes of wastes containing sulfates, carbonates and phosphates with diamond anodes, the hydroxyl group can be transformed into a peroxo group allowing the production of peroxosulfates, peroxocarbonates and peroxophosphates [14]. This helps to explain the much better efficiencies observed in the diamond electrolysis of wastewater when these anions are present, in particular when results are compared to those obtained by the Mixed Metal Oxides electrodes (MMO).

The situation reverses when chloride is the key anion in the waste. Electrolysis with diamond does not stop in the formation of chlorine (which later disproportionate to give hypochloric acid /hypochlorite) but it continues up to the formation of chlorates and perchlorates, which despite are more powerful oxidants for the thermodynamic point of view, they exhibit a lower effect, because they are kinetically slower at room temperature [15, 16].

Up to now, the description of the electrochemical processes faced in most of the work published in the literature is phenomenological, simply describing the observations made. However, the chemistry of mediated processes is important, and its study needs for some additional work which gives insights about the mechanisms followed. Previous studies on the treatment of mixtures are reported using contaminants with similar chemical properties [17-19]. However, in terms of degradation, the key difference between pollutants is based on their aromatic or aliphatic structure [20-23]. Hence, when a comparison is to be done, it is good to select two very different models of pollutants to be oxidized.

In this work, we are going to face the evaluation of the competitive electrochemical oxidation by comparing the degradation of propylene glycol, an aliphatic short chain molecule (with easily-oxidizable alcohol groups), with that of methyl paraben, an aromatic molecule, whose degradation in simpler wastewater was previously carried out by our group [24]. We aim to determine if these species are degraded simultaneously or if there is any preference for the oxidation of one of them during the electrolysis and how the ratio between the concentrations of both species influence on the rate of oxidation of each of them.

Results and discussion

Propylene glycol was chosen as an organic interfering in order to evaluate its effect on the degradation of methyl paraben. For that, MeP and PG were firstly studied individually (100 mg dm^{-3} and 1 g dm^{-3}, respectively), then two mixtures of MeP-PG were prepared using the proportions: 1:10 (w/w), referred as M1 and 1:100 (w/w), referred as M2, in which the initial concentration of MeP was always 100 mg dm^{-3}. **Fig. 1** shows the removal of pure MeP and pure PG in chloride and sulfate medium, in which better removal efficiency is observed in the presence of Cl^- anions for both compounds.

It is well stablished that electrolysis with BBD anodes, in chloride medium will generate hydroxyl radicals ($^\bullet OH$) and active chlorine species (Cl_2, HClO and ClO^-) as main oxidants (Eqs. 1-5), which can promote fast chlorination of the organic molecules [4, 16, 25].

$$H_2O \rightarrow {}^{\bullet}OH + e^- + H^+ \qquad (1)$$

$$2\ Cl^- \rightarrow Cl_2 + 2\ e^- \qquad (2)$$

$$Cl^- + {}^{\bullet}OH \rightarrow ClO^- + H^+ + e^- \qquad (3)$$

$$Cl_2 + H_2O \leftrightharpoons HOCl + H^+ + Cl^- \qquad (4)$$

$$HOCl \rightleftharpoons H^+ + ClO^- \qquad (5)$$

On the other hand, in sulfate medium, the main oxidants are ${}^{\bullet}OH$ and persulfate ($S_2O_8^{2-}$) and/or persulfate radicals ($SO_4^{-\bullet}$), according to Eqs. 6-8 [4, 26, 27]. Those species promote the rupture of the organic molecule, which is a slower mechanism than halogenation and, thus, slower removal of MeP and PG are obtained [28]. Electrochemical oxidation of PG showed *pseudo*-first order kinetic with two regimes, in which the transition occurs at 120 min of treatment, as presented in **Fig. 1b**. The kinetic change can be attributed to two phenomena: *i*) the formation of reactive intermediates, that may be favored to be oxidized under specific conditions, with respect to PG and *ii*) the higher concentration of intermediates compared to PG, which will also decrease its removal. Likewise, MeP presents *pseudo*-first order kinetic for its electro oxidation, as it was reported in previous studies [24, 29].

$$2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e^- \qquad (6)$$

$$SO_4^{2-} + {}^{\bullet}OH \rightarrow SO_4^{-\bullet} + OH^- \qquad (7)$$

$$S_2O_8^{2-} + {}^{\bullet}OH \rightarrow 2\ HSO_4^- + SO_4^{-\bullet} + ½\ O_2 \qquad (8)$$

Although chloride medium clearly favored the removal of MeP and PG, it is important to verify the mineralization obtained in each condition. **Tab. 1** resumes the results for the removal of organic matter. MeP was 100% mineralized in both media before ending the treatment (8 hours), differently from PG, that even after 8 hours there was still TOC remaining. Anyhow, sulfate medium showed better results for both systems, which can be explained by the oxidation mechanism in each case. Persulfate radicals react more selectively by electron transfer, promoting the rupture of carbon bonds, therefore, the removal of TOC takes place almost simultaneously to the compound elimination. Even though the addition of a Cl atom to the compounds is a faster process, it will result in organochlorinated compounds, which means that no organic carbon is removed and the mineralization tends to be slower [24].

Steter *et al.* [30] also studied MeP degradation on a BDD anode with air-diffusion cathode, in order to evaluate electro-Fenton and photoelectro-Fenton processes.

Electrochemical process achieved 77% and 86% of mineralization, in 6 hours, for sulfate and chloride medium, respectively. Even at the best condition, photoelectro-Fenton process using sulfate as electrolyte, the organic matter was not completely mineralized after 360 min (97% TOC removal was attained). It is interesting, though, that chloride was found as a better medium for electro-mineralization than sulfate, differently from the results here presented. To explain that, it is necessary to take into account the scavenger effect of $ClO^-/HClO$ on H_2O_2. Hydrogen peroxide is also produced in the medium due to the recombination of $^{\bullet}OH$ radicals (Eq. 9). However, hypoclorite and hypochlorous acid can react with those species, decreasing the oxidizing power of the solution, according with Eqs. 10-11 [31].

$$2\ ^{\bullet}OH \rightarrow H_2O_2 \qquad (9)$$

$$ClO^- + H_2O_2 \rightarrow Cl^- + O_2 + H_2O \qquad (10)$$

$$HClO + H_2O_2 \rightarrow Cl^- + O_2 + H_2O + H^+ \qquad (11)$$

Fig. 2 presents the oxidation of MeP and PG when the mixtures (M1 and M2) were treated by electrochemical process. Complete removal was achieved for MeP regardless of the medium complexity (**Fig. 2a**). In M1 the results are the same as MeP pure: faster elimination in chloride than sulfate medium, achieving 100% of removal before 40 min and before 360 min for Cl^- and SO_4^{2-}, respectively. However, when PG concentration is increased (M2), the removal of MeP is not favored by Cl^- presence, and the behavior observed is the same for both media. **Fig. 2b** shows the removal of PG with two kinetic regions and the total percentage achieved (*inset* of **Fig. 2b**). In agreement with MeP results, PG presents the same behavior in M1 as well as in pure solution, as it can be confirmed by the kinetic constants presented in **Tab. 2**, where k_1 and k_2 are the constants for the first end second regions, respectively. Similar values of both constants are observed for pure PG and in M1. However, in M2 its oxidation is favored, leading to an increased kinetic rate (up to $9.2.10^{-3}$ min^{-1}) and almost complete removal (up to 96.5%). These results suggest that methyl paraben molecule can be oxidized easier than PG due to its carbonyl group and aromatic ring. However, at higher concentrations of PG, MeP molecules are statically less available to be oxidized, which decreases its degradation and accelerate the oxidation rate of PG. Similar results were obtained by Abdessamad *et al.* [17], which studied the anodic oxidation of a mixture of dyes and observed that the increase in one dye proportion results on its faster removal, due to its predominance in solution.

It is interesting to note that in the cases of PG individually and in M1, the kinetic changes to a lower rate, whereas in M2 the opposite behavior is observed. After 2 hours of treatment, approximately 50-60% of PG and 80-100% of MeP were already removed (M1), hence, the concentration of byproducts may be comparable to the reminiscent propylene glycol. This condition favors the degradation of react intermediates and, consequently, decreases the kinetic rate of PG removal, as it was mentioned before. On the other hand, M2 could be treated by two hypotheses, due to the very high initial concentration of PG (10 g L^{-1} initial): *i*) oxidant species are not in great excess and, thus, the oxidation reaction is dependent of both reactants (second order kinetic) or *ii*) the concentration of oxidants is still very high with respect to PG, resulting in *pseudo*-first order kinetics. In the first case, the data could still fit first-order model, however the kinetic constant would be different when the initial concentration is varied (M1 to M2), which is not verified in this specific case (k_1 values in **Tab. 2** are very similar). Hence, the second hypothesis must be true; in that case, the change on the kinetics is attributed to the intermediates formation, as mentioned before. However, if the intermediates are, by any means, not favored to be oxidized with respect to PG, it may accelerate its removal. In other words: it means that the intermediates do not interfere in PG oxidation because they are not simultaneously removed.

This theory is confirmed by the TOC results presented in **Fig. 3a**, in which no removal of organic matter is observed for M2, whereas TOC is highly removed in M1. Gozzi *et al.* [18] studied the oxidation of mixtures of two pesticides at different ratios and also observed that the increase of one compound results in slower removal of TOC. This effect was attributed not only to the higher organic content of the solution, but also to the fact that the intermediates resulted from the predominant compound are more recalcitrant than the ones from the other compound. As mentioned before, PG is an aliphatic molecule more difficult to oxidized than the aromatic structure of MeP. Hence, it is expected that PG intermediates, also aliphatic, are more recalcitrant than MeP products, which agrees with the fact that PG and its intermediates are not simultaneously oxidized. Overall, **Fig. 3b** confirms those results: 100% of COD is removed in M1 in contrast to only 30% in M2. However, chloride medium seems to be slightly better than sulfate. In COD analysis, organic compounds are almost completely oxidized under drastic conditions applied (stronger oxidant species and very high temperature). However, during the analysis some volatile molecules can evaporate and remain in the gas phase, where no oxidation occurs [32]. The formation of volatile intermediates would explain greater removals of COD when compared to TOC, mostly in chloride medium, where small chlorinated compounds (volatile disinfection byproducts) are likely to be formed.

By any means, as already observed for the MeP and PG individually, the mineralization is favored by sulfate medium, achieving 97% in contrast with 87% obtained in the presence of chloride, probably because of the formation of organochlorinated intermediates, which are more hardly degradable compounds. The fact that higher concentration of PG resulted in its faster removal, but null mineralization, when compared to M1 behavior, indicates that the oxidation mechanism is different in each mixture. Therefore, either the electrolyte nature or the concentration of the organic compounds will lead the degradation to a different oxidation route, affecting the efficiency of the process.

At this point, it is interesting to note that MeP and PG were detected in different HPLC systems. MeP was analyzed in a C18 column with UV detection, in which was possible to observe the formation of some intermediates and their follow removal (not shown), during the 8 hours, in all studied cases. According to the methodology used, these results are indicative about the complete or almost complete degradation of any aromatic byproducts, which means that the remaining organic matter (when TOC removal < 100%) have aliphatic characteristics. Though, any confirmation on intermediates nature needs to be done by identification of those compounds. On the other hand, PG was analyzed in a biphenyl column with RID (refractive index detector). In this case, very few intermediates could be detected for PG pure and M1, in contrast to a great amount of products observed in M2. These results reinforce the previous discussion about how the high concentrations of PG inhibit the oxidation of the intermediates.

Previous studies [29, 30] reported the electrochemical mechanistic route of MeP mineralization with diamond anodes in both sulfate and chloride media. A schematic representation of those findings is presented in **Fig. 4**. Steter *et al.* found that methyl paraben in $^\bullet$OH presence, may firstly undergo two reactions: i) direct hydroxylation of the aromatic ring by hydroxyl radicals, and ii) nucleophilic attack of $^\bullet$OH, leading to the release of $-OCH_3$ group and yielding *p*-hydroxy benzoic acid (MeP precursor). After that, decarboxylation reaction may take place to form hydroquinone, followed by the rupture of the aromatic ring and the generation of small carboxylic acids (left scheme in **Fig. 4**). In the presence of $HClO/ClO^-$, those reactions will similarly occur due to $^\bullet$OH, which are produced in high concentrations. However, the compounds will also suffer chlorination as presented in the right side of **Fig. 4**. One or more atoms of Cl can be added to both MeP and the *p*-hydroxy benzoic acid, which will further cleavage into aliphatic polychlorinated compounds. Hence, in both media the mechanism leads to the formation of small carboxylic acids, which are the last byproducts before mineralization. Furthermore, PG is an aliphatic alcohol and, thus, its oxidation intermediates will also be small aliphatic compounds. Those compounds are usually more difficult to be oxidized and tend to remain in the solution, restraining the complete mineralization.

Hence, considering those pathways, chromatography analyses were carried out to determine carboxylic generated as main byproducts on the degradation of the mixtures, and their respective behavior during the process. Intermediates with the highest concentrations and detected in most of the samples are presented in **Fig. 5**, as I1 to I6. Compounds 1 to 3 are produced in almost all conditions, 4 and 5 only appear in chloride medium, which suggests that they are organochlorinated compounds, and 6 could only be detected as byproduct of M2 degradation. Intermediates of M1 degradation are produced and removed during the treatment, meanwhile in M2 it is observed the accumulation of the byproducts I2 and I6, achieving very high concentrations. These findings agree with previous results, where no mineralization is attained for M2, and intermediates are simultaneously removed with PG and MeP in M1, which changes the respective kinetics of oxidation.

Fig. 6 represents the intermediates that could be identified by external standard analysis: I1, I2, I3, I5 and I6 as oxalic, acetic, tartronic, dichloroacetic and formic acids, respectively. Firstly, it is important to remember that is not possible to state that those compounds are certainly products of MeP or PG, only that they were generated by the oxidation of these analytes. However, all of those are certainly reasonable to be products of PG oxidation and, thus, the possible conversions between them are also represented. According to that, propylene glycol could undergo via two mainly pathways: a) via tartronic acid, leading to oxalic or formic acids before mineralization or b) via acetic acid, yielding oxalic acid or dichloroacetic acid, when in the presence of $HClO/ClO^-$, which are further directly mineralizied.

In fact, oxalic acid is the main carboxylic acid expected as byproduct from electro oxidation with diamond anodes, thus its formation in almost all conditions were already anticipated [33, 34]. However, it was possible to observe that in chloride medium lower concentrations of this compound were achieved, and even no oxalic acid was detected for M1 in the presence of Cl^-. This result seems to indicate that the chlorination reaction is favored under those conditions, producing several halocarboxylic acids before the complete mineralization is attained. Those compounds are likely to be recalcitrant and non-volatile, which also explains the lower efficiency of this medium for mineralization.

It is important to remember that besides the identified intermediates other byproducts were also formed, however in much lower concentrations. As the best of the authors knowledge, there is no description of electrooxidation of PG by $^{\bullet}$OH radical or active chlorine species on the literature. However, compounds such as hydroxyacetone, latic acid and pyruvic acid were already reported as main byproducts of PG by other oxidation methods, and could also be expected as intermediates on this study [35-38]. Furthermore, it must be considered that treatments with active chlorine species, usually yield small stable byproducts, which most of them are volatile, such as chloroform, and cannot be detected by this study.

Conclusions

From this work, the following conclusions can be drawn:

- Methyl paraben and propylene glycol can be completely exhausted from wastewater, regardless of the complexity of the wastewater in which these pollutants are contained.
- Higher removals of MeP and PG were attained in chloride medium. However, the mineralization is favored under the presence of sulfate radicals.
- The main intermediate in the MeP oxidation is the formation of hydroquinone, which is followed for the rupture of the aromatic ring and the generation of several aliphatic carboxylic acids. The presence of chloride ions does not change the oxidation mechanism but favors the production of polychlorinated compounds.
- PG undergoes two main oxidation pathways that produce oxalic and formic acids as last products before the complete mineralization. The presence of chloride anions favors the acetic acid path and inhibits the oxalic acid formation, favoring the production of small chlorinated byproducts.
- There is a limit concentration in each one organic compound interferes on the degradation of a pollutant. The interference effect of PG on MeP oxidation was only observed for low MeP/PG ratios.
- Higher concentrations of organic matter promoted faster abatement of initial pollutants. However, it hinders the mineralization process, which accumulates great content of small aliphatic compounds, mainly acetic and formic acids.

Experimental section

Chemicals

All solutions were prepared with ultrapure water (resistivity >18M cm at 25 ºC) from a Millipore Milli-Q system. Methyl paraben and propylene glycol were purchased from Sigma-Aldrich and studied individually (100 and 1000 mg dm^{-3}, respectively) and in mixtures of 1:10 and 1:100 (w/w) of MeP:PG. Sodium sulfate (3.0 g dm^{-3}) and chloride (3.7 g dm^{-3}) , both obtained from Panreac, were used as supporting electrolyte. Acetonitrile for chromatography were obtained from VWR Chemicals. All reactants were used as received.

Experimental set-up

Experiments were carried out in an electrochemical system described elsewhere [39]. Electrodes of boron doped diamond (BDD) and stainless steel, both with 75 cm^2, respectively, were used to treat 1 dm^{-3} of working solution for 8 hours. A peristaltic pump (PERCOM-I, JP Selecta, Barcelona, Spain) maintained the flow rate at 7 cm^{-3} s^{-1}. A HQ-Power PS3010 power supply (0-30 V, 0-10 A) provided the applied current and a thermostatic bath (Digiterm 100, JP Selecta) maintained the solution temperature at 25 ºC.

Analytical techniques

High performance liquid chromatography was used monitor the concentration of MeP and PG and to identify intermediates by internal standard method. MeP was determined with an Eclipse Plus C18 column (3.5 µm, 4.6 x 100 mm) and mobile phase of acetonitrile:water (60:40 v/v), at 25 ºC, flow rate of 1 cm^3 min^{-1} and UV detector set in 280 nm. PG was analyzed in a Kinetex biphenyl column (5 µm, 4.6 x 150 mm) with 1 cm^3 min^{-1} of water as mobile phase, at 25 ºC and refraction index detector. Its signal (2.2 min) was quantified by a mathematical model of deconvolution, developed based on the chromatograms of water, pure PG and PG solution in all studied media. Small carboxylic acids were determined in an Agilent Hi-Plex H column (7.7 x 300 mm) and 5 mmol dm^{-3} of H_2SO_4 (flow rate of 0.5 cm^3 min^{-1}), at 30 ºC and UV detector set in 220 nm. Total organic carbon (TOC) was quantified in a Multi N/C 3100 Analytik Jena analyzer. Inorganic anions (SO_4^{2-}, ClO_3^- and ClO_4^-) were measured by ion chromatography using a 930 Compact IC Flex (Metrohm).

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Keywords

competitive oxidation; electrolysis; diamond anodes; methyl paraben; propylene glycol.

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Table 1 Removal of organic matter for the degradation of methyl paraben (100 mg dm^{-3}) and propylene glycol (1000 mg dm^{-3}) in 3.0 g dm^{-3} of Na_2SO_4 and 3.7 g dm^{-3} of NaCl

Medium	MeP (time for mineralization)	PG (TOC removal after 8h)
SO_4^{2-}	5 hours	97%
Cl^-	6 hours	87%

Table 2 Kinetic constants for the electrochemical removal of PG in pure solution and in the mixtures M1 (1:10) and M2 (1:100), using 3.0 g dm^{-3} of Na_2SO_4 or 3.7 g dm^{-3} of NaCl

Medium	k_1 (10^{-3} min^{-1})	k_2 (10^{-3} min^{-1})
PG - SO_4^{2-}	4.4	1.5
PG - Cl^-	7.5	3.0
M1 - SO_4^{2-}	4.6	1.5
M1 - Cl^-	6.9	3.1
M2 - SO_4^{2-}	5.0	5.8
M2 - Cl^-	4.3	9.2

Figure 1 Electrochemical removal of **a)** MeP (100 mg dm^{-3}) and **b)** PG (1000 mg dm^{-3}), using 3.7 g dm^{-3} of NaCl (empty symbols) and 3.0 g dm^{-3} of Na_2SO_4 (full symbols).

Figure 2 a) Electrochemical removal of MeP (100 mg dm^{-3}) and **b)** kinetics of PG electrooxidation, in (■) M1 (1:10) and (▲) M2 (1:100), using 3.7 g dm^{-3} of NaCl (empty symbols) and 3.0 g dm^{-3} of Na_2SO_4 (full symbols). Inset: Percentage of removal of PG in each studied mixture (Na_2SO_4 (left) and NaCl (right)).

Figure 3 Removal of **a)** TOC and **b)** COD of (■) M1 (1:10) and (▲) M2 (1:100), using 3.7 g dm^{-3} of NaCl (empty symbols) and 3.0 g dm^{-3} of Na_2SO_4 (full symbols).

Figure 4 Resume of the possible oxidation mechanism of methyl paraben on a BDD anode, in sulfate (left) and chloride (right) media. Adapted from Steter *et al*., 2014 (figure 6) and Steter *et al*., 2016 (figures 9 and 10) [29, 30].

Figure 5 Concentration of the main aliphatic intermediates detected during the treatment of M1 (**a** and **b**) and M2 (**c** and **d**) in 3.0 g dm^{-3} of Na_2SO_4 and 3.7 g dm^{-3} of NaCl. ● I1, ▲ I2, × I3, ○ I4, * I5 and ◇ I6.

Figure 6 Carboxylic acids identified as intermediates of the degradation of MeP and PG mixtures in 3.0 g dm^{-3} of Na_2SO_4 and 3.7 g dm^{-3} of NaCl.

FIGURE 1

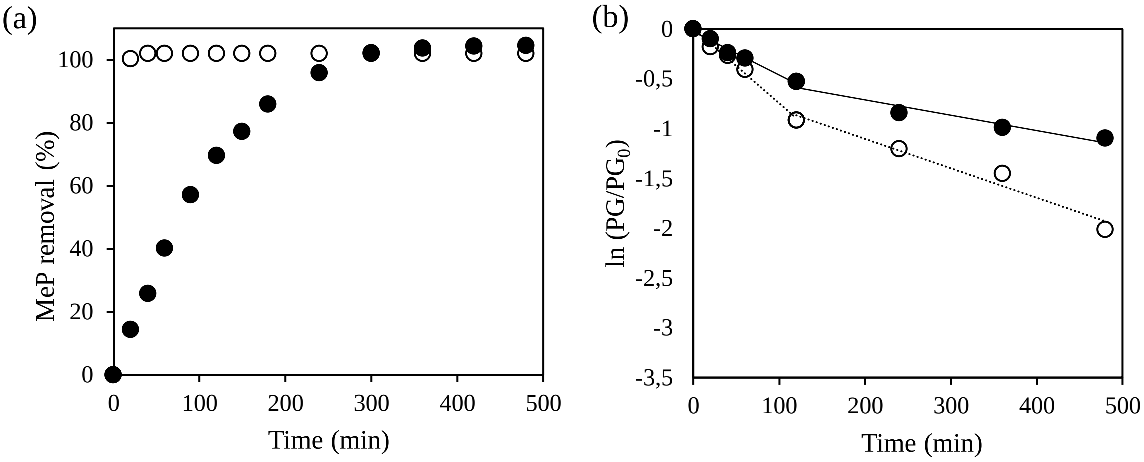

(a)
MeP removal (%)
0
20
40
60
80
100
0
100
200
300
400
500
Time (min)
(b)
ln (PG/PG$_0$)
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
0
100
200
300
400
500
Time (min)

FIGURE 2

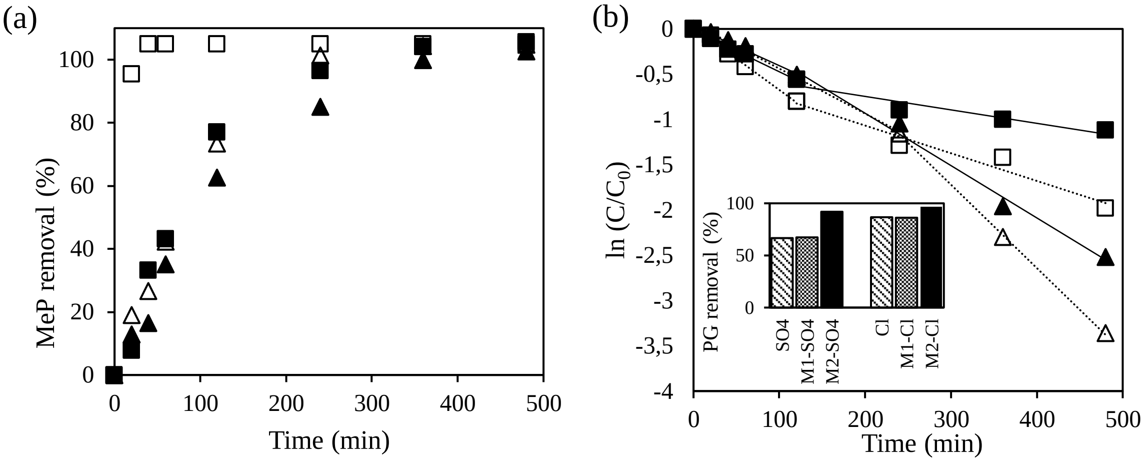

(a)
MeP removal (%)
0
20
40
60
80
100
0
100
200
300
400
500
Time (min)
(b)
ln (C/C$_0$)
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
-4
0
100
200
300
400
500
Time (min)
PG removal (%)
0
50
100
SO4
M1-SO4
M2-SO4
Cl
M1-Cl
M2-Cl

FIGURE 3

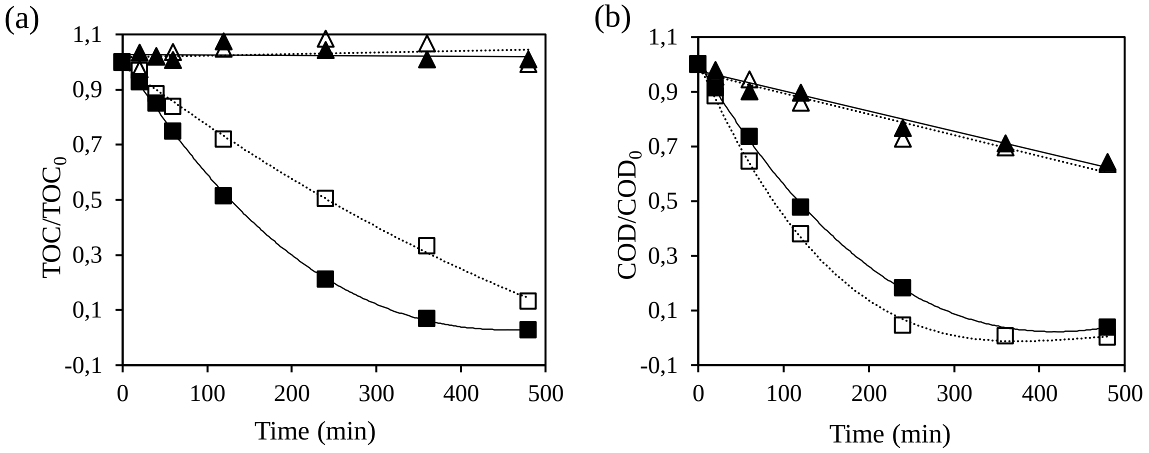

(a)
1,1
0,9
0,7
0,5
0,3
0,1
-0,1
TOC/TOC$_0$
0
100
200
300
400
500
Time (min)
(b)
1,1
0,9
0,7
0,5
0,3
0,1
-0,1
COD/COD$_0$
0
100
200
300
400
500
Time (min)

FIGURE 4

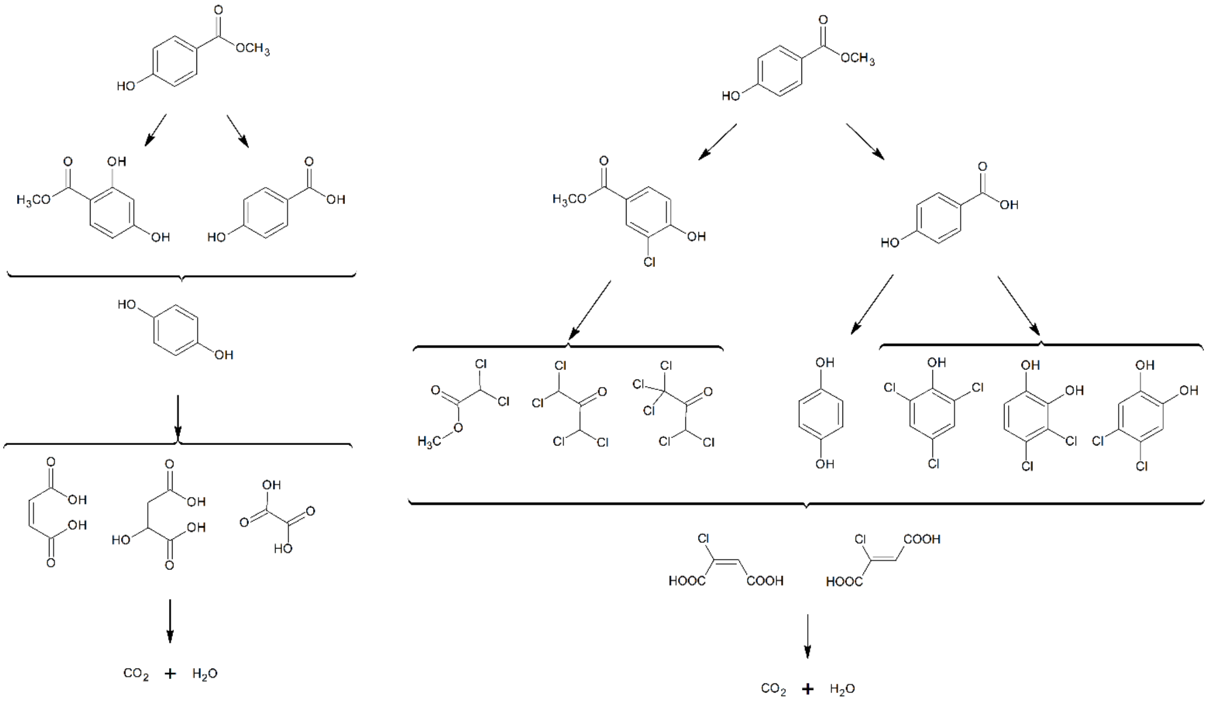


FIGURE 5

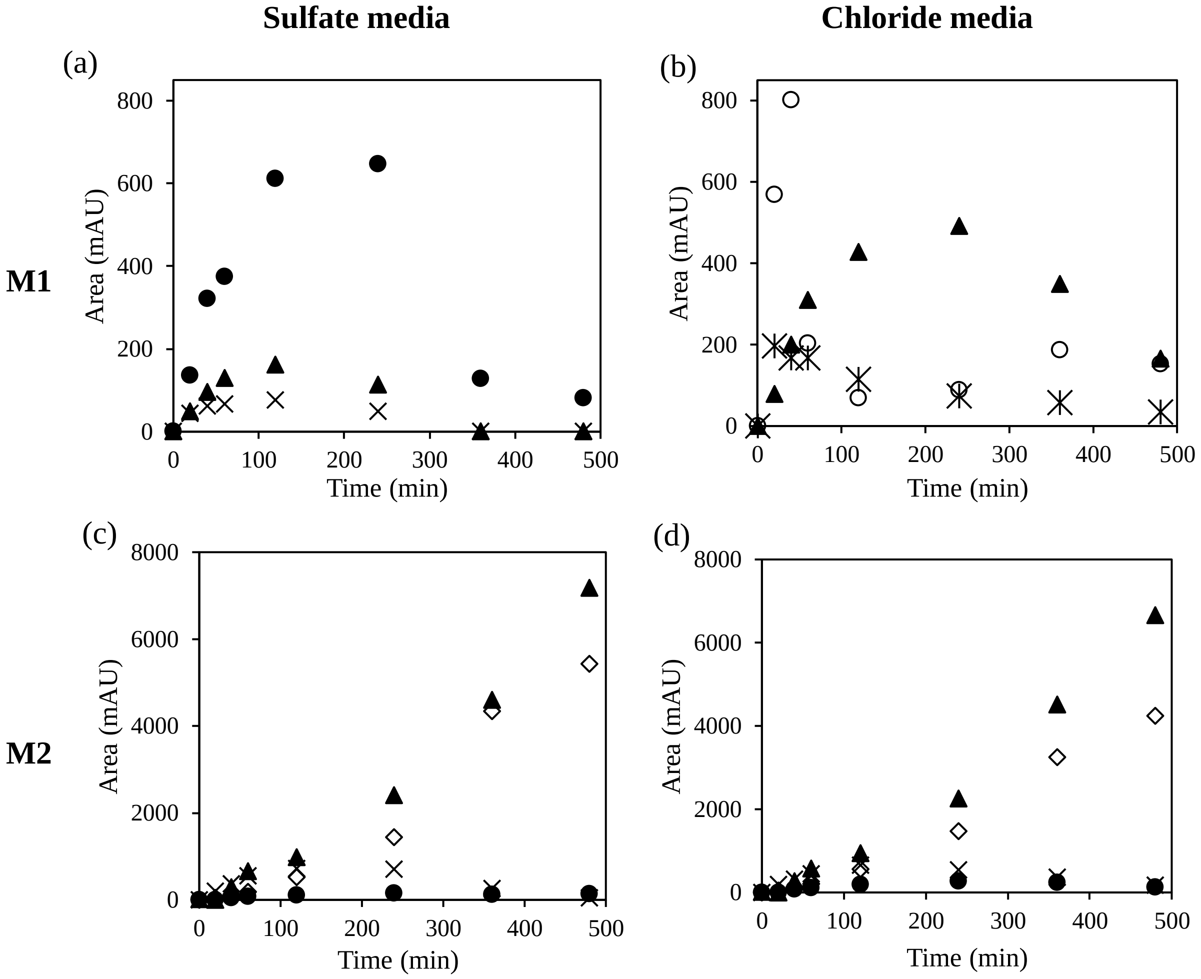

Sulfate media
Chloride media
M1
M2
(a)
(b)
(c)
(d)
Area (mAU)
Time (min)
0
100
200
300
400
500
200
400
600
800
2000
4000
6000
8000

FIGURE 6

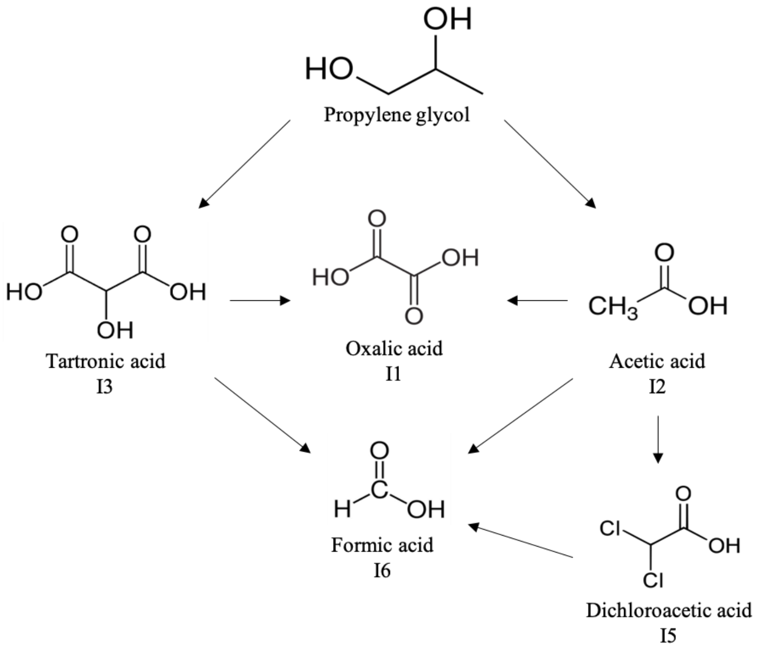
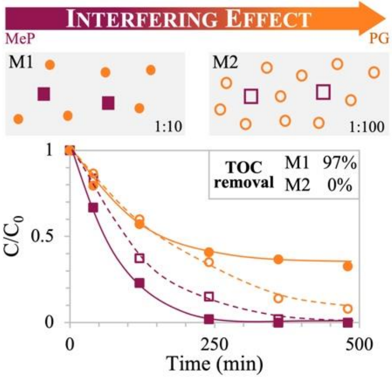

Propylene glycol
Tartronic acid
I3
Oxalic acid
I1
Acetic acid
I2
Formic acid
I6
Dichloroacetic acid
I5

Table of Contents

ARTICLE

What is the effect of the competitive oxidation of pollutants? There is a limit concentration in which an organic compound interferes on the degradation of a contaminant. Interference effect of PG (propylene glycol) on MeP (methyl paraben) oxidation was only observed for low ratios of MeP/PG. Higher concentrations of organic matter promoted faster abatement of initial pollutants but completely hinders the mineralization process.



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Competitive anodic oxidation of methyl paraben and propylene glycol: keys to understand the process