Electrochemical oxidation of butyl paraben on boron doped diamond in environmental matrices and comparison with sulfate radical-AOP

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Abstract

The electrochemical oxidation (EO) of butyl paraben (BP) over boron-doped diamond (BDD) anode was studied in this work. Emphasis was put on degradation performance in various actual water matrices, including secondary treated wastewater (WW), bottled water (BW), surface water (SW), ultrapure water (UW), and ultrapure water spiked with humic acid (HA). Experiments were performed utilizing 0.1 M Na_2SO_4 as the electrolyte. Interestingly, matrix complexity was found to favor BP degradation, i.e. in the order WW~BW>SW>UW, thus implying some kind of synergy between the water matrix constituents, the reactive oxygen species (ROS) and the anode surface. The occurrence of chloride in water matrices favors reaction presumably due to the formation of chlorine-based oxidative species, and this can partially offset the need to work at increased current densities in the case of chlorine-free electrolytes. No pH effect in the range 3-8 on degradation was recorded. EO oxidation was also compared with a sulfate radical process using carbon black as activator of sodium persulfate. The matrix effect was, in this case, detrimental (i.e. UW>BW>WW), pinpointing the different behavior of different processes in similar environments.

Keywords: aqueous matrix; anodic oxidation; carbocatalysis; electrolytes; emerging contaminants; persulfate

1. Introduction

Advanced oxidation processes (AOPs, e.g. heterogeneous and homogeneous photocatalysis, electrochemical oxidation (EO), ozonation, ultrasound irradiation, Fenton and alike reactions, amongst others) have been investigated for the removal of emerging organic pollutants during the last decades (Klavarioti et al., 2009). Micropollutants' removal from water matrices has been recognized as an important environmental and health issue. Water matrix may exert influence on the electrochemical treatment on boron-doped diamond (BDD) anode. This is due to the high concentrations of numerous interfering organic and inorganic species, which are usually present in real effluent samples (Tsantaki et al., 2012). So far, the majority of studies concerning the application of AOPs for water/wastewater treatment have been performed (and still are) in ultrapure water. The rationale behind this is associated with the need to obtain basic knowledge with respect to the degradation kinetics, mechanisms and pathways excluding the water matrix effect. Nonetheless, the effect itself may be unpredictably important, thus leading to erroneous conclusions. In most cases, treatment efficiency decreases with increasing water matrix complexity. This is due to the fact that the target pollutant is likely to compete with the non-target constituents of the matrix (e.g. organics, inorganics and microorganisms) for the precious oxidant species, as well as (in the case of heterogeneous processes) for the active sites of the catalysts/activators (Frontistis and Mantzavinos, 2017). In the study of Kenova et al. (2018), on the electrooxidation of Mordant Blue 13 azo dye in different water matrices, both electrode material and water matrix parameters have been reported to significantly affect COD removal and dye decolorization.

Electrochemical oxidation has emerged as an environmentally clean technology and BDD has been shown to be one of the most auspicious anodes for environmental applications (Frontistis et al., 2017; Sarkka et al., 2015). BDD anodes are known to enhance the generation of ROS compared to other anodic materials (Pecková et al., 2009); this facilitates the effective conversion of organic micropollutants of emerging concern and, subsequently, their mineralization. However, the exact mechanisms of O_2 and $^{\bullet}OH$ production have not been completely elucidated (Henke et al., 2019; Kraft et al., 2003).

Sulfate radical oxidation processes (SR-AOPs) have recently been developed for water treatment. Sulfate radicals can be produced after activation of compounds belonging to the group of persulfates. Activation can occur via numerous methods including, amongst others, heat, transition metals, light irradiation and ultrasound irradiation (Matzek and Carter, 2016). In recent years, metal-free carbonaceous materials have been proposed as alternative catalytic materials for environmental applications (Abid et al., 2016), including persulfate activation. Activated carbon, graphene, multi-walled carbon nanotubes and biochars are some characteristic examples. Carbon black (CB), mainly consisting of fine particles of carbon, has recently been proposed as a low-cost

alternative to expensive carbon materials, such as graphene, in the field of electrochemistry showing great performance as an electric conductive agent (Lounasvuori et al., 2018).

Parabens are synthetic chemicals used as preservatives in a wide variety of products, like pharmaceuticals, cosmetics and food. Parabens are excreted through urine as 4-hydroxybenzoic acid (Fransway et al., 2019b), and are considered contaminants of emerging concern (Frontistis et al., 2017). In medications, they are recommended at concentrations of no more than 0.1%, and they are allowed as preservatives in cosmetics at concentrations up to 0.4% when used alone (in the United States). The acceptable daily intake (ADI) has been calculated to be 10 mg/kg of body weight (Fransway et al., 2019a, 2019b; Reeder and Atwater, 2019; Liao et al., 2013).

Concerns exist regarding the endocrine discruption or carcinogenicity associated with parabens. However, it should be noted that controversial results have been reported for their health effects (Reeder and Atwater, 2019; Haman et al., 2015). Since parabens are ubiquitous in environmental matrices worldwide, efficient treatment processes must be employed for their elimination and to avert their accumulation (Haman et al., 2015).

Few articles exist on parabens treatment by advanced oxidation processes, and specifically by electrochemical methods (Gomes et al., 2016), and even less dealing with BDD oxidation (Frontistis et al., 2017; Dominguez et al., 2016; Steter et al., 2014a; 2014b). It should be noted that the studies of Steter et al. (2014a; 2014b) focus on the elimination and mineralization of an unrealistically high concentration of methyl paraben for environmental samples (100 mg/L). Much lower parabens concentrations (in the range of μg/L) have been measured in influent of domestic wastewater treatment plants (WTP) (Giger et al., 2009). Dominguez et al. (2016) examined parabens decomposition efficiency by BDD oxidation in aqueous matrices and found that the initial concentration was the most important factor. Notably, an increase of the initial paraben concentration caused a decrease of the efficiency of their removal. Interestingly, a synergistic effect on the efficiency of removal has been recorded in surface water (river). This finding was attributed to the probable presence of chloride ions, the resulting rise of solution conductivity and the formation of additional secondary oxidant species that diffuse in the bulk solution (Dominguez et al., 2016).

In one of our previous studies (Frontistis et al., 2017) regarding the BDD mediated oxidation of ethyl paraben at environmentally rational concentration (at the μg/L concentration level), we found that the removal rate followed a pseudo-first order kinetic expression concerning paraben concentration and depended on the type of supporting electrolyte, the current density, and the complexity of the water matrix. In the context of the same study, reaction mechanisms were postulated by identifying major transformation by-products and elucidating reaction pathways with different electrolytes.

In the present study, we further focused on the water matrix effect on the BDD anodic oxidation for the degradation of BP at a concentration level of 0.5 mg/L, by studying various water matrices, including bottled water, secondary effluent, surface water, ultrapure water and ultrapure water spiked with humic acid. Moreover, anodic oxidation was compared to SR-AOP concerning process efficiency in actual matrices to highlight how possible interferences amongst target and non-target water constituents may dictate treatment performance.

2. Experimental and analytical

2.1. Chemicals

Butyl paraben (BP) ($HO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}(CH_2)_3\text{-}CH_3$, CAS no: 94-26-8) was provided by Sigma-Aldrich. Solutions were prepared by using ultrapure water (UW, pH=6.5) which was derived from a Millipore Milli-Q Gradient A10 system. To test the effect of matrix, various actual water matrices, including WW, BW, SW, UW, and UW spiked with HA were used. For experiments with BW, a commercially available natural mineral water was used. WW was sampled from the WTP of the University of Patras, while SW was collected from the region of Attica, Greece (TOC = 2.7 mg/L, pH = 7.5). More details on BW, WW and SW characteristics are given elsewhere (Frontistis et al., 2017; Tsiampalis et al., 2019). Technical grade humic acid (HA, CAS no: 1415-93-6) was supplied from Sigma-Aldrich. Sulfuric acid or sodium hydroxide used for pH adjustment, sodium chloride, sodium sulfate, sodium bircabonate, sodium persulfate (SPS: $Na_2S_2O_8$), methanol and t-butanol were purchased from Sigma-Alrdich. Carbon black (CB: Vulcan XC72R) was supplied by Cabot.

2.2. Reactor setup and experimental procedure

The experimental set up of the electrochemical reactor consised of two electrodes (a boron doped diamond electrode served as the anode and a 304 stainless steel electrode served as the cathode, both with a surface area of 8 cm^2). More information can be found in other studies of our group (Kouskouki et al., 2018; Frontistis et al., 2017). In specific expirements, stainless steel and platimum with a surface area of 8 cm^2 were also used as anode to examine the effect of the anodic material.

In order to evaluate the influence of operating conditions on BP removal, experiments were conducted at 1.4-143 mA/cm^2 current density, 0.1 M electrolyte concentration and 250-2000 μg/L BP concentration. Experiments were performed at their inherent pH, except of the experiments that were conducted at acidic or alkaline conditions with the addition of the appropriate volume of H_2SO_4 or NaOH.

For SR-AOP experiments, a pyrex vessel of 250 mL capacity open to the atmosphere was employed. In a typical run, 120 mL of an aqueous solution containing 0.5 mg/L BP was loaded in

the vessel followed by the addition of CB and SPS. The solution was under continuous magnetic stirring.

From either reacor, samples of 1.2 mL were collected at specific times, filtered with a 0.22 μm syringe filter (PVDF) and then measured as follows.

2.3 Determination of BP

High performance liquid chromatography (Waters Alliance 2695) interfaced with a photodiode array detector (Waters 2996) was used for the detection of BP. Separation was achieved on a Kinetex XB-C18 100A column (2.6 μm, 2.1 mm x 150 mm) and a 0.5 μm inline filter (KrudKatcher Ultra) both purchased from Phenomenex. The mobile phase, consisting of 50:50 UW:acetonitrile, eluted isocratically at 0.25 mL/min and 45°C, while the injection volume was 100 μL.

3. Results and discussion

3.1. Effect of operating conditions on degradation

3.1.1. Effect of the anodic material

Wide variations exist between different electrode materials as it concerns their efficiency to oxidize water to $^{\bullet}OH$ or O_2, and the nature of adsorbed radicals/electrode surface interaction.

In the present study, preliminary experiments were performed to investigate the effect of anodic material (BDD, stainless steel, platinum) on the degradation of 0.5 mg/L BP at 50 mA/cm^2 current density with 0.1 M Na_2SO_4 in UW and the results are presented in Figure 1. As can be seen, complete destruction of BP was achieved in 15 min of treatment with BDD anode, while the removal was about 40% and 18% for steel or platinum anode, respectively. BP removal was solely due to electrochemical processes and not just adsorption on the BDD surface as preliminary equilibration experiments had shown.

The results are in agreement with the work of Kouskouki et al. (2019), who observed complete removal of 245 μg/L piroxicam at 26.7 mA/cm^2 on BDD after 15 min of electrooxidation, while only 15% removal occurred in the presence of platinum.

The better efficiency of BDD anodic material compared to that of steel or platinum, may be attributed to the larger production of $^{\bullet}OH$ on its surface. BDD is classified as "non-active" electrode, thus the surface of the BDD has only a physical interaction with $^{\bullet}OH$ and, consequently, a greater production of hydroxyl radicals without forming higher oxides (Murugananthan et al., 2008). Likewise, a much better efficiency of BDD in comparison to RuO_2, glassy carbon, Pt, and PbO_2, anodes has been described by Burgos-Castillo et al. (2018) and Murugananthan et al. (2008). Frontistis et al. (2018) reported that BDD was found to be more effective than platinum, since ampicillin abatement after 10 min of electrolysis was 39% and 68% for platinum and BDD,

respectively. Similarly, BDD was found to have a significantly higher efficiency compared to platinum for the EO and mineralization of salicylic acid (Guinea et al., 2008). In the study of Barazesh et al. (2016), degradation rates normalized per surface area of BDD anode were several times (i.e. 100−2500%) greater than in Ti−IrO_2.

BDD is considered as an ideal anodic material due to outstanding chemical, physical and electrochemical properties compared to other conventional electrode materials. The results of the present study confirm this finding, further supporting the technology of EO over BDD anodes which holds great promise to provide efficient wastewater treatment solutions.

3.1.2. Effect of applied current

Since electrons represent the energy input of the system, the role of the applied current is vital. The increase in current density favors the formation of $^{\bullet}OH$, which in turn may maximize the mineralization of organic pollutants. Figure 2 shows the effect of applied current density on 0.5 mg/L BP degradation in UW with 0.1 M Na_2SO_4. As seen in Figure 2A, which shows concentration-time profiles, an increase in current density results in increased conversion. Complete oxidation of BP can be accomplished within 5 min at 107-143 mA/cm^2, 10 min at 71 mA/cm^2, and 15 min at 50 mA/cm^2. Figure 2B shows the effect of current density on the apparent rate constant, k_{app}, assuming that the electrochemical decomposition of BP follows pseudo-first order kinetics. Apparent rate constants are calculated from the slope of the straight lines associated with the plot of the logarithm of normalized concentrations over time (plots are not shown for brevity). Frontistis et al. (2018) showed that the rate of the degradation of antibiotic ampicillin remarkably increased by increasing current density. Similarly, a three-fold increase in the oxidation rate of ethyl paraben over BDD was recorded when the current augmented from 10 to 70 mA/cm^2 (Frontistis et al., 2017). Dominguez et al. (2016) showed that current density affected BDD oxidation of parabens in a statistically significant manner, in both UW and river water; in other studies (Dominguez et al., 2010), the influence of current on carbamazepine degradation over BDD was found to be the single most important variable followed by the concentration of salt and the flow rate. Abdelhay et al. (2017) showed that increasing applied current density positively affected the removal of color, COD, and turbidity of slaughterhouse wastewater. In the study of Deligiorgis et al. (2008), on BDD electrolysis of table olive processing wastewater, a statistically significant effect of the current, the initial COD, and the contact time on the degradation of phenols and COD was recorded. In another study, Murugananthan et al. (2008) found that bisphenol A (BPA) oxidation was a current-controlled process and occurred faster at greater current densities. In the study of Kenova et al. (2018), the decolorization of Mordant Blue 13 dye followed exponential decay with k_{app} increasing with increasing applied current density. According to the authors, a remarkable increase in the dye

removal rate at higher current density was due to the formation of additional radicals and other oxidizing species, (e.g. sulfate radicals, peroxodisulfate anions, H_2O_2). The removal of COD was increased with specific charge. However, the variation of current density had almost no effect on COD removal. This finding suggests the crucial role of mediated oxidation in the electrochemical oxidation. Interestingly, the work of Anglada et al. (2011) on the BDD electrolysis of landfill leachate showed that no statistically significant effect of the applied current on the removal of the pollutants was noted, under the studied conditions.

3.1.3. Effect of BP concentration

Figure 3 shows the influence of BP concentration on its degradation at 50 mA/cm^2 current density in UW with 0.1 M Na_2SO_4. Increasing initial concentration decreases the rate, which implies that the concentration of oxidants generated during the process is a limiting factor for the decomposition of organics. In fact, the rate that the oxidants are produced is expected to be nearly constant at fixed operating conditions, i.e. current density and the electrolyte used. Thus, the rate BP is degraded is a function of its concentration relative to the oxidants available for reaction and it decreases at higher BP concentrations. It should be noted here that although degradation data can still be fitted adequately to a pseudo-first order kinetic model from which k_{app} values are computed (shown next to the respective profiles in Figure 3), it is clear that the reaction is not true first order since rate constants change with initial BP concentration. In fact, this behavior implies a transition of rate order in regards to BP from first to zeroth.

Dominguez et al. (2016) showed that the initial parabens concentration was the unique most influential factor for their electrochemical removal in ultrapure water and river water; an increase in the organics concentration resulted in a decline in the efficiency. Frontistis et al. (2018) found that nearly complete degradation of ampicillin could be reached after 20 min of treatment, independently of the initial concentration in the range 0.8-3 mg/L. Moreover, the percent removal was higher for lower concentration of ampicillin. This finding indicates that ampicillin removal did not follow true first order kinetics with regards to the concentration of ampicillin. In another study of Murugananthan et al. (2008), it was shown that BPA conentration could affect its mineralization, especially at the early stages of the reaction. An increase of the mineralization current efficiency (which is a measure of energy consumption) was recorded with increasing pollutant concentration, and decreasing current density (Murugananthan et al., 2008).

3.1.4. Effect of water matrices

Since electrochemical oxidation aims at treating real wastewater, the efficiency of the method in real aqueous matrices and not only in synthetic wastes is of particular interest. Figure 4A shows the

effect of various actual water matrices, including WW containing ca 10 mg/L organic carbon and inorganics, BW containing mainly ca 250 mg/L bicarbonate, SW, UW, and UW spiked with 10 mg/L HA (i.e. to simulate the natural organic matter of waters), on the degradation of 0.5 mg/L BP at 50 mA/cm^2 current density with 0.1 M Na_2SO_4. Interestingly, matrix complexity seems to favor BP degradation, i.e. the rate decreases in the order WW~BW>SW>UW, thus implying some kind of synergy between the organic and/or inorganic water matrix constituents, ROS and the anode surface. The findings of the present study are in agreement with previous studies of our group (Frontistis et al., 2017), where the researchers examined the BDD electrooxidation of 200 μg/L ethyl paraben in 0.1 M Na_2SO_4. The promotion of oxidation reactions in the bulk solution as a result of the indirect formation of reactive oxygen species, produced by the presence of different inorganic ions like SO_4^2, Cl^-, etc, may be the reason behind this finding (Katsaounis and Souentie, 2013; Velegraki et al., 2010).

Indeed, Dominguez et al. (2016), in their study on parabens BDD oxidation, observed a great synergistic effect on the oxidation efficiency in the river water matrix, possibly due to the presence of chloride ions at high concentration (40.4 mg/L), which augments the solution conductivity and favors the formation of secondary oxidants such as HClO/ClO^- or chlorine.

Regarding the presence of HA, it is well known that HA negatively affects the oxidation process by competing with BP for reactive species and electrode surface sites, leading to reduced degradation rates (Frontistis et al., 2018; Fernandes et al., 2016b). For example, Woisetschläger et al. (2013) noted that glucose degradation became progressively inhibited by increasing the amount of HA. Similarly, in the study of Frontistis et al. (2018) on the BDD electrochemical destruction of antibiotic ampicillin, the presence of 10 mg/L of HA led to a decrease in the observed kinetic constant by 40%. It must be noted here that although HA is typically selected as an analogue of the natural organic matter in water matrices, the effluent organic matter in WW may also contain other species such as soluble microbial products and traces of non-biodegradable pollutants. In this view, the use of HA may not be fully representative of the organic content in WW matrices.

Figures 4B and 4C show the effect of the addition of NaCl and $NaHCO_3$, respectively, while Figure 4D shows the effect of the addition of sodium persulfate (SPS) in UW which is a mild oxidant (redox potential of 2.1 V) and has the ability to oxidize organic pollutants (Ioannidi et. al., 2018). Furthermore, SPS activation causes the production of sulfate radicals with a redox potential of (2.5–3.1) V, according to reaction (1), which can be used for the elimination of organic pollutants (Matzek and Carter, 2016; Ghanbari et al., 2017).

$$S_2O_8^{2-} + e^- \rightarrow 2SO_4^{2-} + SO_4^{-\bullet} \qquad (1)$$

The presence of bicarbonate anion slightly slows down the rate of oxidation of BP (Figure 4C) possibly as a result of the fact that the bicarbonate anion scavenges hydroxyl radicals (Wu and Linden, 2010). In contrast, the addition of chloride (Figure 4B) favors the reaction presumably due to the formation of chlorine-based oxidative species, including chlorohydroxyl radicals according to reactions (2-7). In bibliography, the positive effect of Cl^- has often been underlined (Garcia-Espinoza et al., 2018; Frontistis et al., 2017; Katsaounis and Souentie, 2013). Garcia-Espinoza et al. (2018), focused on the effect of electrocatalytically generated active chlorine on carbamazepine destruction.

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

$$Cl^- \rightarrow Cl^\bullet + e^- \quad (3)$$

$$Cl^\bullet + Cl^\bullet \rightarrow Cl_2 \quad (4)$$

$$Cl^\bullet + O_2 \rightarrow ClO_2 \quad (5)$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \quad (6)$$

$$HClO \overrightarrow{\leftarrow} ClO^- + H^+ \quad (7)$$

Similar results with the present study were reported by Lebik- Elhadi et al. (2018). They investigated the BDD anode oxidation of thiamethoxam with 0.1 M Na_2SO_4 and mentioned that the addition of NaCl at concentrations reaching 100 mg/L increased degradation. They also reported that the k_{app} was 0.72 min^{-1} at 100 mg/L NaCl and 0.22 min^{-1} without NaCl. A similarly positive but less pronounced effect was recorded for the addition of 100 and 200 mg/L sodium persulfate (Figure 4D). This behavior can be attirbuted to the electrochemical activation of persulafte for the generation of selective sulfate radicals (Frontistis et al., 2018; Chen et al., 2018).

Candia-Onfray et al. (2018) showed recently that high concentrations of sulfate and chloride support the production of oxidants (e.g. active chlorine species, hydroxyl radicals) that can eventually oxidize the organic loading of winery wastewater in the bulk solution. In the work of Oliveira et al. (2018) focusing on the electrooxidation of industrial phenolic wastewaters, it was shown that the presence of chloride in the wastewater favored the electrogeneration of strong oxidant species, (mainly hypochlorous acid, but also chlorine, and hypochlorite) and increased the efficiency of the process. The effect of the presence of chloride ion on the oxidation process of various synthetic samples was also studied by Fernandes et al. (2016a), who reported that the presence of chlorides enhanced the removal of organic matter and nitrogen. The same research group (Fernandes et al., 2016b) studied the EO of HA and sanitary landfill leachate samples. It was

312 shown that the conversion of organics and nitrogen increased with the chloride ion concentration,
313 and the applied current density.
314 However, it should be noted that although electrochemical degradation is usually enhanced by
315 chloride ions, this is unfortunately accompanied by the formation of undesired organochlorinated
316 by-products. These products alongside with residual chlorine may both be incriminated for elevated
317 post-treatment ecotoxicity (Garcia-Segura et al., 2015; Katsoni et al., 2014; Boudreau et al., 2010).
318 Barazesh et al. (2016) showed that transformation rates for the vast majority of the contaminants in
319 industrial wastewater increased with chlorides, but high concentrations of HCO_3^- frequently altered
320 transformation rates because of the creation of selective oxidants. Electron-poor contaminants were
321 found to have a decreased reactivity, while compounds with phenolic and amine moieties were
322 characterized by increased reactivity. In the same study, it was found that the addition of 10 mM
323 HCO_3^- declined the degradation of different pollutants by 50% to 75% relative to the conversion in
324 10 mM NaCl (Barazesh et al., 2016).
325 Treatment performance may also be affected by effluent pH (Tsantaki et al., 2012), whose effect
326 hinges on the nature of the implicated organics. Since the various matrices have different pH values
327 (between 6 and 8), experiments were performed in UW at initial pH values between 3 and 8.
328 Interestingly, Figure 4E shows no pH effect on degradation of 0.5 mg/L BP. In all cases complete
329 degradation can be reached within 15 min. Similar results about the slight influence of initial pH on
330 the oxidation of organic micropollutants using BDD oxidation were reported by Frontistis et. al.
331 (2017), Pereira et al. (2012) and El-Ghenymy et al. (2012). However, other studies reported
332 contradictory results concerning the pH effect on the BDD EO (Siedlecka et al., 2018; Abdelhay et
333 al., 2017; Garcia-Segura et al., 2015). pH was found to have a remarkable role on the removal rate
334 of BPA, which was favored at pH 10 (Murugananthan et al., 2008). Moreover, the electrochemical
335 abatement of sulfonamides was strongly affected by pH, alongside other operating conditions such
336 as temperature and inorganic ions (Fabianska et al., 2014).
337 Finally, representative experiments were performed in the presence of 1000 mg/L t-butanol, whose
338 affinity for hydroxyl radicals is well-documented (Li et al., 2013). The results are shown in Figure
339 4F in terms of apparent rate constants in the absence (black bars) and in the presence (dashed bars)
340 of alcohol. It must be noted here that the latter values have been multiplied 100 times to allow for
341 clarity. Evidently, the reaction is nearly completely quenched in the presence of alcohol irrespective
342 of the water matrix, thus implying that hydroxyl radicals are the dominant oxidizing species.
343
344 *3.1.5. Effect of low current in various water matrices*
345 One of the major disadvantages of electrolysis is the need for large amounts of energy. For this
346 reason, the performance of the process in different aqueous matrices was studied at a lower current

density.

The effect of low current density (1.4 mA/cm^2) on 0.5 mg/L BP concentration with 0.1 M Na_2SO_4 and various matrices (WW, WW without the addition of electrolyte, BW, UW and 200 mg/L NaCl in UW) is shown in Figure 5; the rate decreases in the order UW with NaCl>WW without salt>WW>BW>UW. Concerning WW, BW and UW, it is noticed that the degradation follows the same trend as in Figure 4A, but the time needed for the removal of BP is increased. For WW, the time required for BP removal was augmented from 3 min at 50 mA/cm^2 to more than 15 min at 1.4 mA/cm^2. The addition of 0.1 M Na_2SO_4 slightly decreased the degradation rate in WW, as can be seen in Figure 5. It should be emphasized that the decreased current density does not significantly affect the conversion of BP since it becomes 100% and 90% in 5 min at 50 mA/cm^2 and 1.4 mA/cm^2, respectively. This result confirms the significance of chloride during BDD anodic oxidation as it leads to the formation of active chlorine species (Zhang et al., 2016).

Contrarily, the degradation rate of BP in BW and UW was suspended. A possible explanation for this result is the strong dependence between current density and the generation of hydroxyl radicals that are the principal oxidizing species in the absence of chlorides. As already mentioned, the formation of hydroxyl radicals is favored by the augmentation of current density, which in turn may maximize the mineralization of organic pollutants.

3.1.6. Comparison with SR-AOPs

As already demonstrated in Figure 4D, the presence of SPS can promote the electrochemical oxidation of BP due to the formation of sulfate radicals. Since SR-AOPs have recently gained attention in water treatment, we decided to compare the EO of BP with that of persulfate oxidation activated by carbocatalysis, as follows (Dimitriadou et al., 2019):

$$2S_2O_8^{2-} \xrightarrow{\text{CB}} S_2O_8^{\bullet-} + SO_4^{2-} + SO_4^{\bullet-} \quad (8)$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \quad (9)$$

The concentration levels of the oxidant and the activator are critical for the efficient degradation of BP, as this is demonstrated in Figure 6. The degradation rate increases with increasing either SPS or CB concentration within the concentration ranges tested, however the maximum rate recorded in either case (Figure 6B and 6D) is lower than that of EO at current densities ≥50 mA/cm^2 (Figure 2B). It is also noted that CB behaves as adsorbent since about 35% BP removal occurs after 45 min in the absence of SPS (Figure 6A); this is consistent with its considerable specific surface area of 216 m^2/g (Dimitriadou et al., 2019). On the other hand, SPS itself is a mild oxidant as 30% degradation occurs after 45 min without activator (Figure 6C).

The performance of the SR-AOP in actual matrices is demonstrated in Figure 7A; unlike what happens in EO, degradation efficiency decreases with matrix complexity, i.e. UW>BW>WW. This also is consistent with the negative impact of bicarbonate (Figure 7B) and chloride (Figure 7D) on BP degradation. Bicarbonate may scavenge the highly active sulfate and/or hydroxyl radicals producing the less reactive carbonate radicals ($HCO_3^{\bullet}$) (Ma et al., 2018). On the other hand, sulfate radicals may react with chloride (Lutze et al., 2015) to form other less reactive radicals such as chlorine and dichloride radicals ($Cl^{\bullet}$, $Cl_2^{\bullet-}$) (Metheniti et al., 2018), thus lowering degradation rates. Noticeably, the effect of HA on degradation was found to be commonly detrimental for both EO (Figure 4A) and SR-AOP (Figure 7C); in the latter case, HA may occupy active sites of the CB surface, thus limiting availability for SPS and/or BP.

To evaluate indirectly the relative contribution of sulfate and hydroxyl radicals to BP degradation, experiments were conducted with methanol and t-butanol as radical scavengers and the results, in terms of apparent rate constants, are summarized in Figures 7E and 7F, respectively. Noticeably, methanol inhibits considerably BP degradation and this is more pronounced at 1000 mg/L concentration, however, this seems not to be the case with t-butanol. Given that butanol has a 6-fold greater affinity for hydroxyl radicals than methanol (Li et al., 2013), it can be hypothesized that sulfate radicals play a key role in degrading BP.

4. Conclusions

This work demonstrates the efficient application of BDD anodic oxidation for the destruction of butyl paraben, a representative endocrine disrupting compound of the parabens family, in environmentally relevant matrices and levels. The process is expectedly favored (i) at increased current densities, where the rate of ROS production is accelerated, and (ii) in the presence (intrinsic or deliberate) of ions such as chloride that can electrochemically generate additional chlorine-based oxidative species. As a matter of fact, there appears to be a reaction rate trade-off between high current densities and chlorine-free electrolytes and vice versa. What is less expected is the fact that matrix complexity seems to favor paraben degradation. This finding underlines the existence of some kind of synergy between the organic and/or inorganic water matrix constituents, ROS and the anode surface. This positive interplay, however, seems to be process-specific as has been demonstrated through the application of an SR-AOP, where persulfate was carbocatalytically activated and the resulting sulfate radicals could degrade butyl paraben; in this case, matrix complexity was detrimental to degradation.

Nowadays, an issue of great concern is the design of advanced technologies for the removal or persistent pollutants from different water matrices. The obtained results showed the water matrix

effect on the degradation of BP and underlined the need for further work on the in-depth examination of the EO of organic compounds and the application of this technology in real life systems.

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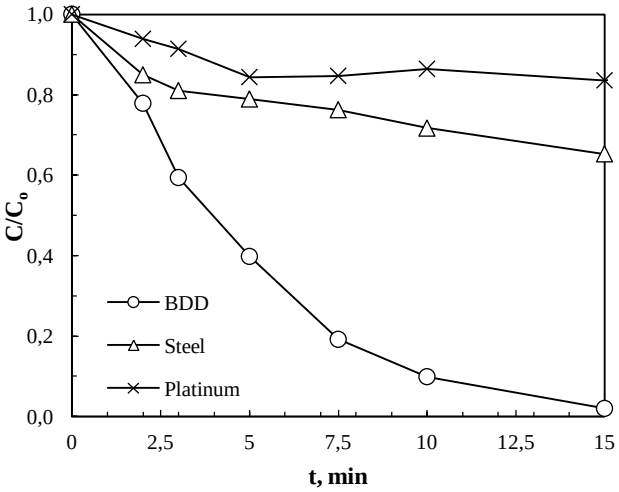

Figure 1. Degradation of 0.5 mg/L BP at 50 mA/cm^2 current density with 0.1 M Na_2SO_4 in UW as a function of anodic material.

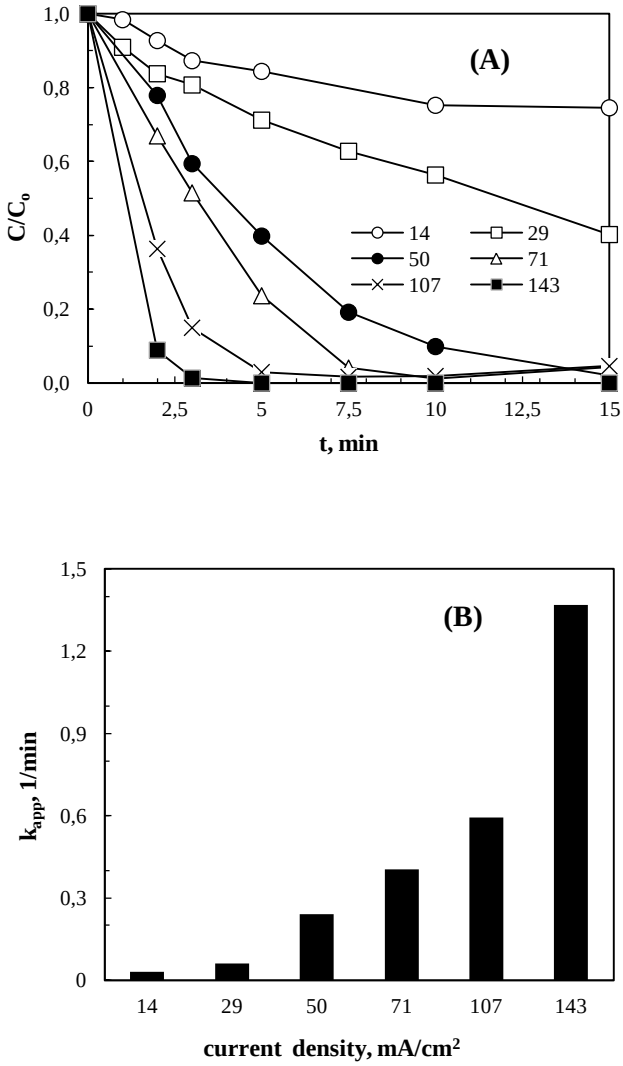

Figure 2. Effect of current density (in mA/cm^2) on 0.5 mg/L BP degradation in UW with 0.1 M Na_2SO_4. (A) Concentration-time profiles; (B) Apparent rate constants.

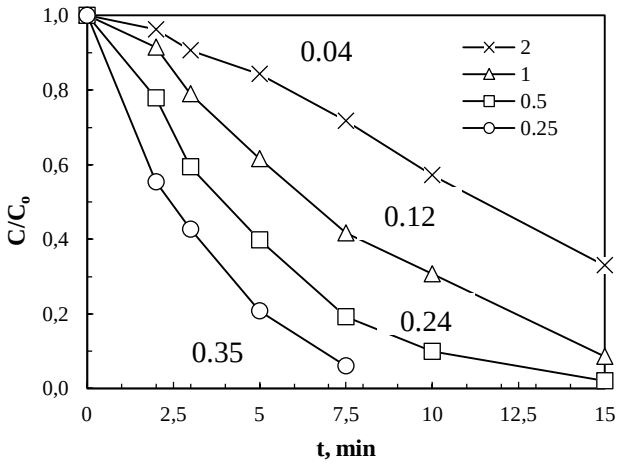

Figure 3. Effect of BP concentration (in mg/L) on its degradation at 50 mA/cm^2 current density in UW with 0.1 M Na_2SO_4. Numbers next to profiles show apparent rate constants (in 1/min).

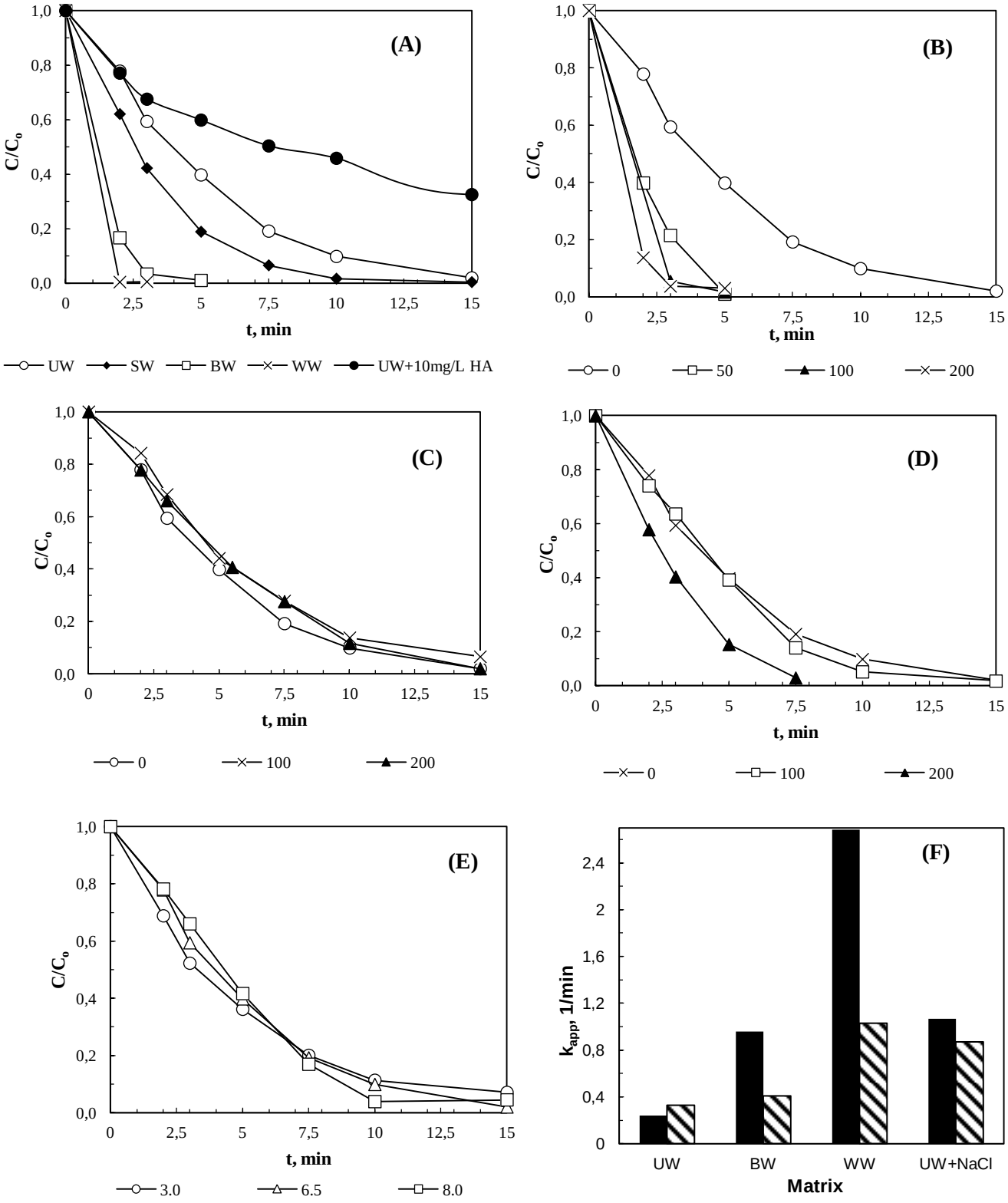

Figure 4. Degradation of 0.5 mg/L BP at 50 mA/cm^2 current density with 0.1 M Na_2SO_4. (A) Various actual water matrices and UW spiked with 10 mg/L HA; (B) Addition of chloride (in mg/L) in UW; (C) Addition of bicarbonate (in mg/L) in UW; (D) Addition of sodium persulfate (in mg/L) in UW; (E) Various initial pH values of UW. (F) Apparent rate constants for runs without (black bars) and with (dashed bars) 1000 mg/L tert-butanol. Values for runs with butanol have been multiplied by a factor of 100 for clarity.

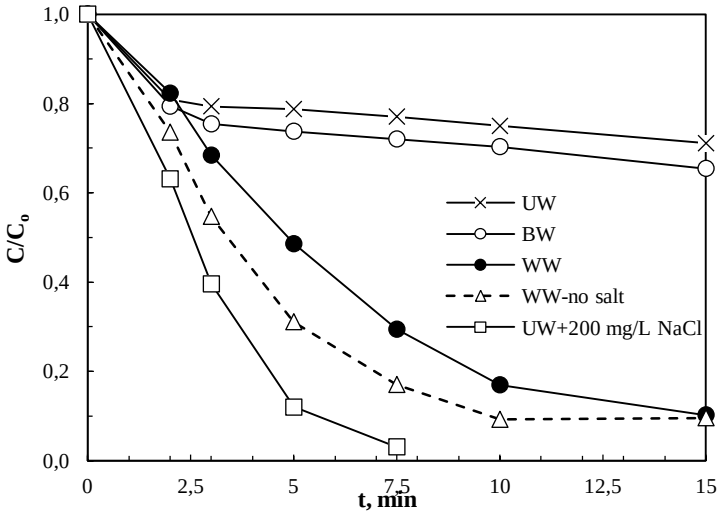

Figure 5. Effect of low current density (1.4 mA/cm^2) on 0.5 mg/L BP concentration with 0.1 M Na_2SO_4 and various matrices. Dashed line shows experiment without addition of electrolyte.

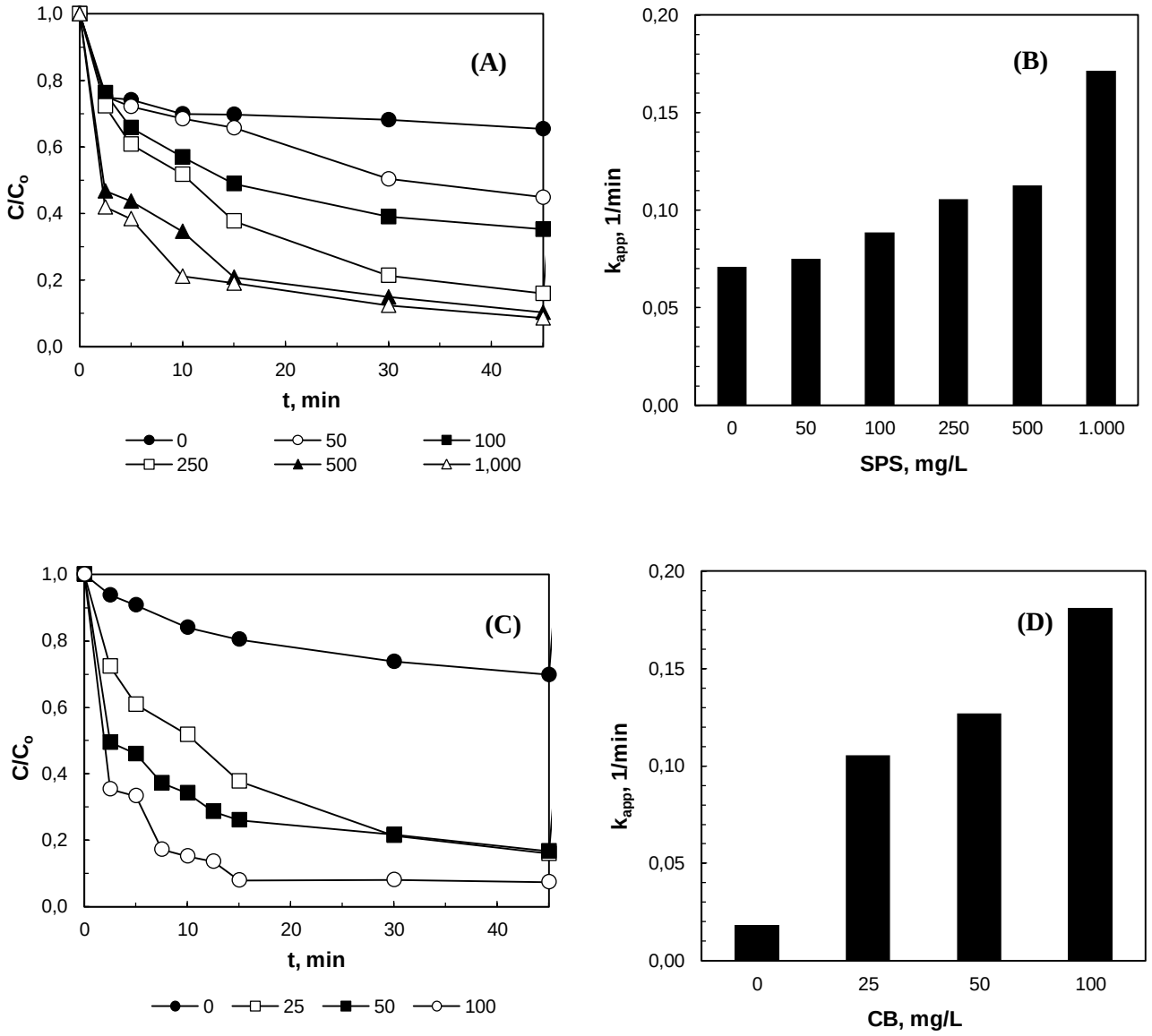

Figure 6. Degradation of 0.5 mg/L BP in UW as a function of SPS ((A) and (B)) or CB ((C) and (D)) concentration. For (A) and (B), CB=25 mg/L; for (C) and (D), SPS=250 mg/L.

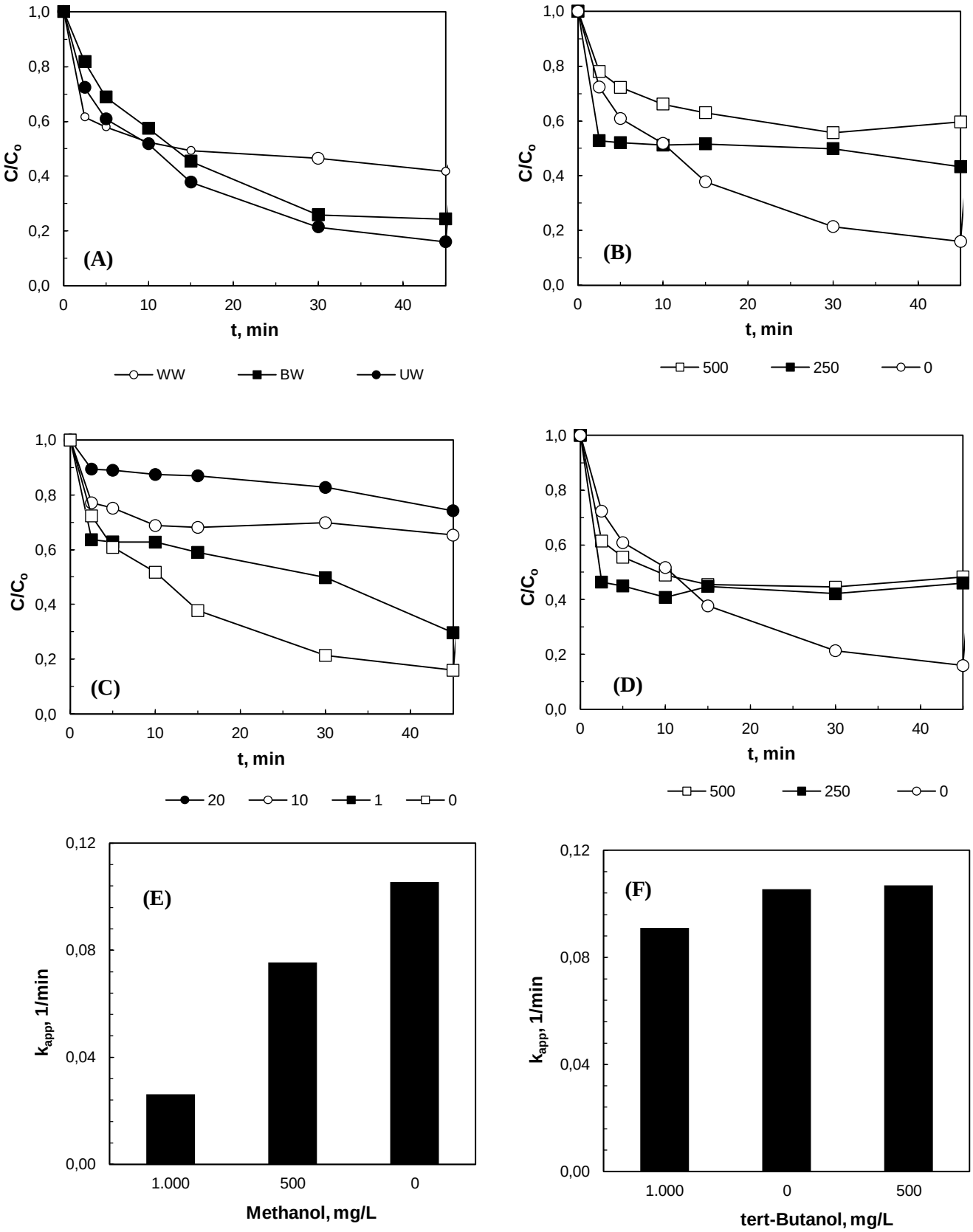

Figure 7. Effect of (A) actual water matrix or UW spiked with (B) bicarbonate; (C) humic acid; (D) chloride; (E) methanol; (F) t-butanol on the degradation of 0.5 mg/L BP with 250 mg/L SPS and 25 mg/L CB. All concentrations in (B)-(F) are in mg/L.