

Electrochemical Degradation of Acetaminophen in the Presence of Different Redox Mediator Systems

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This study focuses on the electrochemical degradation of acetaminophen (AP) in the presence of individual redox mediators. The oxidation peaks of Fe(II), Ag(I), and sulfate were detected on a Windsor boron-doped diamond (BDD) electrode in 1 M Na₂SO₄. The AP degradation performance using a single mediator was in the following order: Ce(IV) (from Ce(SO₄)₂) > Fe(III) (from Fe(NO₃)₃ or FeCl₃) > Co(II) (from CoCl₂) ≈ Ag(I) (from AgNO₃). *p*-BQ due to AP degradation was observed in 1 M Na₂SO₄ in the presence of Ce(IV) and Fe(III), while the former exhibited more and faster *p*-benzoquinone (*p*-BQ) generation than the latter. In the presence of individual mediators in 1 M Na₂SO₄ or NaNO₃, the performance of electrochemical AP degradation, *p*-BQ removal, and TOC mineralization on a Diachem BDD anode occurred in the following order: Fe(III) > Ce(IV) > Fe(II) ≈ Co(II) > Ag(I), but the performance decreased when replacing Na₂SO₄ with NaNO₃ as the electrolyte. The Cl₂/Cl⁻ redox mediator could also enhance AP degradation and TOC mineralization. The apparent pseudo first-order rate constants for AP electrochemical degradation in these solutions ranged from 2.92×10⁻⁴–4.34×10⁻² 1/s. An Fe(III) dosage of 100 ppm (Fe(III)/AP mole ratio = 2.7) at 0.25 A/cm² is suggested for this electrochemical process although Fe(III) dosage in the range of 50–500 ppm could be considered. Fe(III) has good potential for use in the electrochemical advanced oxidation process (EAOP) to significantly improve organic pollutant degradation performance.

Keywords: electrochemical degradation; acetaminophen (AP); *p*-benzoquinone (*p*-BQ); redox mediator; boron-doped diamond (BDD) electrode

1. INTRODUCTION

Acetaminophen (AP) is a nonprescription analgesic and antipyretic medicine widely used for mild-to-moderate pain and fever therapy [1]. Because of its presence in urine or feces without alteration after use [2] and/or improper disposal of medicines in homes, AP can enter and contaminate groundwater, rivers, and lakes through wastewater treatment plants and may even contaminate drinking water [1], which causes potential risks for aquatic environments. As one of the emerging pharmaceutical

contaminants, AP has been frequently detected with concentrations from several to tens of ppb levels (even $>100 \mu\text{g/L}$) in sewage and surface water in several areas [3–6]. Usually, municipal wastewater treatment plants (WWTPs) are not designed to remove emerging pharmaceutical pollutants [7], so WWTP effluent is regarded as the main source of AP in surface waters [8].

Therefore, to achieve high-quality treated effluents, there is a great need to develop reliable methods for the degradation of prioritized pharmaceuticals (e.g., AP) in WWTP effluents [9]. Although pharmaceuticals exhibit various removal efficiencies in some modern WWTPs [10], the degradation of AP can be achieved by different physiochemical approaches, such as advanced oxidation processes (AOPs) (e.g., TiO_2/UV [11,12], $\text{UV}/\text{H}_2\text{O}_2$ [13], ozonization [13], electrochemical oxidation [14–17]), and mediated electrochemical oxidation (MEO) [18,19].

However, attention has rarely been paid to the electrochemical degradation of AP in the presence of different metal ion redox mediators, i.e. (Fe(II), Fe(III), Co(II), Ag(I), or Ce(IV)). The present work investigates the degradation of AP on a boron doped diamond (BDD) anode in solution in the presence of one of these mediators. For comparison, *p*-benzoquinone (*p*-BQ), one of intermediates generated from AP electrochemical degradation, was also tested and discussed.

2. MATERIALS AND METHODS

2.1. Chemicals and materials

Figures 1a and b show the chemical structures of acetaminophen (AP) ($\text{C}_8\text{H}_9\text{NO}_2 = 151 \text{ g/mol}$) (Sigma) and *p*-benzoquinone ($\text{C}_6\text{H}_4\text{O}_2 = 108 \text{ g/mol}$) (Alfa), respectively. Sodium sulfate (Sigma) was used to prepare the supporting electrolyte. Fe(III) chloride, Fe(II) sulfate, Fe(III) nitrate, and Ag(I) nitrate were purchased from Sigma, while cerium(IV) sulfate 4-hydrate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) and sodium chloride were purchased from Panreac Quimica (EU) and Nihon Shiyaku (Japan), respectively. Acetonitrile was supplied from ECHO Chemical Co. Ltd. (Taiwan). Sulfuric acid (65%) (Scharlau, Spain) was used as received without further purification.

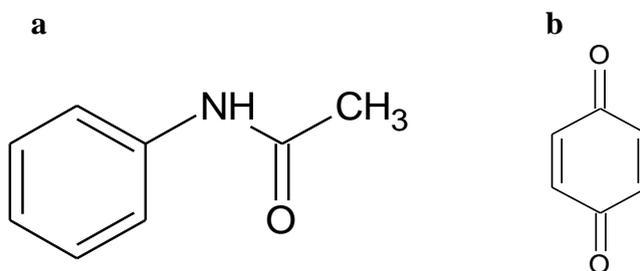


Figure 1. Molecular structures of acetaminophen [19] and *p*-benzoquinone.

2.3. Cyclic voltammetric measurements and degradation experiments

The electrochemical behavior of the metal ions (redox mediators) of interest in prepared solutions was measured using cyclic voltammetry (CV). The potential sweep range was $0.3 \leftrightarrow 2.3$, $-1.0 \leftrightarrow 1.6$, or $-1.1 \leftrightarrow 1.6 \text{ V}$ (starting/ending at the same potential with a scan rate = 100 mV/s) for the CV

measurements. The cyclic voltammetric measurements were performed using a CHI 660B electrochemical work station. A BDD disk (0.07 cm², Windsor Scientific Co. Ltd. (UK)) and a platinum wire were used as the working and counter electrodes, respectively, while the reference electrode was an Ag/AgCl one (3 M KCl, 0.207 V vs. a standard hydrogen electrode (SHE) at 25°C).

The electrolysis experiments were conducted at 25°C in a thermostated cell divided by a Nafion-212 separator (Dupont) with magnetic stirring. The anolyte and catholyte used the same electrolyte, 1 M Na₂SO₄, NaNO₃, or NaCl (100 mL), while the anolyte was spiked with 100 mg/L AP. A BDD electrode (Nb/BDD, Diachem (Condias GmbH, Germany)) served as the anode while the cathode was a Ti plate used for the AP degradation in the presence of single redox mediator species in solutions galvanostatically operated using a DC power supply (Good Will Instrument Co. Ltd. GPS-2303). The cell voltage and current over time were recorded based on the DC power supply readings. Samples taken from the anolyte at intervals during electrolysis were measured for the concentrations of AP, *p*-benzoquinone (*p*-BQ), and total organic carbon (TOC).

The AP degradation efficiency, TOC removal efficiency, and apparent pseudo first-order rate constant (*k*) of AP degradation can be calculated as follows:

$$\text{AP degradation efficiency} = [1 - (C_{\text{AP}}/C_{\text{AP}_0})] \times 100\% \quad (1)$$

$$\text{TOC removal efficiency} = [1 - (\text{TOC}/\text{TOC}_0)] \times 100\% \quad (2)$$

$$C_{\text{AP}} = C_{\text{AP}_0} e^{-kt}, \quad (3)$$

where *C*_{AP} and TOC are the residual concentrations of AP and TOC at a given electrolytic time *t*, respectively, and *C*_{AP₀} and TOC₀ are the initial concentrations of AP and TOC, respectively.

2.4. Analysis

The titration method using a redox potential titrator (Metrohm 702 SM Titrino) was adopted to determine the Ce(IV) concentrations of the samples [18,19]. The concentrations of AP and *p*-BQ in the samples were analyzed by a HPLC analyzer (Hitachi Chromaster 5420). The compound separations were performed on a Mightysil RP-C18 column (250 mm×4.6 mm, particle size, 5 μm). The mobile phases were acetonitrile/water (45:55, v/v) (ECHO Chemical Co) and water/acetonitrile (55:45, v/v) (ECHO Chemical Co) for the analyses of AP and *p*-BQ, respectively. The flow rate was 1.0 mL/min, and the injection volume was 20 μL. The retention times of AP (254 nm) and *p*-BQ (245 nm) were 3.0 and 4.2 min, respectively, and their method detection limits were 0.05 and 0.02 mg/L, respectively. At a carrying gas (purified air) flow rate = 150 mL/min, a Shimadzu 5000 Model TOC analyzer (combustion temperature = 680°C) was used to detect the TOC concentrations of the samples.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetric (CV) measurements

CV analyses were performed to examine the electrochemical behavior of AP on BDD in sodium sulfate solution or metal ions (redox mediators) of interest in prepared supporting electrolytes. For the voltammogram of the solution that only contained a background electrolyte (BK, 1 M Na₂SO₄), an

oxidation peak was detected at 1.722 V vs. Ag/AgCl before the oxygen evolution (Figure 2a), which could be attributed to the oxidation of sulfate to persulfate.

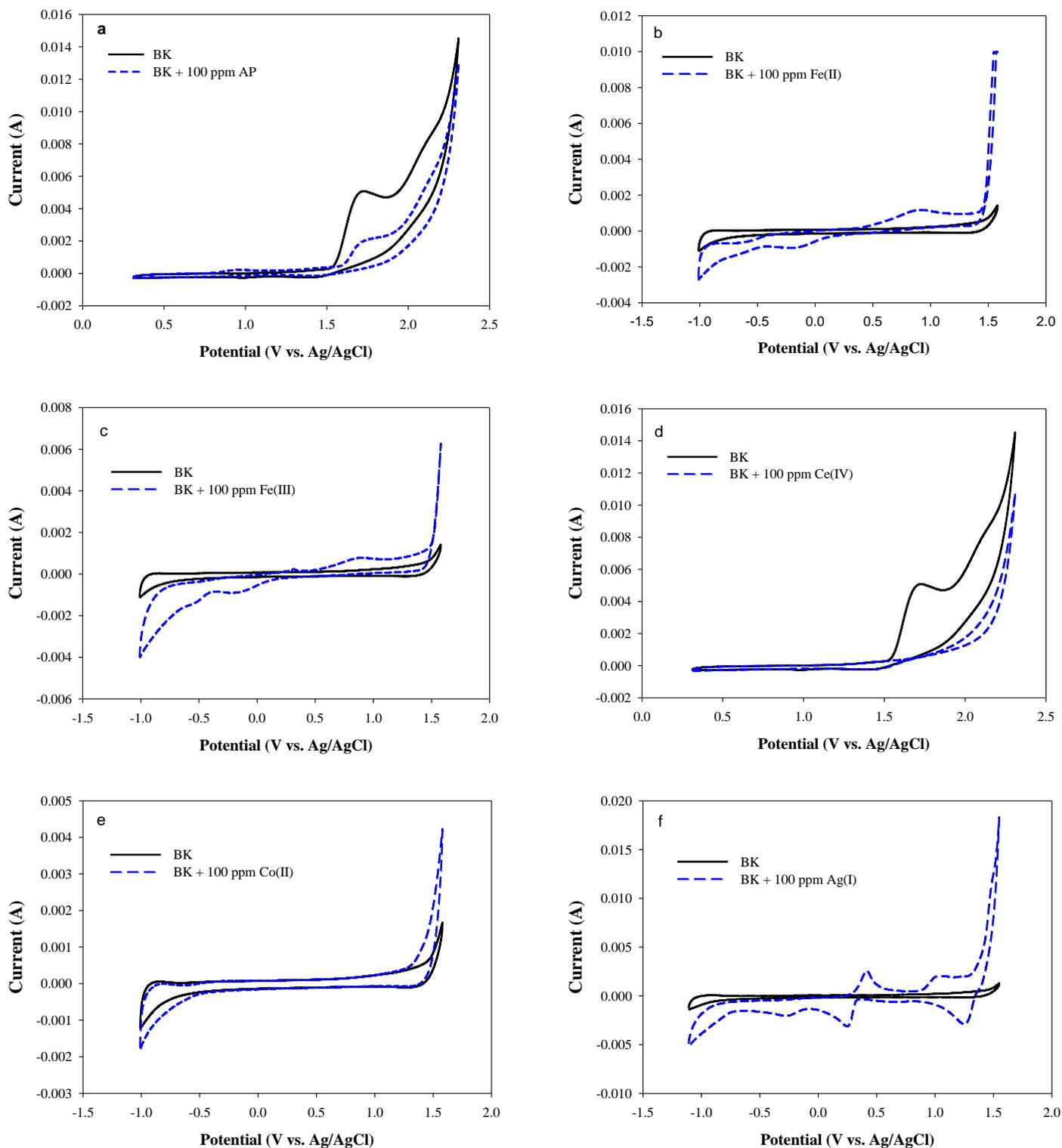


Figure 2. Cyclic voltammograms on BDD in different solutions containing AP (a) or different metal ions (Fe(II) (b), Fe(III) (c), Ce(IV) (d), Co(II) (e), and Ag(I) (f)) (scan rate = 100 mV/s at 25°C).

This finding is similar to that reported in a solution containing 5g/L Na₂SO₄ using a BDD electrode [20]. The cyclic voltammogram of 100 mg/L AP in 1 M Na₂SO₄ was roughly similar to that of BK, but one more oxidation peak was observed at about 0.964 V vs. Ag/AgCl, revealing that AP could be directly oxidized on BDD. In addition, the oxidation peak of sulfate to persulfate was smaller in the presence of AP in 1 M Na₂SO₄, similar to those addressed in the literature for the anodic oxidation of some aromatic compounds such as phenol, nitrophenols, chlorophenols, polyhydroxybenzene, and 17 β -estradiol [11–16]. This result was associated with the partial deactivation of active sites on the surface of the BDD, which was deposited or covered with organic films formed during the CV scans.

Figure 2b shows the voltammograms of 1 M Na₂SO₄, with and without the addition of FeSO₄. No oxidation or reduction peak was found in the absence of Fe(II). In the presence of Fe(II), anodic and cathodic peaks were detected at 0.900 and –0.210 V vs. Ag/AgCl, respectively. The former reflected the oxidation of Fe(II) to Fe(III), while the latter indicated an opposite reaction (reduction). A similar tendency was also observed when FeSO₄ was replaced with either Fe(NO₃)₃ or FeCl₃ (Figure 2c). For the 1 M Na₂SO₄ containing mediator Ce(IV) (from adding Ce(SO₄)₂), the BDD surface deactivation phenomenon also appeared during the CV sweeps, and no obvious anodic or cathodic peak was detected (Figure 2d). This result was dissimilar to our earlier observation of the redox reaction peaks of Ce(III)/Ce(IV) coupled on a Diachem BDD in 0.1 M Ce(III)/4 M HNO₃ [18] and 0.3 M Ce(III)/5 M HNO₃ [21]. The deactivation status of the BDD surface and the differences in the supporting electrolytes should be mainly responsible for the discrepancies among different works.

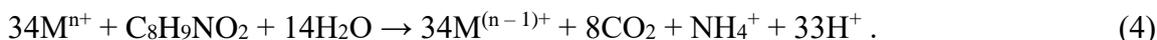
The voltammograms of 1 M Na₂SO₄ in the absence and presence of Co(II) were similar, and no oxidation or reduction peak for Co(II)/Co(III) transformation was detected (Figure 2e). For 1 M Na₂SO₄ in the presence of Ag(I), the anodic peaks appeared at 0.417 and 1.063 V vs. Ag/AgCl, corresponding to the cathodic peaks at –0.270 and 0.249 V vs. Ag/AgCl, respectively (Figure 2f). The former (oxidation) peaks presented the oxidation of Ag(0) to Ag(I) and Ag(I) to Ag(II), respectively, while the latter ones were their respective reverse (reduction) reactions [22]. This finding indicates that the Ag(I) can be electrochemically converted into mediator Ag(II), which is also useful for AP degradation when the sodium sulfate solution contains Ag(I).

3.2. The degradation of AP and *p*-BQ by mediators

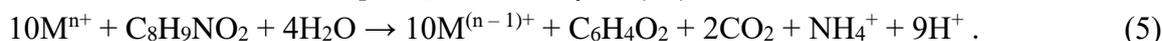
Before each AP electrochemical degradation test in the presence of an ion species or mediator, the degradation of AP (100 mg/L) using each ion species or the mediator alone (500 mg/L) was performed at 25°C and an initial pH of 3.00 in 1 M Na₂SO₄. As can be seen from Figure 3a, the AP degradation performance by a single ion species or mediator occurred in the following order: Ce(IV) (from Ce(SO₄)₂) > Fe(III) (from Fe(NO₃)₃ or FeCl₃) > Co(II) (from CoCl₂) \approx Ag(I) (from AgNO₃). AP could hardly be degraded in 1 M Na₂SO₄ in the presence of Co(II) or Ag(I), suggesting that AP could hardly be oxidized by Co(II) or Ag(I). Dissimilarly, Fe(III) could oxidize partial AP; however, the AP degradation efficiency was 12% for Fe(NO₃)₃, slightly greater than that for FeCl₃ (10%), revealing that NO₃[–] might contribute to poor AP degradation while Cl[–] could not. On the other hand, Ce(IV) could oxidize AP very fast (degradation efficiency = 100% at $t = 3$ min). Similar observations were also reported for the degradation of AP by Ce(IV) [18,19], which is commonly used to decompose organic

pollutants in MEO processes [23–25]. Our finding was attributed to the fact that the oxidation potentials of Co(III)/Co(II), Ce(IV)/Ce(III), and Fe(III)/Fe(II) couples are 1.83–1.92, 1.74, and 0.77 V vs. standard hydrogen electrode (SHE) [23,26], respectively, although Co(II) in place of Co(III) was used in this study.

For simplification, if CO_2 and NH_4^+ are the main final products, the direct degradation of AP ($\text{C}_8\text{H}_9\text{NO}_2$) by mediator M^{n+} (Ce^{4+} or Fe^{3+} ; $n = 4$ or 3) can be expressed by the following reaction:



However, the oxidation of AP into *p*-BQ and CO_2 by Ce(IV) can be described below:



Both reactions tended to increase the acidity of the solution.

Like the tendency toward AP degradation, the rates of AP-derived *p*-BQ generation for the above mentioned solutions also varied in the following order: $\text{Ce}(\text{SO}_4)_2 > \text{Fe}(\text{NO}_3)_3 > \text{FeCl}_3 > \text{CoCl}_2 \approx \text{AgNO}_3$ (Figure 3b). In the presence of Co(II) or Ag(I) in 1 M Na_2SO_4 containing AP, almost no *p*-BQ formed. The *p*-BQ formation rate was significantly greater in the presence of $\text{Fe}(\text{NO}_3)_3$ than in the presence of FeCl_3 in 1 M Na_2SO_4 , supporting the aforementioned inference that NO_3^- was devoted to AP degradation while Cl^- was not although the concentration of *p*-BQ hardly increased in the former solution at $t > 20$ min, while that in the latter solution still slowly increased with reaction time. When Ce(IV) was present in 1 M Na_2SO_4 containing AP, the concentration of *p*-BQ quickly reached a maximum and then approached to a plateau up to the end of reaction. This phenomenon was also observed in our earlier work performed at AP = 10 mg/L and Ce(IV) = 200 mg/L in a temperature range of 25–80°C [19].

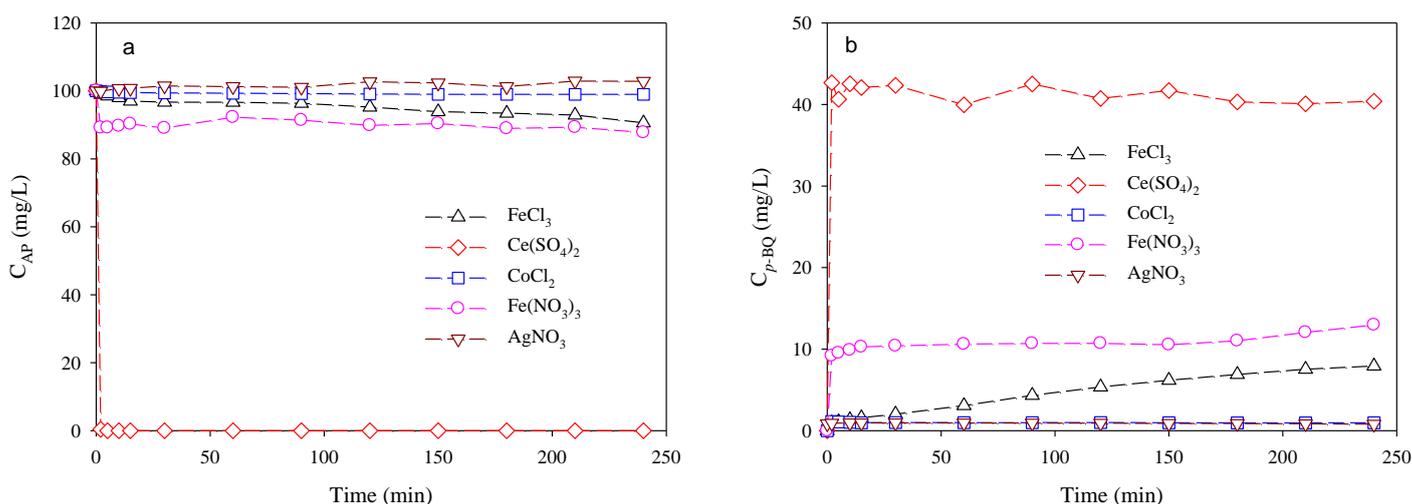


Figure 3. Chemical degradations of AP (100 ppm) and AP-derived *p*-BQ in the presence of single Fe(III), Ce(IV), or Co(II) in 100 mL 1 M Na_2SO_4 at 25°C.

3.3. Electrochemical degradations of AP, *p*-BQ, and TOC in the presence of single redox mediators

Figure 4 shows the variations in the AP concentrations over time during electrochemical degradation on a Diachem BDD (working area = 2 cm²) at 0.25 A/cm² and 25°C in the presence/absence of single ion species or mediator in 1 M Na_2SO_4 (100 mL). In the absence of any mediator, the AP degradation efficiency in 1 M Na_2SO_4 increased with increases in time, and the complete AP degradation

(efficiency = 100%) occurred at 30 min. In addition, its apparent pseudo first-order rate constant (k) was 1.02×10^{-3} 1/s (Table 1), which was lower than that (1.55×10^{-3} 1/s) found in our earlier study using a greater current density (0.50 A/cm^2) [19], which should have led to more $\bullet\text{OH}$ generation [24] or formation of oxidizing species (persulfate or sulfate radical) [27,28]. The complete AP degradation was also achieved at 30 min when NaCl or CoCl_2 was present in 1 M Na_2SO_4 . However, their k values (2.99×10^{-3} and 3.72×10^{-3} 1/s, respectively) were greater than that found with electrolysis alone. Co(III) is a typical mediator [29], so this finding suggests that the mediator Co(III) may be generated from the Co(II) and may contribute to AP degradation although the oxidation potential for Co(II)/Co(III) is 1.83–1.92 V vs. SHE [24]. It is also possible that in the presence of chloride and active chlorine can be electro-generated based on the following reactions [30,31]:



The produced HOCl can be used to oxidize organic compound R via the following reaction [31]:

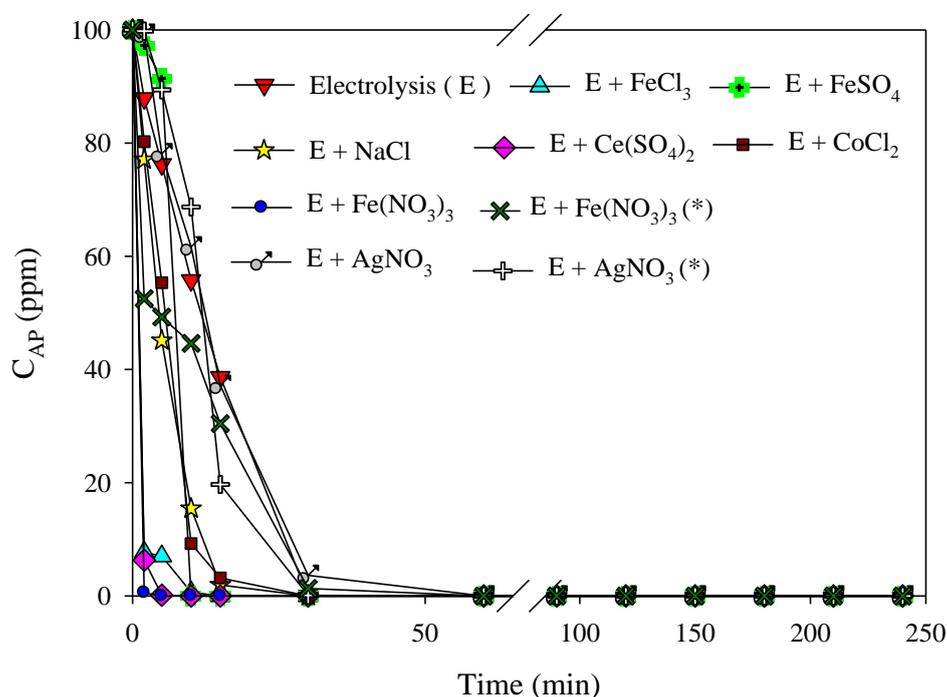


Figure 4. Electrochemical degradations of AP (100 ppm) in the presence of single redox mediators in 100 mL 1 M Na_2SO_4 or NaNO_3 (marked with *) (anode area = 2 cm^2 at 0.25 A/cm^2 and 25°C).

According to these reactions, Cl^- (anion) can be electrochemically converted into a mediator. When NaCl or CoCl_2 was replaced with FeCl_3 , the AP degradation efficiency was further improved with a k value of 8.43×10^{-3} 1/s because Fe(III) is another typical mediator [29]. This result demonstrates that the presence of mediator Fe(III) in a sodium sulfate solution enhances the degradation of AP, which in addition to electrolysis may have been beneficial to AP degradation due to Fe(III) oxidation replacing FeCl_3 with $\text{Fe}(\text{NO}_3)_3$, thus achieving more AP degradation in 1 M Na_2SO_4 and obtaining the highest k

value of 4.34×10^{-2} 1/s among the tested chemicals or species. However, the AP degradation was not as good when the 1 M Na₂SO₄ was replaced with 1 M NaNO₃.

This phenomenon was also observed in the case of AP degradation in the presence of AgNO₃ in 1 M Na₂SO₄, relative to 1 M NaNO₃. Typical mediators also include Ag(II) and Ce(IV) [29]. In this study, Ag(I) (instead of Ag(II)) and mediator Ce(IV) were also tested for the purpose of comparison. The AP degradation efficiency in the presence of AgNO₃ in 1 M Na₂SO₄ was slightly lower than that in the absence of AgNO₃ (electrolysis only), while their AP degradation curves were similar to each other. Therefore, the Ag(II) generated from Ag(I) oxidation on the Diachem BDD in a 1 M Na₂SO₄ electrolyte should be negligible although the oxidation of Ag(I) to Ag(II) was detected on the Windsor Scientific BDD in the CV analysis (Figure 2f). On the other hand, the presence of Ce(IV) (from adding Ce(SO₄)₂) significantly increased the degradation of AP in 1 M Na₂SO₄, attaining the second highest k (2.25×10^{-2} 1/s) of all the mediator tests. The pseudo first-order rate constants (k) of AP electrochemical degradation ranged from 2.92×10^{-4} – 4.34×10^{-2} 1/s (Table 1).

Table 1. The apparent pseudo-first-order rate constants (k) for electrochemical AP degradation (100 ppm) in the presence of single redox mediators at 0.25 A/cm² and 25°C in 1 M Na₂SO₄ or NaNO₃ (marked with *). (The value of k was 1.02×10^{-3} 1/s in the absence of any redox mediator.)

FeCl ₃	FeSO ₄	NaCl	Ce(SO ₄) ₂	CoCl ₂	Fe(NO ₃) ₃	Fe(NO ₃) ₃ *	AgNO ₃	AgNO ₃ *
8.43×10^{-3}	2.92×10^{-4}	2.99×10^{-3}	2.25×10^{-2}	3.72×10^{-3}	4.34×10^{-2}	1.43×10^{-3}	8.10×10^{-4}	5.75×10^{-4}

During the electrolysis in Na₂SO₄, *p*-BQ was detected, and its concentration increased with time to reach a maximum ($C_{p\text{-BQ-max}}$) at $t_{\text{max}} = 15$ min and decreased with time until it could not be detected (ND) ($t_{\text{ND}} = 60$ min) (Figure 5a). The *p*-BQ was one of intermediates derived from AP electrochemical destruction. In the presence of NaCl, CoCl₂, or FeCl₃ in Na₂SO₄, their t_{max} values were ≤ 15 min and their t_{ND} values were > 60 min; however, their $C_{p\text{-BQ-max}}$ data were all greater than those obtained for electrolysis alone. The magnitude of $C_{p\text{-BQ-max}}$ values of these cases were in the following order: FeCl₃ $>$ CoCl₂ $>$ NaCl $>$ electrolysis alone (E), with an opposite trend for their t_{max} values, so the presence of Fe(III) or possibly Co(III) in 1 M Na₂SO₄ enhanced the formation of *p*-BQ. This phenomenon was also found for the presence of Fe(III) in Na₂SO₄, but not for that in NaNO₃, which had a larger t_{max} and t_{ND} , suggesting that persulfate and/or a sulfate radical might also be involved in the formation and degradation of *p*-BQ.

Replacing Fe(NO₃)₃ with AgNO₃ in NaNO₃ did not change the t_{max} , but the highest $C_{p\text{-BQ-max}}$ and residual *p*-BQ values were found among the tested chemicals. However, the replacement of NaNO₃ with Na₂SO₄ in order to dissolve AgNO₃ was found to potentially increase the degradation of *p*-BQ, also supporting the previously mentioned inference, and persulfate and/or the sulfate radical enhanced the degradation of *p*-BQ. Among the tested conditions, the presence of FeSO₄ in Na₂SO₄ resulted in the lowest $C_{p\text{-BQ-max}}$ and shortest t_{ND} , corresponding to the lowest formation and the fastest degradation of *p*-BQ. This result indicates that most of the added Fe(II) should be electrochemically oxidized to Fe(III). Consistent with the trends shown in figures 4 and 5a, the electrochemical degradation of AP in Na₂SO₄ in the presence of Fe(III) (from Fe(NO₃)₃) exhibited the quickest TOC removal and mineralization rates among the tested conditions, and it achieved complete TOC removal at $t_{\text{ND}} = 150$ min although those in

the presence of FeSO_4 , NaCl , and $\text{Ce}(\text{SO}_4)_2$ and in the absence of any one of these chemicals also had $t_{\text{ND}} = 150$ min (Figure 5b). In the presence of FeCl_3 or CoCl_2 , the t_{ND} was 210 min. Again, the TOC removal was significantly lower in the presence of AgNO_3 and in the NaNO_3 electrolyte during electrolysis. Accordingly, the 1 M Na_2SO_4 with the addition of $\text{Fe}(\text{NO}_3)_3$ was chosen for the subsequent AP degradation and mineralization tests.

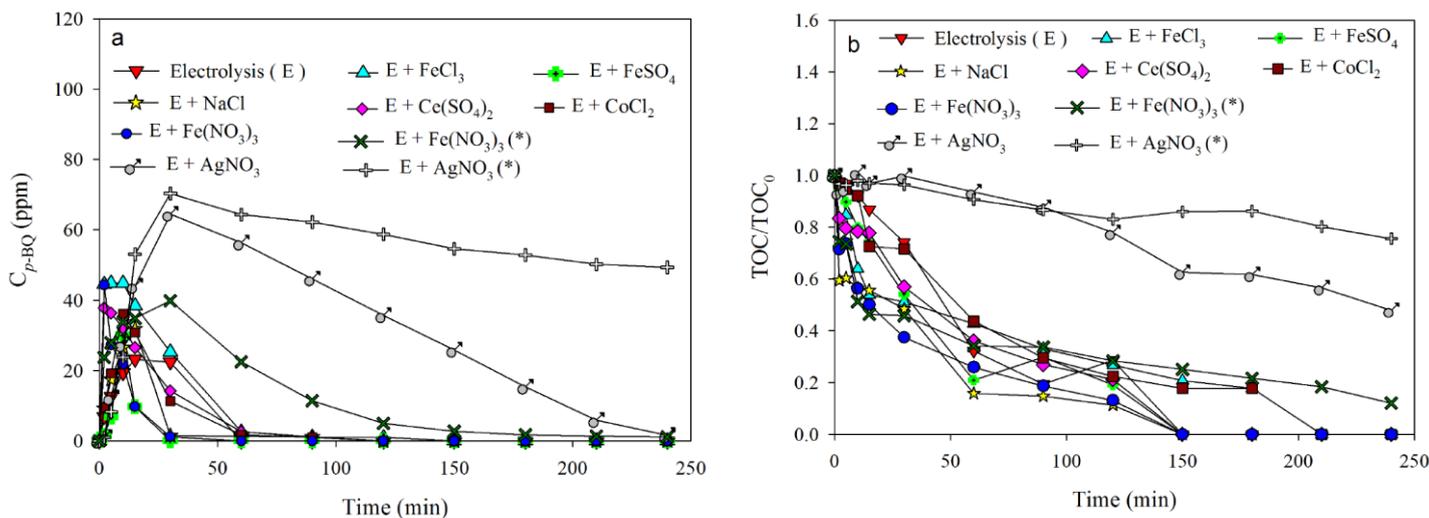
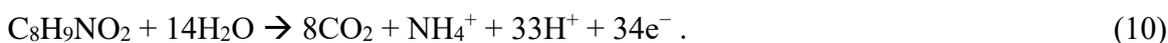


Figure 5. Electrochemical degradations of AP-derived $p\text{-BQ}$ (a) and TOC (b) in the presence of single redox mediators in 100 mL 1 M Na_2SO_4 or NaNO_3 (marked with *) (AP = 100 ppm and anode area = 2 cm^2 at 0.25 A/cm^2 and 25°C).

3.4. Electrochemical degradations of AP, $p\text{-BQ}$, and TOC in the presence of $\text{Fe}(\text{III})$ at different concentrations

If the mineralization of all AP involves its conversion into CO_2 and mainly NH_4^+ , the overall reaction can be written as follows [14]:



However, $\text{Fe}(\text{III})$ should account for the mineralization of partial AP based on reaction 4. Therefore, we tested the appropriate $\text{Fe}(\text{III})$ dosage range in 1 M Na_2SO_4 for AP degradation. It was found that both the AP degradation efficiency and the rate increased with increases in the $\text{Fe}(\text{III})$ dosage from 50 to 250 mg/L (ppm) and that the AP degradation efficiency was not further raised by increasing the $\text{Fe}(\text{III})$ dosage to 500 and 750 ppm (Figure 6a).

Nevertheless, increases in the $C_{p\text{-BQ-max}}$ value approximately corresponded to increases in the $\text{Fe}(\text{III})$ dosage in the range 50–750 ppm. In addition, these $C_{p\text{-BQ-max}}$ values were greater and degraded $p\text{-BQ}$ faster than was the case without $\text{Fe}(\text{III})$ addition in 1 M Na_2SO_4 (Figure 6b). According to the comparison of TOC removal rate and efficiency shown in Figure 6c, the appropriate $\text{Fe}(\text{III})$ dosage ranged from 50 to 500 ppm, which corresponded the mole ratios of $\text{Fe}(\text{III})/\text{AP} = 1.35\text{--}13.5$ and was significantly lower than that (34) in reaction 4 because the AP degradation and TOC mineralization relied on the electrochemical advanced oxidation accompanied with the presence of $\text{Fe}(\text{III})$. An $\text{Fe}(\text{III})$ dosage

of 100 ppm was selected for subsequent experiments because the same t_{ND} was obtained for 100% TOC removal at 100 and 500 ppm Fe(III).

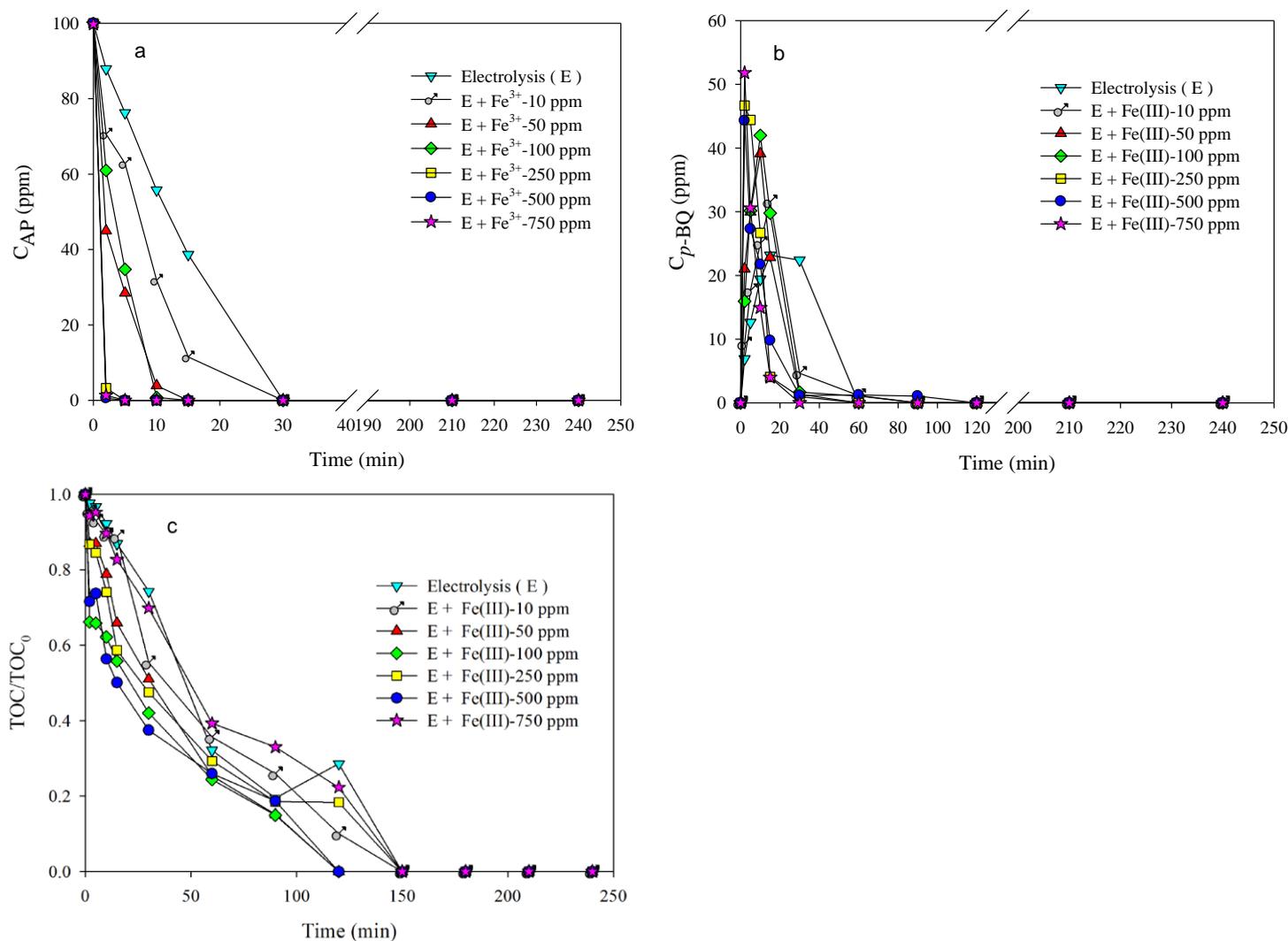


Figure 6. Electrochemical degradations of AP (100 ppm) (a), AP-derived *p*-BQ (b), and TOC (c) in the presence of Fe(III) with different concentrations (10 to 750 ppm) in 100 mL 1 M Na₂SO₄ (anode area = 2 cm² at 0.25 A/cm² and 25°C).

To improve the AP degradation and TOC mineralization in 1 M Na₂SO₄, electrolytic experiments under different current densities were performed at an Fe(III) dosage of 100 ppm. An increase in the current from 0.5 to 2.0 A on the 2 cm² BDD anode significantly increased the AP degradation, *p*-BQ destruction, and TOC mineralization in 1 M Na₂SO₄ (figures 7a, b, and c). This result was attributed to greater production of •OH and oxidizing species for AP abatement by increasing the current density and was similar to the observations of organic pollutant degradation in electrochemical advanced oxidation processes (EAOPs) [19,24,27]. In the presence of 100 ppm Fe(III) in 1 M Na₂SO₄, reducing the current achieved comparable (at 0.5 and 1.0 A) or even better (at 1.5 A) performance for AP abatement in terms of AP degradation, *p*-BQ destruction, and TOC mineralization. Accordingly, an Fe(III) dosage of 100

ppm (Fe(III)/AP mole ratio = 2.7) at 0.5 A is suggested for this electrochemical AP removal process ($k = 7.08 \times 10^{-3} \text{ 1/s}$) because the t_{ND} values for complete TOC removal were the same (120 min) at currents = 0.5–1.5 A and a current = 2 A without the addition of Fe(III).

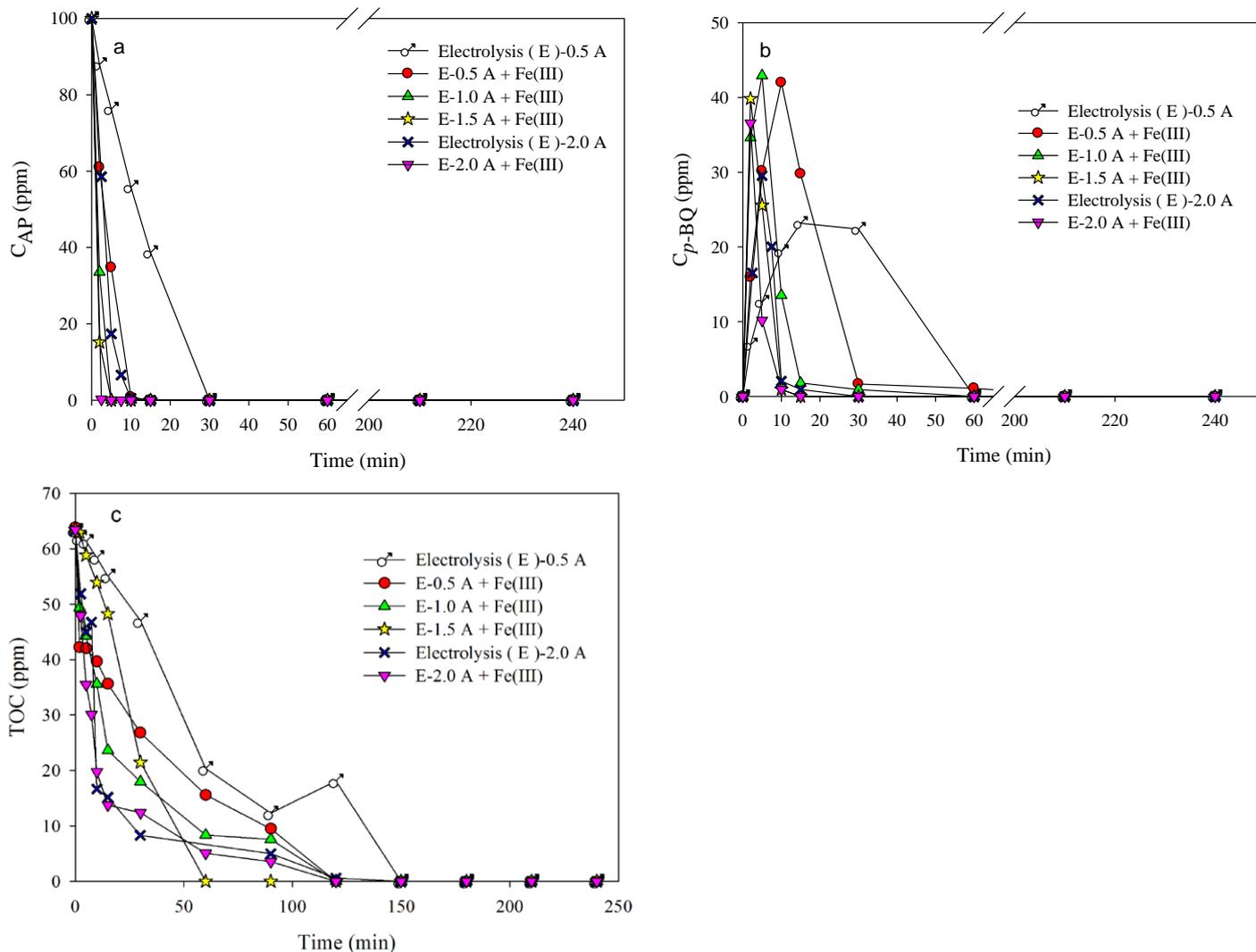


Figure 7. Electrochemical degradation of AP (100 ppm) (a), AP-derived *p*-BQ (b), and TOC (c) in the presence of 100 ppm Fe(III) in 1 M Na₂SO₄ at different currents (0.5–2.0A) (anode area = 2 cm² and 25°C).

4. CONCLUSIONS

This study tested the degradation of AP, the formation/degradation of *p*-BQ resulting from AP degradation, and the mineralization of TOC on BDD in the presence of redox mediators in 1 M Na₂SO₄ or NaNO₃. Based to the CV analysis, Fe(II)/Fe(III) redox peaks and Ag(I)/Ag(II) could be detected on a Windsor BDD in 1 M Na₂SO₄, and the oxidation peak of sulfate to persulfate could also be observed. The performance of AP degradation by a single redox mediator occurred in the following order: Ce(IV) (from Ce(SO₄)₂) > Fe(III) (from Fe(NO₃)₃ or FeCl₃) > Co(II) (from CoCl₂) ≈ Ag(I) (from AgNO₃). NO₃⁻

may contribute to slight AP degradation. The *p*-BQ from AP degradation was observed in 1 M Na₂SO₄ in the presence of Ce(IV) and Fe(III), while greater and faster *p*-BQ generation appeared for the former than for the latter.

In the presence of individual redox mediators in 1 M Na₂SO₄ or NaNO₃, the performance (or apparent pseudo first-order rate constant, *k*) of AP degradation and TOC mineralization on a Diachem BDD anode occurred in the following order: Fe(III) > Ce(IV) > Fe(II) ≈ Co(II) > Ag(I), although replacing Na₂SO₄ with NaNO₃ as the electrolyte lowered this performance. The presence of Cl⁻ in 1 M Na₂SO₄ also improved the AP degradation and TOC mineralization. The *k* values for AP electrochemical degradation in these solutions ranged from 2.92×10⁻⁴–4.34×10⁻² 1/s. The appropriate Fe(III) dosage ranged from 50 to 500 ppm, which corresponded the mole ratios of Fe(III)/AP = 1.35–13.5 to increase the electrochemical AP degradation and TOC mineralization in 1 M Na₂SO₄. However, an Fe(III) dosage of 100 ppm (Fe(III)/AP mole ratio = 2.7) at 0.25 A/cm² is suggested for this electrochemical process. The addition or presence of Fe(III) in aqueous solution could significantly increase the performance of electrochemical degradation of AP.

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