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Electrochemical Degradation of Acetaminophen in the Absence/Presence of Ce(IV)

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This study investigates the degradation of acetaminophen (AP) using Ce(IV) oxidation with/without the aid of electrolysis on a Ti/PbO_2 anode in Na_2SO_4+H_2SO_4 solutions under different operating conditions. The results show that *p*-benzoquinone (*p*-BQ) is an intermediate generated from AP dergadation. Increases in temperature (25−80°C) did not accelerate the degradation of AP but increased the rate of *p*-BQ degradation. The AP degradation efficiencies all achieved 100% within 2 min despite the difference in Ce(IV) concentration (100−4000 ppm) and initial AP concentration (AP_o =10−100 ppm). The *p*-BQ degradation was noticeably quicker at higher Ce(IV) concentrations than at lower ones at AP_o =10 ppm, while the optimal Ce(IV) concentration range was 375−500 ppm, which showed better *p*-BQ degradation rates than the other Ce(IV) concentrations at AP_o =100 ppm. At AP_o = 10 mg/L, the increase in the current density without the addition of Ce(IV) increased the rate of AP degradation (pseudo-first-order rate constant (*k*) = 1.55×10^{-3}–6.04×10^{-3} s^{-1}) and *p*-BQ formation/degradation at 0.5–1.5 A/cm^2 and 25°C, but the electrochemical degradation efficiency of AP decreased with an increase in temperature (20–80°C) ($k = 1.55\times10^{-3}$–3.58×10^{-4} s^{-1}). The AP degradation efficiency was lower using electrolysis alone at 0.5–1.5 A/cm^2 and 20–80°C than when using only Ce(IV) oxidation at 80°C. Compared with the Ce(IV) oxidation method (without electrolysis), the electrochemical plus Ce(IV)-mediated (E+Ce(IV)) process achieved faster *p*-BQ degradation at lower temperatures. This E+Ce(IV) process was also more efficient for AP degradation and *p*-BQ formation/degradation than electrolysis alone. At AP_o = 100 ppm, 25°C, and 0.5 A/cm^2, the TOC removal ($k = 8.83\times10^{-5}$–1.65×10^{-4} s^{-1}) increased with increases in Ce(IV) concentrations (200–375 ppm) using the E+Ce(IV) process for AP degradation. For AP and *p*-BQ degradation, the Ce(IV) electrochemically regenerated from a spent Cr-etching solution was as good as the purchased one.

Keywords: degradation; acetaminophen (AP); *p*-benzoquinone (*p*-BQ); Ce(IV); PbO_2 electrode

1. INTRODUCTION

In recent years, pharmaceuticals and personal care products have been of great concern, and many of them are regarded as emerging (environmental) contaminants. Among these contaminants, acetaminophen (AP) has obtained considerable attention because it is frequently used in many countries [1−3] and is one of the most commonly detected compounds in sewage and surface water [2,4−6]. The highest concentrations of AP were found to be ~6 µg L^{-1} in European sewage treatment plant (STP) effluents [7], ~10 µg/L in natural waters in the USA [8], and >65 µg/L in the Tyne river, UK [9]. AP, a common analgesic and anti-inflammatory drug, is widely used for the relief of pain and fever. In addition, ~5 % of therapeutic AP doses are excreted unchanged in urine [10]. The frequent presence of AP in STP effluents poses a potential risk to aquatic and terrestrial organisms.

Therefore, reliable methods to achieve AP degradation are greatly needed. Thus, the degradation of AP has already been tested in several advanced oxidation processes (AOPs), such as TiO_2/UV [11,12], UV/H_2O_2 [13], ozonization [13], and electrochemical oxidation [14−17]. Ce(IV) (E^o = 1.61 V) can be used in mediated electrochemical oxidation (MEO) processes for organic pollutant destruction in acid solutions, and the Ce(III) from Ce(IV) reduction after use may be electrochemically regenerated in a subsequent procedure [18−20]. Therefore, the Ce(IV)-MEO is an environmentally friendly approach to organic pollutant abatement.

However, the degradation of AP using Ce(IV) with/without the aid of electrolysis has not been addressed as yet. Moreover, an acidic environment is favored for the oxidation of organic pollutants using Ce(IV) [18−20]. Therefore, the aim of the present work is to explore the degradation of AP and its degradation intermediate – *p*-benzoquinone (*p*-BQ) using Ce(IV), electrolysis, or Ce(IV) plus electrolysis in 1 M Na_2SO_4 at pH = 1 (suitable for Ce(IV) acting as an oxidant) [18−20] under different operating parameters (initial AP concentration, Ce(IV) concentration, temperature, and current density). For comparison, Ce(IV) electrochemically regenerated from a spent thin-film transistor liquid-crystal display (TFT-LCD) Cr-etching solution was also tested for AP degradation.

2. MATERIALS AND METHODS

2.1. Chemicals and materials

The acetaminophen (AP) ($C_8H_9NO_2$ = 151 g/mol), shown in Figure 1, was purchased from Sigma, and the *p*-benzoquinone purchased from Alfa, was used for the quantification of this intermediate. Na_2SO_4 (Showa, Japan) was used to prepare the supporting electrolyte. Cerium(IV) sulphate 4-hydrate ($Ce(SO_4)_2 \cdot 4H_2O$) was provided by Panreac Quimica (EU). Acetonitrile and sulfuric acid (98%) were supplied from ECHO Chemical Co. Ltd. (Taiwan) and Scharlau (Spain), respectively.

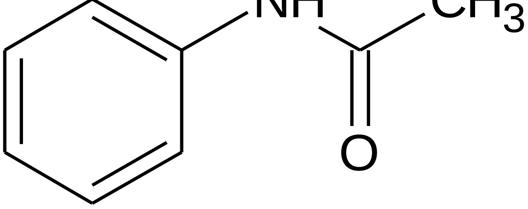

Figure 1. Molecular structure of acetaminophen (AP).

2.3. Degradation experiments

The AP degradation batch experiments by Ce(IV) were carried out by adding different amounts of Ce(IV) into solutions (with the pH = 1 adjusted using H_2SO_4), which initially contained 10 or 100 mg/L AP in a reactor. The solution was uniformly mixed using a magnetic stirrer. Samples were taken at intervals with immediate addition of excess ferrous ions to prevent the subsequent oxidation of AP by residual Ce(IV).

Electrolysis experiments were performed in a divided, thermostated cell (separator: Nafion-212 (Dupont)) with magnetic stirring. With the pH adjusted to 1 using H_2SO_4, the anolyte (100 mL) was 1 M Na_2SO_4 spiked with 10 or 100 mg/L AP, while the catholyte was only 1 M Na_2SO_4 solution. The Ti/PbO_2 electrode (1 cm^2) was used as the anode, and a Ti plate served as the cathode for the degradation of AP under different operating conditions galvanostatically operated with a DC power supply (Good Will Instrument Co. Ltd. GPS-2303). The Ti/PbO_2 electrode fabrication method has been described elsewhere [21]. The cell voltage and current data were obtained from the DC power supply readings. For the electrochemical degradation of AP in the presence of Ce(IV), the electrolysis was performed simultaneously with the addition of Ce(IV) into anolyte containing AP. The samples collected during the experiments were analyzed for the concentrations of AP, *p*-benzoquinone (*p*-BQ), and total organic carbon (TOC).

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

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

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

$$\mathrm{Ln}(Co/C) = kC \quad (3)$$

where AP and TOC are the residual concentrations of AP and TOC at a given electrolytic time, respectively, and AP_o and TOC_o are the initial concentrations of AP and TOC, respectively.

2.4. Analysis

Ferrous ammonium sulfate solutions (in 1 M nitric acid) were used to quantify the Ce(IV) concentrations of samples based on titration (Metrohm 702 SM Titrino) [22]. The concentrations of total cerium were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Perkin Elmer Optima 2100 DV). The concentrations of residual AP and those of *p*-BQ generated from AP degradation in the samples were analyzed using an HPLC analyzer (Hitachi Chromaster 5420). The compound separations were performed on a Mightysil RP-C18 column (250 mm×4.6 mm, particle size, 5µm). 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 and injection volume were 1.0 mL/min and 20 µL, respectively. The AP retention time (254 nm) was 2.9 min, while that of *p*-BQ (245 nm) was 4.3 min. Mineralization of AP was evaluated according to the removal of the corresponding TOC determined using a TOC analyzer (Shimadzu 5000) operated at 680°C. Purified air was used as the carrying gas, with a flow rate of 150 mL/min.

3. RESULTS AND DISCUSSION

3.1. Effect of temperature on the degradation of AP and p-BQ

Figure 2 shows the AP destruction curves at various temperatures (25−80°C). The degradation of AP by Ce(IV) oxidation was fast because the AP totally disappeared within 2 min at Ce(IV) = 200 ppm (mg/L). This AP degradation behavior by Ce(IV) oxidation is faster than or similar to that of the degradation of some organics by Ce(IV) or other metal ion oxidants in MEO processes [20,23,24].

At Ce(IV) = 200 ppm, the concentrations of *p*-BQ generated from AP degradation at three tested temperatures all reached maximum values at 2 min, and then the *p*-BQ concentration decreased over time at 50°C and 80°C although a different trend was observed at 25°C (Figure 2 inset). The C/C_{max} of *p*-BQ began to increase after 15 min. On one hand, the degradation of AP led to the formation of *p*-BQ. On the other hand, the oxidation of *p*-BQ by Ce(IV) resulted in a decrease in *p*-BQ concentration. In this study, C_{max} denotes the maximum concentration of *p*-benzoquinone at reaction time $t = t_{max}$. At $t < t_{max}$, the rate of *p*-BQ generation from AP degradation was greater than that of *p*-BQ consumption by Ce(IV) oxidation, but at $t > t_{max}$, an opposite trend appeared. As a result, the ratio of C/C_{max} of *p*-BQ quickly increased during the initial 2 min of reaction. However, after 2 min, the C/C_{max} decreased with increases in the reaction time.

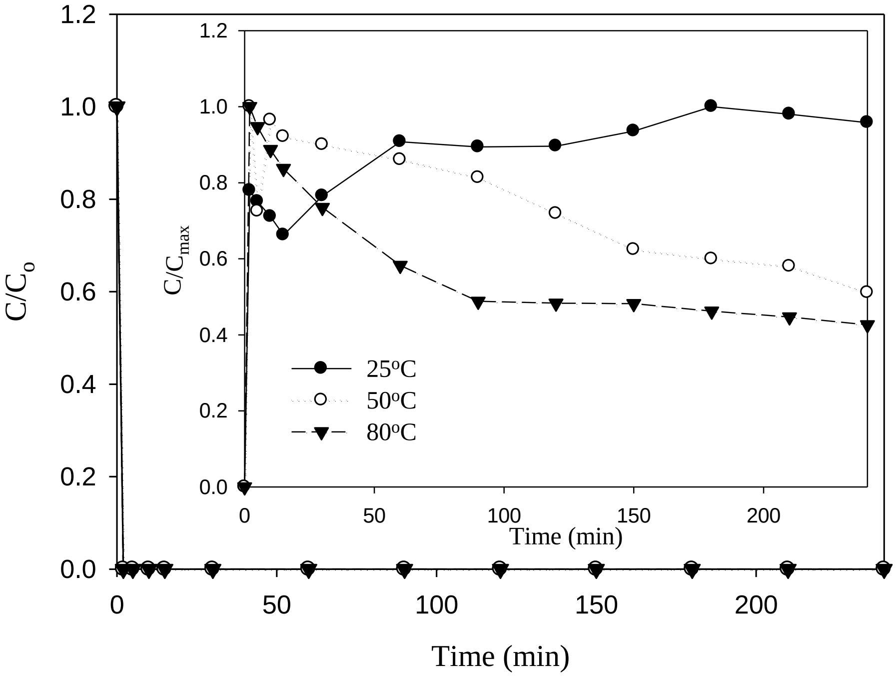

Figure 2. Degradation of AP and *p*-BQ generated from AP degradation (inset) by Ce(IV) (200 mg/L) oxidation at different temperatures (AP_o = 10 ppm).

According to the inset in Figure 2, it can be inferred that the increase in temperature speeded up the formation and subsequent removal of *p*-BQ and shortened the time to reach the C_{max} of *p*-BQ. Similarly, the increasing destruction or mineralization with increases in temperature due to Ce(IV) oxidation was also found for benzoic acid (25−45°C) in 0.2 M H_2SO_4 [25] and for ethylenediaminetetraacetic acid (EDTA) (70−95ºC) [26] and phenol (25−90ºC) [27] in 3 M nitric acid. This finding was attributed to the greater reaction rate at the higher temperature. After a 240 min reaction between 10 ppm AP and 200 ppm Ce(IV) at 80ºC, the C/C_{max} did not reach zero, indicating that more Ce(IV) was necessary to accelerate the formation and degradation of *p*-BQ and the mineralization of AP. Therefore, Ce(IV) concentration tests were performed in subsequent experiments at 80ºC.

3.2. Effect of Ce(IV) concentration on the degradation of AP and p-BQ

For simplification, if CO_2 and NH_4^+ are the main final products, the direct degradation of AP ($C_8H_9N_2O$, 151 g/mol) by Ce(IV) (140 g/mol) can be expressed by the following reaction:

$$33Ce^{4+} + C_8H_9N_2O + 15H_2O \rightarrow 33Ce^{3+} + 8CO_2 + 2NH_4^+ + 31H^+ \quad (4)$$

However, if *p*-BQ (intermediate, $C_6H_4O_2$) appears during the oxidation of AP by Ce(IV), and CO_2 and NH_4^+ are the main final products, this type of AP degradation can be described using:

$$9Ce^{4+} + C_8H_9N_2O + 5H_2O \rightarrow 9Ce^{3+} + C_6H_4O_2 + 2CO_2 + 2NH_4^+ + 7H^+ . \quad (5)$$

If NH_4^+ is further oxidized to NO_3^-, then the reaction is:

$$23Ce^{4+} + C_8H_9N_2O + 11H_2O \rightarrow 23Ce^{3+} + C_6H_4O_2 + 2CO_2 + 2NO_3^- + 27H^+ . \quad (6)$$

The initial concentration of AP (10 ppm) was significantly lower than that of Ce(IV) (200 ppm), corresponding to the mole or molar concentration ratio of Ce(IV) to AP = ~22/1, which was close to that of Reaction 3. Theoretically, the required mole ratio of Ce(IV)/AP is 33/1 for complete AP mineralization (Reaction 4).

The degradation efficiencies of 10 ppm AP were all 100% at 2 min when the initial concentrations of Ce(IV) ranged from 100−800 ppm (Figure 3a). This range of Ce(IV) concentration corresponded to Ce(IV)/AP mole ratios ranging between approximately 11/1 and 86/1 at AP = 10 ppm, covering those of reactions 4 to 6 (33/1, 9/1, and 23/1, respectively). The *p*-BQ formation rates were similar at the four tested Ce(IV) concentrations. At Ce(IV) = 100 and 200 ppm, the *p*-BQ degradation rates were also similar (Figure 3a inset). Nevertheless, the *p*-BQ degradation was noticeably quicker at higher Ce(IV) concentrations of 400 or 800 ppm, where complete degradation of *p*-BQ was achieved at ~90 min. Benzoquinone ($C_6H_4O_2$) is usually detected as an intermediate in the oxidative degradation of phenolic compounds in aqueous solutions. For example, the oxidation of phenol by H_2O_2 generated benzoquinone [28] and the *p*-BQ intermediate has also been observed during the electrochemical degradation of bisphenol A [27,29,30]

At a ten-fold initial AP concentration (AP_o =100 ppm), 100% AP degradation was still observed within 2 min for concentrations of Ce(IV) ranging from 100−800 ppm (Figure 3b). At Ce(IV) = 200 ppm, the reaction time for reaching *p*-BQ C_{max} was similar for $[AP]_o$ =10 and 100 ppm (Ce(IV)/AP mole ratios = 22 and 2.2, respectively); however, the *p*-BQ degradation rate was significantly faster for the former than for the latter (Figure 3b inset). When the Ce(IV) concentration increased from 200 to 375 ppm, the *p*-BQ degradation rate significantly increased. The optimal Ce(IV) concentration range was 375−500 ppm (Ce(IV)/AP mole ratios = 4.0−5.4), showing better *p*-BQ degradation rates than the Ce(IV) concentrations of 1000, 2000, and 4000 ppm, which corresponded to Ce(IV)/AP mole ratios of 11, 22, and 43, respectively. Interestingly, the time required for the complete disappearance of *p*-BQ was only double (180 min) when the initial concentration of AP increased from 10 to 100 ppm, and the concentration of Ce(IV) did not have to be proportionally increased.

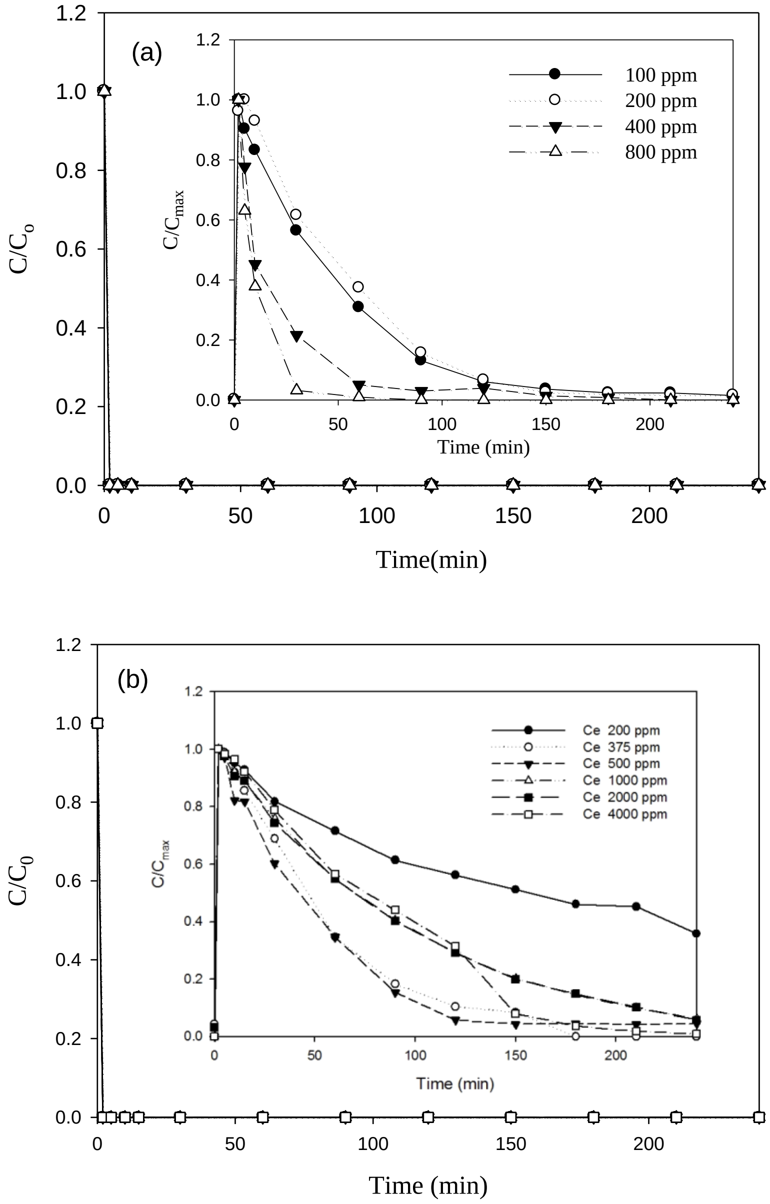

Figure 3. Degradation of AP and *p*-BQ generated from AP degradation (inset) by Ce(IV) at different concentrations and initial AP concentrations (AP_o =10 (a) and 100 (b) mg/L) (80°C).

3.3. Effect of current density and temperature on electrochemical degradation of AP and p-BQ

Figure 4a shows the variations in AP (AP_o = 10 mg/L) and *p*-BQ concentrations during electrochemical degradation on Ti/PbO_2 at 0.5–1.5 A/cm^2 and 25°C. The AP degradation increased with increases in current density. It only took 10 min to achieve complete AP degradation (efficiency = 100%) at 1.5 A/cm^2, while 30 min was required to obtain 100% AP degradation efficiency at 0.5 and 1.0 A/cm^2. This result is consistent with the fact that the rate of organic pollutant degradation generally increases with increases in current density in the case of electrochemically advanced oxidation processes (e.g., the AP electrochemical degradation using Ti/PbO_2 in this study), which are associated with •OH generation [26] since more oxidizing species are formed at any given time [31]. The pseudo first-order rate constants (k) of AP electrochemical degradation ranged from 1.55×10^{-3}–6.04×10^{-3} s^{-1} (Table 1); furthermore, the k value obtained at 0.5 A/cm^2 in 1 M Na_2SO_4 in this study was slightly smaller than that (1.94×10^{-3} s^{-1}) reported in a 4.8×10^{-4} M H_2SO_4 + 1 M Na_2SO_4 solution [22]. Increases in current density also resulted in increases in the rates of *p*-BQ formation and degradation (Figure 4b). The *p*-BQ generated from AP degradation totally disappeared after 15 min at 1.5 A/cm^2, while double the amount of time was needed at 0.5 or 1.0 A/cm^2.

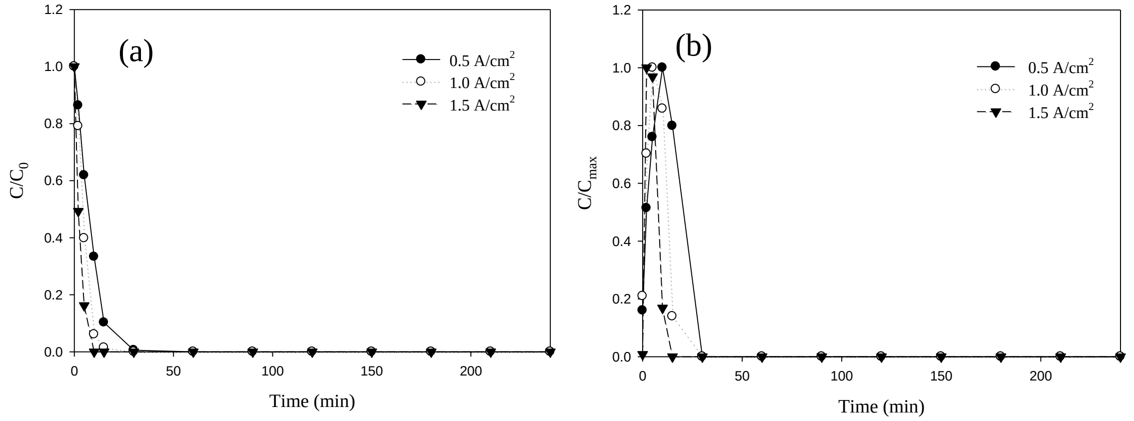

Figure 4. Electrochemical degradation of AP (a) and *p*-BQ generated from AP degradation (b) at different current densities (AP_o = 10 mg/L and 25°C).

Table 1. Pseudo-first-order rate constants (k, 1/s) for electrochemical AP degradation without the addition of Ce(IV) at different current densities (25°C) and temperatures (0.5 A/cm^2) (AP_o = 10 mg/L) and for TOC removal with the addition of Ce(IV) at different concentrations (25°C and 0.5 A/cm^2) (AP_o = 100 mg/L).

Current density (A/cm^2)			Temperature (°C)			Ce(IV) concentration (ppm)		
0.5	1.0	1.5	25	50	80	200	375	500
1.55×10^{-3}	2.92×10^{-3}	6.04×10^{-3}	1.55×10^{-3}	1.00×10^{-3}	3.58×10^{-4}	8.83×10^{-5}	1.18×10^{-4}	1.65×10^{-4}

Dissimilarly, the AP electrochemical degradation efficiency decreased with increases in temperature (20–80°C) at AP_o = 10 mg/L (Figure 5a). This trend was opposite to that when increasing current density although it was also found for the electrochemical degradation of bisphenol A in our earlier study [30]. This result was possibly related to the dimerization of AP [32] or polymeric product deposition on the surface of the anode [27] although partial AP might be oxidized by electrochemically generated persulfate [31]. At 25–80°C, the k values of AP electrochemical degradation ranged from 1.55×10^{-3}–3.58×10^{-4} s^{-1} (Table 1). The rates of *p*-BQ formation and degradation also decreased as the temperature was increased, which was in accordance with the results for AP electrochemical degradation and indicates that increased temperatures are favorable for the electrochemical degradation and mineralization of AP.

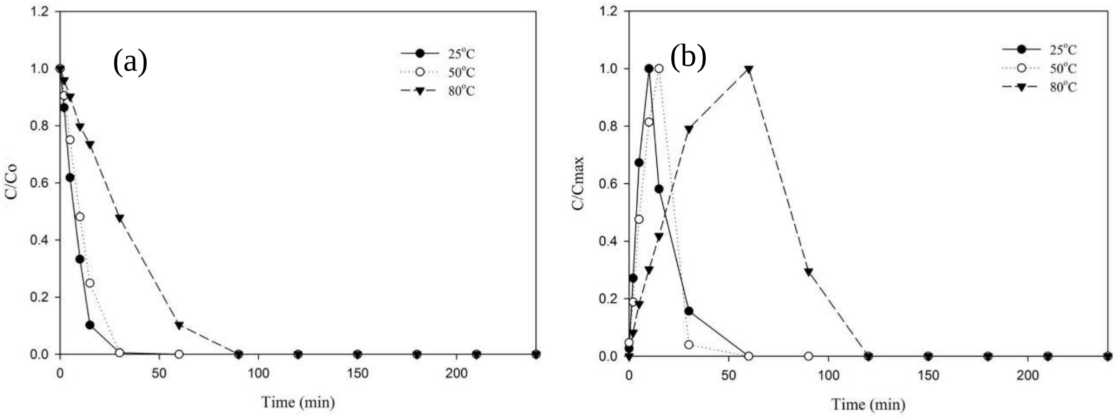

Figure 5. Electrochemical degradations of AP (a) and *p*-BQ generated from AP degradation (b) at different temperatures (AP_o = 10 mg/L and 0.5 A/cm^2).

3.4. AP and p-BQ degradation using an electrochemical plus Ce(IV)-oxidizing (E+Ce(IV)) process

According to the discussion in sections 3.1 and 3.3, the temperatures that were better for the AP (AP_o = 10 mg/L) degradation processes using Ce(IV) and electrochemical oxidation were different (80°C and 25°C, respectively). Therefore, we tested AP and *p*-BQ degradation using an electrochemical plus the Ce(IV)-oxidizing (E+Ce(IV)) process under different temperatures. Within 2 min, the AP degradation efficiencies achieved 100% with only Ce(IV) oxidation at 80°C or E+Ce(IV) oxidation at 0.5 A/cm^2 under different temperatures (20–80°C) (Figure 6).

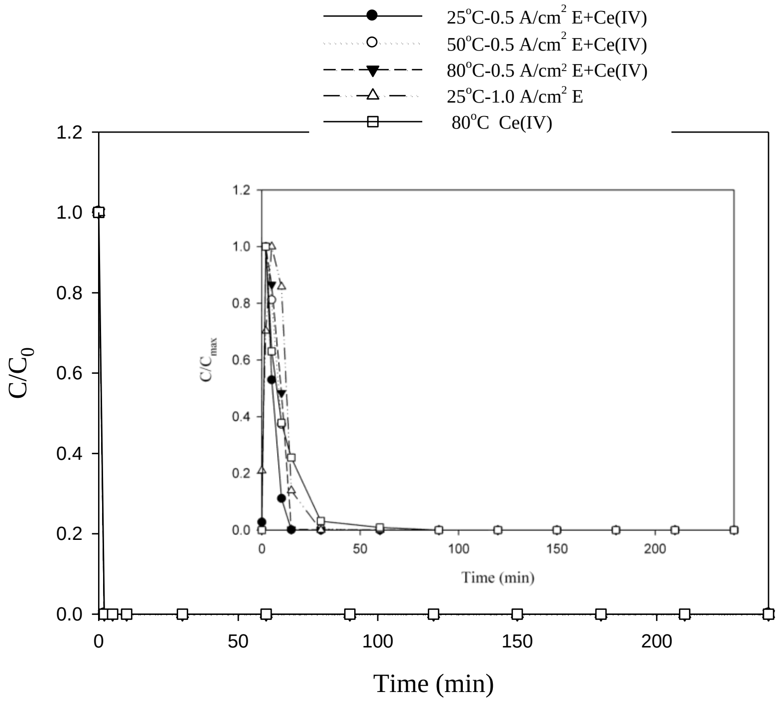

Figure 6. Electrochemical degradation of AP and *p*-BQ generated from AP degradation (inset) with/without Ce(IV) addition at different temperatures and current densities (AP_o = 10 mg/L) ([Ce(IV)] = 200 and 800 mg/L with and without electrolysis, respectively).

A lower AP degradation efficiency was observed when using electrolysis alone, even at a higher current density (1.0 A/cm^2). Without the addition of Ce(IV), the rates of *p*-BQ formation and degradation were also slightly lower (Figure 6 inset). The *p*-BQ degradation rate was also slightly lower when using Ce(IV) without electrolysis. It was noted that the concentrations of Ce(IV) were 200 and 800 mg/L with and without electrolysis, respectively, indicating that a lower Ce(IV) concentration could be used for electrolysis (0.5 A/cm^2) at room temperature (25^{o}C) to obtain a performance similar to that using Ce(IV) alone for AP and *p*-BQ degradation.

Nevertheless, the effect of Ce(IV) concentration on AP degradation was further tested at 25^{o}C and 0.5 A/cm^2 for the E+Ce(IV) process with a greater AP initial concentration (AP_o = 100 mg/L). It was observed that the rates of AP degradation (Figure 7) and *p*-BQ degradation (Figure 7 inset) were significantly lower at Ce(IV) = 200 ppm than at Ce(IV) = 375 and 500 ppm, which had similar rates of AP degradation and *p*-BQ degradation; however, this finding concurred with that discussed in Section 3.2, and was considered attributable to the insufficient amount of Ce(IV) at 200 ppm when increasing the initial concentration of AP from 10 to 100 ppm. However, the trade-off between Ce(IV) concentration and electrolysis still existed because only 60 min was required to reach complete *p*-BQ degradation in the case of the E+Ce(IV) process, while the required time was triple (180 min) for using Ce(IV) alone at Ce(IV) = 375 ppm (as shown in Figure 3b).

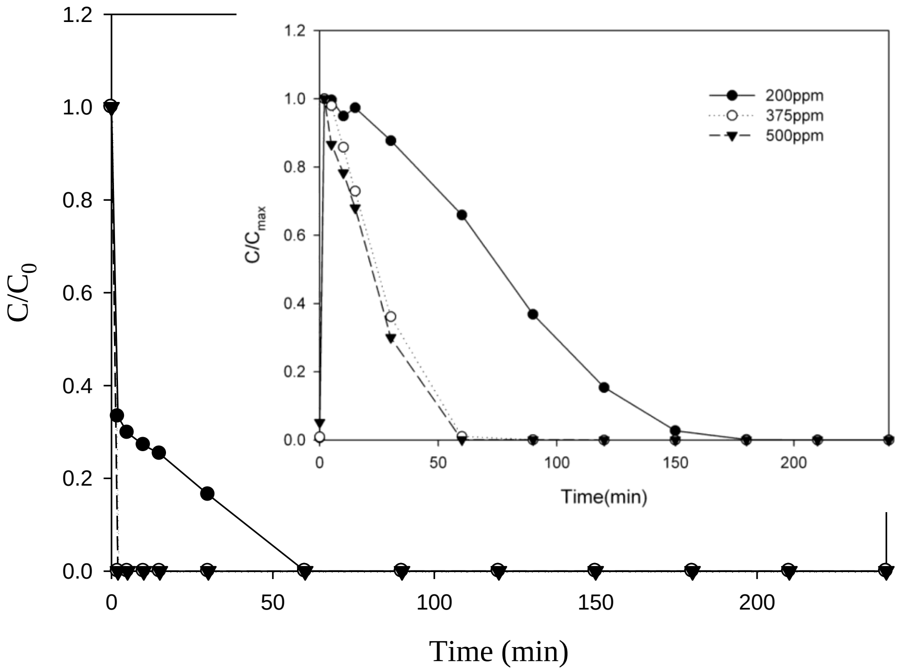

Figure 7. Electrochemical degradation of AP and *p*-BQ generated from AP degradation (inset) at different Ce(IV) concentrations (AP_o = 100 ppm, 25^{o}C, and 0.5 A/cm^2).

Figure 8 shows that the TOC removal efficiency increased with increases in Ce(IV) concentration over time for an initial AP concentration = 100 ppm at 25^{o}C and 0.5 A/cm^2, while the complete mineralization of TOC was obtained at 240 min for the Ce(IV) concentrations of 200, 375, and 500 ppm. However, similar rates of either AP degradation or *p*-BQ degradation were noticed at Ce(IV) = 375 and 500 ppm (Figure 7 inset). This finding is associated with the fact that •OH and Ce(IV) are involved in both AP degradation and TOC mineralization although the former is stronger than the latter for TOC mineralization. At a higher Ce(IV) concentration, the Ce(III) generated from Ce(IV) reduction in AP or intermediate degradation might compete with water for electrochemical oxidation on the anode surface to produce Ce(IV) and •OH, respectively. Therefore, both •OH and Ce(IV) played important roles in the AP degradation and TOC mineralization. The *k* values for TOC removal were 8.33×10^{-5}, 1.18×10^{-4}, and 1.65×10^{-4} s^{-1}, respectively (Table 1).

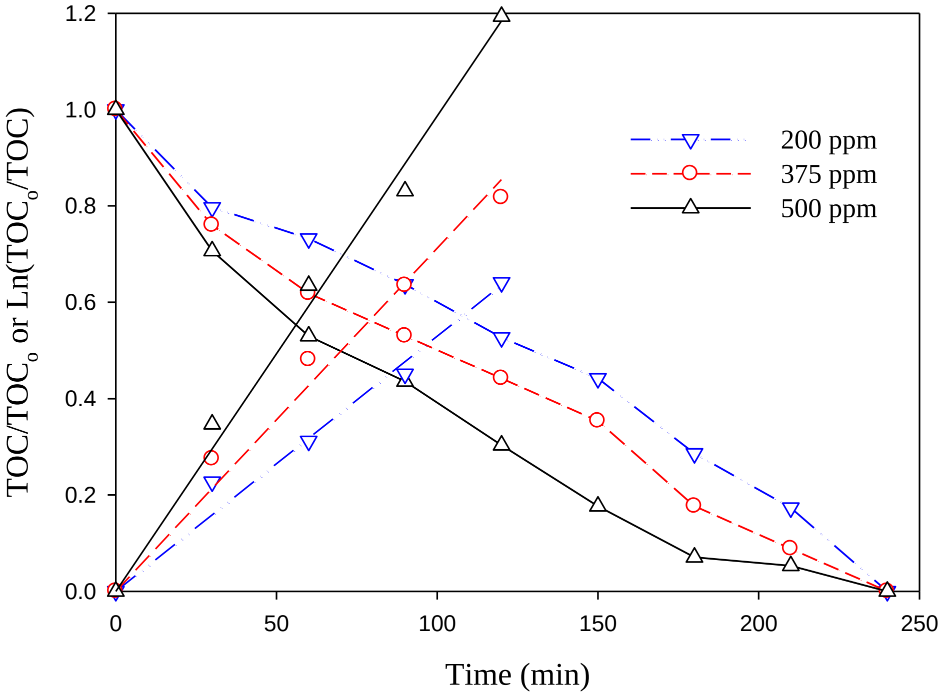

Figure 8. TOC/TOC$_o$ (data with spline curves) or Ln(TOC$_o$/TOC) (data with linear regression lines from the origin) against time for AP electrochemical degradations at different Ce(IV) concentrations (AP_o = 100 ppm, 25°C, and 0.5 A/cm^2).

3.5. Electrochemical degradation of AP and p-BQ with the addition of purchased versus regenerated Ce(IV)

According to our previous studies, Ce(IV) can be electrochemically regenerated from spent thin-film transistor liquid-crystal display (TFT-LCD) Cr-etching solutions [33–35]. Therefore, electrochemical AP degradation with the addition of regenerated Ce(IV) was also tested for comparison. Figure 9 shows the electrochemical degradation of AP and *p*-BQ with the addition of purchased (the same chemical ($Ce(SO_4)_2\cdot4H_2O$) used in the tests in sections 3.1, 3.2, and 3.4) versus regenerated Ce(IV) (500 mg/L) at 25°C and 0.5 A/cm^2. Obviously, both cases exhibited quite similar performance in terms of AP degradation, *p*-BQ formation, and degradation rates, suggesting that the regenerated Ce(IV) has good potential to be used in the E+Ce(IV) process for AP abatement in aqueous solutions.

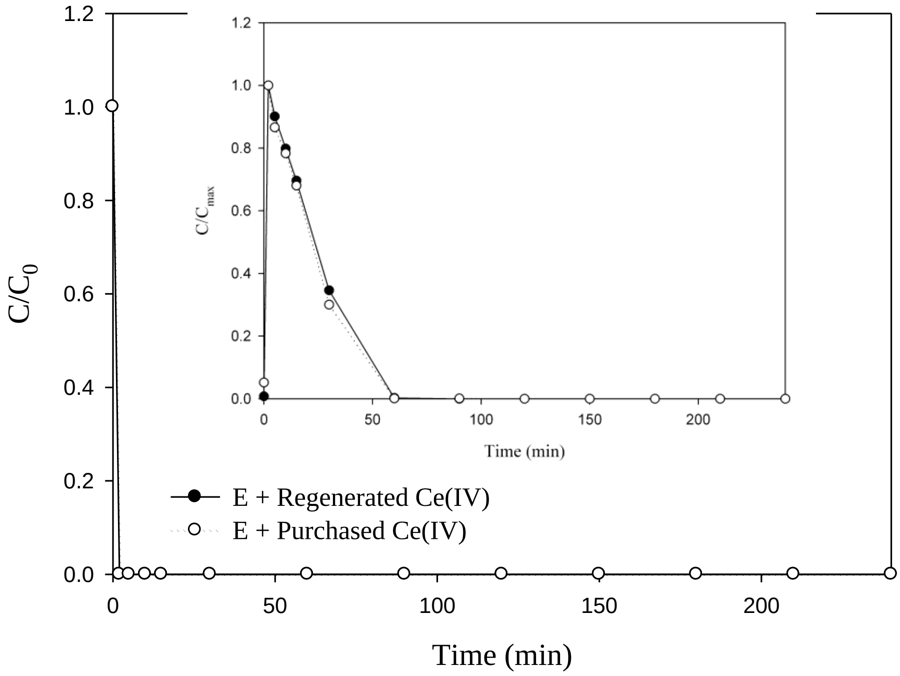

Figure 9. Electrochemical degradation of AP and *p*-BQ generated from AP degradation (inset) with the addition of purchased versus regenerated Ce(IV) (500 mg/L) (25°C and 0.5 A/cm^2).

4. CONCLUSIONS

In this study, the degradation of AP and variations in *p*-BQ on PbO_2 were tested under different operating conditions. It was found that increases in temperature (25−80°C) did not accelerate the degradation of AP but increased the rate of *p*-BQ degradation. The degradation efficiencies of 10 ppm AP were all 100% at 2 min when the initial concentrations of Ce(IV) ranged from 100−800 ppm; additionally, the *p*-BQ degradation was noticeably quicker at higher Ce(IV) concentrations than at lower ones. At AP_o =100 ppm, 100% AP degradation was still obtained within 2 min at Ce(IV) concentrations ranging from 100−800 ppm, while the optimal Ce(IV) concentration range was 375−500 ppm, which exhibited better *p*-BQ degradation rates than the Ce(IV) concentrations of 1000, 2000, and 4000 ppm.

Without the addition of Ce(IV), increasing the current density increased the rates of AP (AP_o = 10 mg/L) degradation (pseudo-first-order rate constant (k) = 1.55×10^{-3}–6.04×10^{-3} s^{-1}) and *p*-BQ formation and degradation on PbO_2 at 0.5–1.5 A/cm^2 and 25°C; conversely, the AP electrochemical degradation efficiency decreased with increases in temperature (20–80°C) ($k = 1.55\times10^{-3}$–3.58×10^{-4} s^{-1}). A lower AP degradation efficiency was observed when using electrolysis alone at 0.5–1.5 A/cm^2 and 20–80°C as compared to using only Ce(IV) oxidation at 80°C. In comparison to the Ce(IV) oxidation method (without electrolysis), the electrochemical plus Ce(IV)-oxidizing (E+Ce(IV)) process only required a lower reaction temperature to achieve faster *p*-BQ degradation. This E+Ce(IV) process was also more efficient for AP degradation and *p*-BQ formation/degradation than electrolysis alone. The TOC removal efficiency increased with increases in Ce(IV) concentration (200–375 ppm) ($k = 8.83\times10^{-5}$–1.65×10^{-4} s^{-1}) using the E+Ce(IV) process for AP degradation at AP_o = 100 ppm, 25°C, and 0.5 A/cm^2.

The Ce(IV) electrochemically regenerated from a spent thin-film transistor liquid-crystal display (TFT-LCD) Cr-etching solution exhibited similar performance for AP degradation and *p*-BQ degradation, suggesting that regenerated Ce(IV) has good potential to be used in the E+Ce(IV) process for AP abatement in aqueous solutions.

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