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Electrochemical Detection and Degradation of Acetaminophen in Aqueous Solutions

Te-San Chen, Kuo-Lin Huang[*]

Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan (ROC)
[*]E-mail: huangkL@mail.npust.edu.tw

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This study presents simple electrochemical approaches used to detect and destroy acetaminophen (AP) in aqueous solutions. The electro-oxidation behavior and efficiency of AP were monitored on a poly(L-serine) (PLS) film-modified glassy carbon electrode (GCE) using cyclic, linear sweep voltammetric, and differential pulse voltammetric techniques. The PLS film was found to exhibit catalytic activity towards the electrochemical oxidation of AP. Under optimized pH condition, AP showed a linear response between 1.0×10^{-6} and 1.0×10^{-5} mol L^{-1} (correlation coefficient > 0.995). The detection limit (DL) of AP was determined as 1.0×10^{-7} mol L^{-1} (S/N = 3) and the average recoveries and relative standard deviation (RSD) were 97.5 and 2.8% ($n = 5$), respectively. In addition, increasing current density and pH favored the degradation of AP. The performance of PbO_2/Ti anode was better than those of Pt/Ti and DSA electrodes for AP degradation.

Keywords: Acetaminophen, Poly(L-serine) film-modified electrode, Electrochemical method, Voltammetry, Degradation.

1. INTRODUCTION

Recently, the presence of pharmaceuticals (referred to emerging environmental pollutants) in the environment has received a lot of attention, because the pharmaceuticals raise risks to environment and concerns for human health [1]. Also, researchers have attributed adverse ecological effects to these compounds [2, 3]. Acetaminophen (AP), one of the most common pharmaceuticals found in households, is used for the relief of pain and fever. Hence, AP is usually present in the effluent of sewage treatment plants and surface water. The presence of AP in municipal sewage is largely attributable to its manufacturing processes and the disposal of unused ones or human excretion. In therapeutic doses, 1–4% of the drug is excreted unchanged in the urine [4]. Over the past few years, AP has received much attention because it is one of most-used medicines in many countries [5, 6] and is also one of most frequently detected pharmaceuticals in sewage [6-9]. In Taiwan, AP has been found to have high detection concentrations (the highest = 100,433 ng L^{-1}) (with a relatively high frequency of detection (over 90 %)) in the some contaminated water samples [6]. Little information is available on the detection and destruction of AP in aquatic environment. So far, different methods have been reported for the determination of AP such as high-performance liquid chromatography [10, 11] chemiluminescence [12], and liquid chromatography–mass spectrometry [5, 13]. Nevertheless, these methods suffer from some disadvantages such as requirement for sample pretreatment, high cost, and long analysis time. Moreover, different methods have been reported for the destruction of AP, such as ozonation and H_2O_2/UV. However, only partial mineralization of 30% and 40% has been found from ozonation and H_2O_2/UV, respectively, in the pH range 2.0–5.5 [14]. Thus, it is also greatly in need to develop reliable processes for the treatment of AP.

It is attractive to apply electrochemical methods for the detection and degradation of AP, because these methods are simplest, rapid, less expensive, and clean for the detection and degradation of emerging environmental pollutants. However, the use of conventional material electrodes usually requires high potentials for the electro-oxidation of target compounds or suffers fouling of electrode surface by the products generated from electrochemical reactions; consequently, the achieved detection limits are relatively high. In order to eliminate these drawbacks, various approaches using different modified electrodes have been proposed [15-30]. However, using a poly(L-serine) (PLS) film-modified glassy carbon electrode (GCE) to detect AP has not been proposed. In recent years, PLS film-modified electrodes have received extensive interest due to their wide application for chemical sensors; these modified electrodes may decrease the over potential, improve the mass transfer, and enrich the substance in electrochemical reactions of interest [31-33]. Song *et al.* [32] reported that a lab-prepared PLS film-modified glassy carbon electrode (GCE) could catalyze electrochemical oxidation of estradiol and its application for sensitive and rapid determination of estradiol was promising. Li [31] also observed that the electrocatalytic activity to the oxidation of tyrosine was excellent on a PLS film-modified GCE, because the peak current was greatly enhanced while the peak-to-peak potential separation turned narrow, when compared with that on a bare glassy carbon electrode. He concluded that the PLS film-modified GCE was a promising device in practical use for the determination of tyrosine. Nevertheless, little is known for the electrochemical detection and degradation of AP in aqueous solutions.

In this study, we applied an electrochemical approach to detect and destruct AP in aqueous solutions. A cyclic voltammetric (CV) technique was used to achieve the electropolymerization of L-serine on GCE surface and prepare the PLS film-modified GCE. CV, linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV) analyses were performed to examine the electrode's responses and sensitivities for determination of AP. DSA (dimensional stable anode, IrO_2/Ti), Pt/Ti, and PbO_2/Ti electrodes were tested and compared for the electrochemical degradation of AP. Some electrolytic variables such as current density, electrolyte pH, and electrode material were evaluated in the degradation of AP in aqueous solutions.

2. MATERIALS AND METHODS

2.1. Chemicals and Materials

AP was purchased from Sigma (USA) while L-serine was obtained from Alfa Aesar (UK). Sodium phosphate dibasic dehydrate ($Na_2HPO_4 \cdot 2H_2O$) and phosphoric acid (H_3PO_4) used for the preparation of phosphate buffer solutions were supplied by Merck. All the reagents (analytical grade) were used as received without further purification. The stock solution (1.0×10^{-2} mol L^{-1}) of AP was prepared by dissolving the chemical into 0.1 M phosphate buffer solution (pH 6.0), and then stored at 4^oC. Deionized distilled water (DDW) was used throughout the experimental works.

2.2. Instruments

The electrochemical behavior measurements and determination of the AP in the prepared solutions were performed using CV and LSV on a 660B electrochemical workstation (American, CH Instruments, Inc) which was connected with a conventional three-electrode system. A PLS film-modified glassy carbon electrode and a platinum wire were used as the working and counter electrodes, respectively. The reference electrode was Ag/AgCl (3 mol KCl dm^{-3}, 0.207 V vs SHE (standard hydrogen electrode) at 25^oC). The electrolyses of the AP aqueous solutions (1 M Na_2SO_4) were carried out in a divided thermostatted cell by a DC power supply (Good Will Instrument CO., LTD GPS-2303).

2.3. Preparation of PLS Film-Modified GCE

The PLS film-modified GCE was prepared as follows. A GCE was polished with 0.05 μm alumina slurry, then rinsed with redistilled water, and finally sonicated in redistilled water to give a clean and mirror surface. The electropolymerization of L-serine on GCE surface was carried out using cyclic sweeps between –0.6 and 2.0 V vs Ag/AgCl in 0.1 mol L^{-1} phosphate buffer (pH 5.0) containing 1.0×10^{-2} mol L^{-1} L-serine. During the electrochemical polymerization process, an oxidation peak was observed at 1.41 V vs Ag/AgCl in the anodic scan and a reduction peak appeared at −0.30 V vs Ag/AgCl in the reverse (cathodic) scan due to the formation of PLS (Fig. 1). As can be seen from Fig. 1, the oxidation and reduction peak currents both increased with increasing voltammetric scan, indicating that an electro-conductive polymer film has been formed on the electrode surface. After 20 scanning cycles, the surface of the electrode was washed with redistilled water to remove physically adsorbed materials. After air-drying, a clear blue PLS film was seen on the electrode surface. The thickness (or sensitivity) of the PLS film could be adjusted by controlling the cyclic number of voltammetric scans. The cyclic voltammogram of acetaminophen (1.0×10^{-4} mol L^{-1}) in 0.1 M phosphate buffer (pH 6.0) reached stable after 20 cycles (data are not shown here), so the optimum scan number of 20-cycle was used in this study.

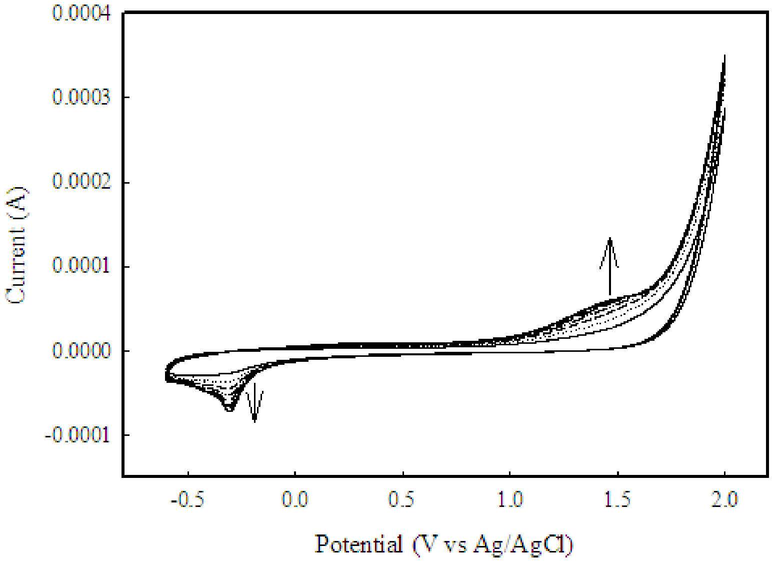


Figure 1. Cyclic voltammograms for the electropolymerization of L-serine on a glassy carbon electrode (GCE). Supporting electrolyte: 0.1 M phosphate buffer (pH 5.0), scan rate: 100 mV s^{-1}, and L-Serine concentration: 1.0×10^{-2} mol L^{-1}.

2.4. Preparation of PbO_2/Ti

Electro-deposition was employed for the preparation of PbO_2 coating on Ti. The titanium sheets (1.0 mm thickness, 99.5% purity) were mechanically polished using abrasive papers of successively finer roughness and then rinsed in two 15 min steps in ultrasonicated acetone and deionized distilled water (DDW). Acid pickling was done in a solution containing sulfuric acid 25% at 85^{o}C for 2 hrs. Electro-deposition experiments were conducted using a two-electrode electrochemical cell, in which the titanium sheet was used as the anode and a copper foil of similar size was used as the cathode. The gap between anode and cathode was fixed at 2 cm. The solution was agitated with a magnet at 200 rpm during the electroplating. The electroplating solution was made up of 16.7 g $Pb(NO_3)_2$, 2.0 g $Cu(NO_3)_2$, and 0.1 g NaF dissolved in 0.1 litter of distilled water. Nitric acid was used to adjust the pH of electrolyte to be 1. The PbO_2 layer was generated in the above mentioned solutions at 80 mA cm^{-2} for 3 hour at 65^{o}C.

2.5. AP Electrolysis

The electro-oxidation of the AP aqueous solution was performed under constant current electrolysis in a divided thermostatted cell. The anolyte (100 ml) was AP in 1 M Na_2SO_4 while the catholyte was 1 M Na_2SO_4. For the divided cell (H-type), the anode and cathode compartments were separated by an ion-exchange membrane separator (AMI-7001). The AMI-7001 is a type of strong base anion exchange membrane with quaternary ammonium functional groups. Prior to use, the AMI-

7001 was heated at 65°C in 1 M (~3%) H_2O_2 for 1 h to remove organic impurities, then the membranes were washed three times with DDWand stored in DDW.

The oxidation of aqueous AP was carried out under different current densities, anode materials, and electrolyte pH at constant temperature (30°C). DSA, Pt/Ti, or PbO_2/Ti was used as the anode whereas a Ti plate was as the cathode for the electrolysis/degradation of AP. These electrodes had the same geometric working surface areas ($1cm^2$). Samples were taken at intervals during the electrolysis for 210 min. For comparison, the residual AP concentrations of samples were analyzed by the PLS film modified GCE and an UV-visible spectrophotometer (at the maximum visible wavelength of 245 nm (SHIMADZU 1601)).

2.6. Electrochemical Measurement

In this study, a cyclic voltammetric (CV) approach and linear sweep voltammetry (LSV) analyses were performed to examine the electrode’s characteristic and response. Differential pulse voltammetry (DPV) has the advantage of increasing analytical sensitivity for applications; therefore DPV was used to obtain detect AP and its linear concentration ranges. Phosphate buffer solutions (0.1 mol L^{-1}, pH = 6.0) were used as the supporting electrolyte for each electrochemical measurement of AP. At first, the PLS film-modified GCE underwent successive cyclic sweeps between 0 and 1.2 V vs Ag/AgCl until the voltammograms were stable. Then, an AP solution was added. The potential scan ranges were 0↔1.2V (starting/ending at 0 V, scan rate 100 mV/s), 0–0.8 V (anodic, scan rate 10 mV/s), and 0–0.8 V (anodic, scan rate 5 mV/s, pulse amplitude of 50 mV and a pulse width of 20 ms) vs Ag/AgCl for CV, LSV, and DPV measurements, respectively. Since the main focus in this work was AP oxidation, for the LSV and DPV measurements, only the data in 0.2–0.7 V and 0.2–0.6 V (vs Ag/AgCl) ranges associated with the AP oxidation were provided.

2.7. COD Measurement

The closed reflux colorimetric method was used to determine COD values. 2 mL of sample was introduced into a commercially available digestion tube and the mixture was then heated 120 min at 150 °C. The amount of oxidizing agent reduced was subsequently determined colorimetrically using a colorimeter (Hach DR/890) and expressed as the COD.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of AP at PLS Film-Modified GCE

The electrochemical behaviors of AP at the bare and PLS film-modified GCEs were investigated using CV. Fig. 2 shows the CVs of 1.0×10^{-3} mol L^{-1} AP in 0.1 mol L^{-1} phosphate buffer (pH = 7.0). At the bare GCE, the redox behavior of AP was electrochemically irreversible with an oxidative peak at E_{pa} = 0.480 V vs Ag/AgCl, and a corresponding reduction peak at E_{pc} = 0.018 V vs

Ag/AgCl. In comparison to the bare GCE, the peak current of AP oxidation at the PLS film-modified GCE greatly increased, and the peak potential separation was reduced. Additionally, the oxidation peak potential was negatively shifted by 123 mV. This phenomenon is similar to that observed by Song *et al.* [32] for electrochemical determination of estradiol using a PLS film-modified GCE. The reasons for such an excellent catalytic activity of the PLS film-modified GCE for AP can be explained as follows. The carbonyl and hydroxyl groups of AP molecules formed hydrogen bonds with both the hydroxyl and amino groups of PLS units. Such bonding increased the adsorption capacity of AP on the surface of PLS film-modified GCE and thus effectively improved detection sensitivity and negatively shifted the oxidation peak potentials. The remarkable oxidation peak current enhancement and negative shift of oxidation peak potential clearly indicate that the PLS film-modified GCE has better electrocatalytic activity to the oxidation of AP than the bare GCE.

Fig. 3 displays the plots of log[(I_L – I)/[I_L I] vs. potential from the LSV scans of 2×10^{-5} mol L^{-1} AP solution, where I is the current and I_L is the limiting current. According to the slope of line (2.3RT/αnF), the calculated αn value for AP was 1.05, where α is the transfer coefficient and n is the number of electrons involved in the electrode reaction; R is the gas constant, T is the absolute temperature, and F is the faraday constant. For a quasi-reversible or irreversible electrode process with α close to 0.5 [31], the value of calculated n was ~2, revealing that two electrons was involved in the oxidation of AP on the PLS film-modified GCE.

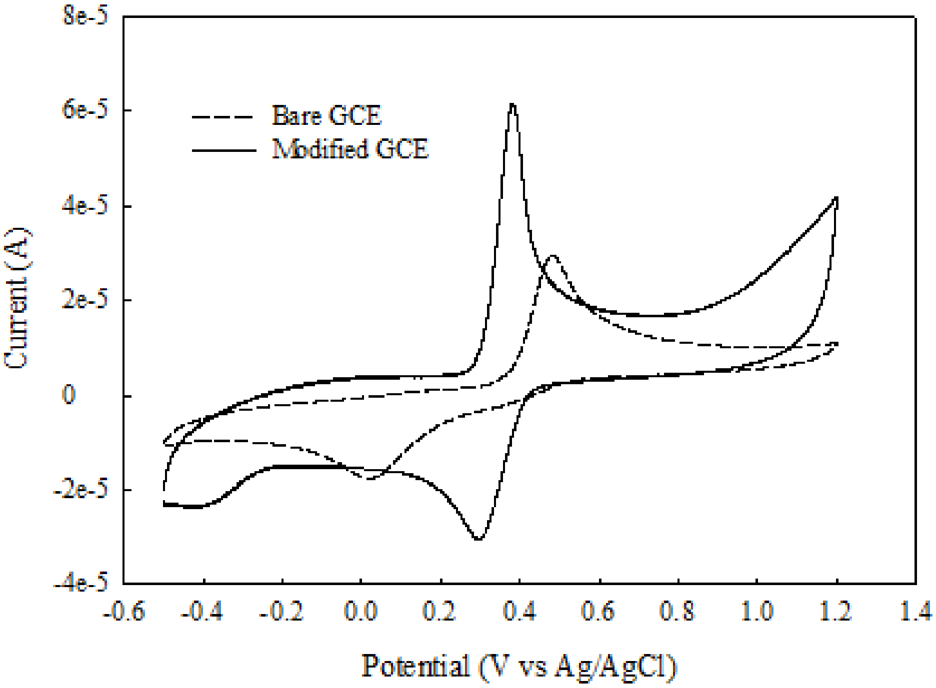


Figure 2. Cyclic voltammograms (scan rate = 100 mV s^{-1}) of 1.0×10^{-3} mol L^{-1} acetaminophen in 0.1 M phosphate buffer (pH 7.0) at the PLS film-modified and bare GCEs.

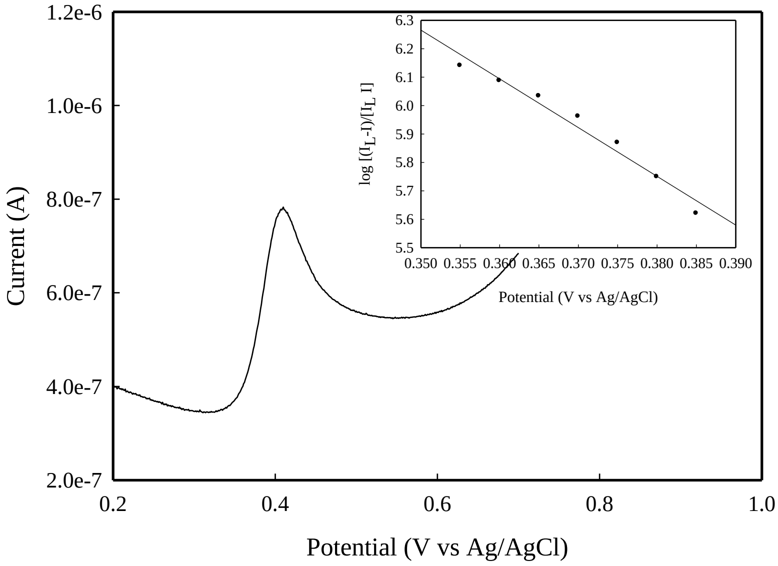


Figure 3. The LSV scan of 2×10^{-5} mol L^{-1} acetaminophen in 0.1 M phosphate buffer (pH 6.0) at the PLS film-modified GCE and its corresponding mass-transfer corrected Tafel plot (inset).

3.2. Effect of pH on the Electrochemical Determination of AP

Electrochemical determination of AP may be affected by several factors, such as electrolyte pH, scan rate, and accumulation time. In this work, the effect of electrolyte pH on the electrochemical determination of AP was examined. The electrochemical oxidation of AP in 0.1 mol L^{-1} phosphate buffers with different pH values was studied using LSV. Fig. 4 shows that the oxidation peak currents and potentials of 1.0×10^{-5} mol L^{-1} AP were related to electrolyte pH. When the pH increased from 4.0 to 6.0, the oxidation peak current of AP at the PLS film-coated GCE increased; however, a further increase of pH decreased the oxidation peak currents. At lower pHs, the relatively high concentration of proton hindered the catalytic oxidation of AP owing to common ion effect (because proton was one of the byproducts of AP oxidation (see more discussion below)), while the decrease in current response at higher pHs was resulted from hydroxylation of mediator [34]. Thus, the pH 6.0 phosphate buffer was used as a supporting electrolyte for the electrochemical determination of AP. Additionally, the linear shift of oxidation peak potential (E_{pa}) towards negative potentials with an increase in pH indicates that protons were directly involved in the oxidation of AP. Such potential shifts give the equation of E_{pa} (V) = –0.052 pH + 0.725 (R = 0.998) (Fig. 4). The slope of 0.052 V/pH is in agreement with the theoretical slope (2.303 mRT/2F) of 59 mV/pH, so the numbers of protons (m) involved in reaction was 2 (equal to the corresponding numbers of electron-transfer). Nematollahi *et al.* [4] and Li and Chen [35] also found $m = 2$ for the initial oxidation of AP in acidic and basic solutions, and they proposed that the initial degradation of AP could be described as the following reaction in which the AP could be oxidized to an intermediate (N-acetyl-*p*-benzoquinone-imine (NAPQI)) due to deprotonation.

$$\text{Acetaminophen} \leftrightarrow \text{NAPQI} + 2H^{+} + 2e^{-} \qquad (1)$$

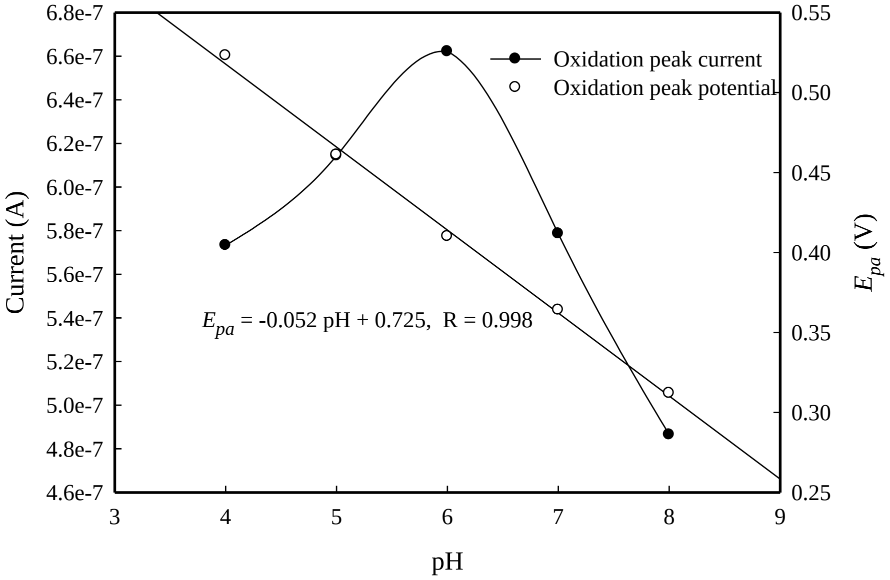


Figure 4. Effect of pH on the oxidation peak current and potential of 1×10^{-5} M acetaminophen in 0.1 M phosphate buffer solution (based on LSV data).

3.3. Linear Range, Detection Limit, and Reproducibility of AP Measurement

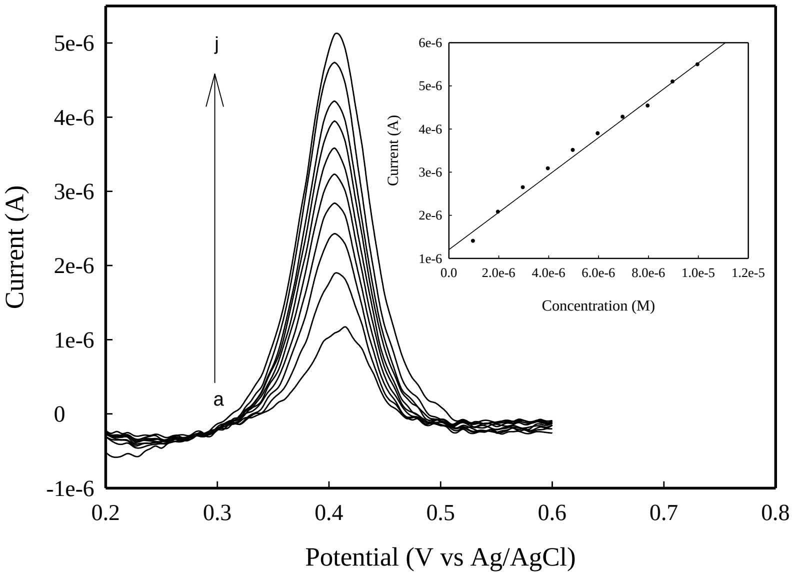


Figure 5. (a) DPVs of AP with different concentrations (in 0.1 M phosphate buffer (pH 6.0)) on the PLS film-modified GCE. Scan rate = 5 mV s^{-1}, pulse amplitude = 50 mV, and pulse width = 20 ms. AP concentrations: (a) 1×10^{-6} (b) 2×10^{-6} (c) 3×10^{-6} (d) 4×10^{-6} (e) 5×10^{-6} (f) 6×10^{-6} (g) 7×10^{-6} (h) 8×10^{-6} (i) 9×10^{-6}, and (j) 10×10^{-6} mol L^{-1}. (b) Variation in peak current versus AP concentration.

Differential pulse voltammetry was used for the quantification of AP since it exhibited better-defined voltammograms with sharper peaks than those obtained by CV and LSV. Under the optimized pH condition mentioned above, the calibration curve was obtained in pH 6.0 phosphate buffer by DPV. The oxidation peak current of AP was proportional to its concentration over the range from 1.0×10^{-6} to 1.0×10^{-5} mol L^{-1} (correlation coefficient > 0.995) (Fig. 5). Also the detection limit (DL) of acetaminophen was determined as 1.0×10^{-7} mol L^{-1} at a signal to noise ratio (S/N) of 3. A comparison of the results for the determination of acetaminophen with different modified electrodes reported in the literature is given in Table 1. The result of this study is close to those reported in literature ((1.0–1.4) $\times10^{-7}$ mol L^{-1}) [19, 22]. The accuracy and reproducibility of AP detection were evaluated by measuring a 5.0×10^{-6} mol L^{-1} AP standard solution for 5 times. The average recovery and relative standard deviation (RSD) were 97.5% and 2.8%, respectively, indicating the excellent accuracy and reproducibility for AP detection.

Table 1. Comparison of detection limits (DLs) of different modified electrodes reported in this and some other studies for AP detection.

Modified electrodes	pH	DL (μM)	Reference
Graphite oxide/GC electrode	2.0	0.04	[15]
C–Ni/GC electrode	3.0	0.6	[16]
Carbon ionic liquid electrode	4.6	0.3	[17]
PANI–MWCNTs/GC electrode	5.5	0.25	[18]
Carbon film resistor	8.0	0.14	[19]
MWCNT–alumina-coated silica/GC electrode	9.0	0.05	[20]
Graphene/GC electrode	9.3	0.032	[21]
CNTs modified screen printed electrode	10.0	0.1	[22]
PAY/nano–TiO2/GC electrode	7.0	2	[23]
Nafion/TiO2–graphene/GC electrode	7.0	0.21	[24]
MWCNT–BPPGE	7.5	0.01	[25]
SWCNT–dicetyl phosphate film/GC electrode	6.5	0.04	[26]
MWCNTs/GC electrode	7.0	0.029	[27]
SWCNT–GNS/GC electrode	7.0	0.038	[28]
f-MWCNTs/GC electrode	8.0	0.6	[29]
nafion/ruthenium oxide pyrochlore chemically modified electrode	unknown	1.2	[30]
PLS/GC electrode	6.0	0.1	This work

3.4. Factors Associated with AP Electro-Oxidation/Degradation

3.4.1. Effect of current density on AP electro-oxidation/degradation

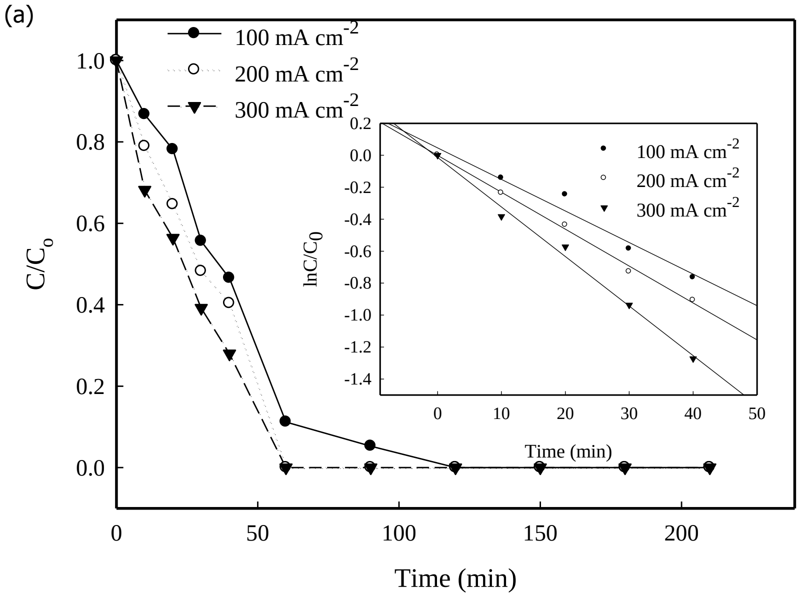
Current density is an important parameter that may influence electrochemical oxidation of AP. Fig. 6 shows the ratios of C/C_0 (C: the residual concentration of AP at a given electrolytic time, and C_0: the initial concentration of AP) for the anodic oxidation of AP and COD decay on the PbO_2/Ti electrode at different applied current densities (I_{appl}) (100–300 mA cm^{-2}). As expected, the AP degradation and COD decay increased with increasing I_{appl}. Nearly 100% AP degradation could be accomplished at 300 mA cm^{-2}, after electrolysis of 1 h, whereas it required more than 2 h of electrolysis to achieve a similar level of AP degradation at 100 mA cm^{-2}. This phenomenon should be related to the fact that increasing current density led to the increase of overpotential and hydroxyl radical (·OH) that was associated with the direct and indirect degradation of AP, respectively. Ai *et al.* [36] observed that ·OH (used to react with salicyclic acid) was formed in a constant and considerable rate in the potential range of 1.0−1.4 V corresponding to the anodic discharge of H_2O at a PbO_2 electrode.

The regressions of AP degradation data were all linear for three different I_{appl} values (initial AP concentration = 10 mg L^{-1}) (the inset in Fig. 6(a)). Accordingly, the degradation of AP, a bimolecular reaction between AP and ·OH, can be regarded as a pseudo-first order reaction and written as follows if the concentration of ·OH does not change significantly.

$$\frac{d[AP]}{dt} = k[AP][\cdot OH] = k_{app}[AP] \qquad (2)$$

The calculated rate constants were 3.3×10^{-4}, 3.9×10^{-4}, and 5.2×10^{-4} s^{-1} at 100, 200, and 300 mA cm^{-2}, respectively. The rate constants almost linearly increased with increasing I_{appl} at a constant initial concentration of AP, revealing that the degradation process of AP was controlled more by electrode kinetics than by mass transfer in the tested current density range.

The degradation of organics can also be evaluated by COD variation. It is interesting to observe that at 100 mA cm^{-2} the value of COD at 10 min electrolysis of AP was slightly greater than that of initial COD, but at 200 mA cm^{-2} the COD values were noticeably higher than initial COD when electrolysis time was less 1 h while at 300 mA cm^{-2} the COD data in ≤0.5 h AP electrolysis were similar to that at 10-min electrolysis at 100 mA cm^{-2} (Fig. 6(b)).



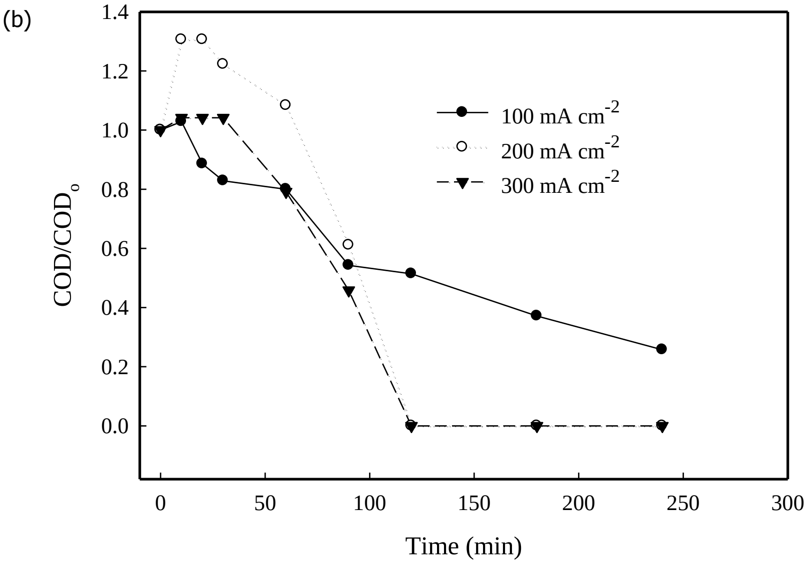


Figure 6. (a) Variation of AP C/C$_o$ with time at different current densities (AP = 10 mg L^{-1}, electrolyte: 1 M Na_2SO_4, temperature = 30 ^oC, anode: PbO_2/Ti 1cm^2, and cathode: Ti 1cm^2); inset: ln(C/C$_o$) against time. (b) Variation of COD/COD$_o$ with time at different current densities for AP electro-oxidation (operating conditions: the same as those of (a), except AP = 30 mg L^{-1}).

This result is possibly associated with that intermediates and products generated from AP electro-/·OH-oxidation were easier to be oxidized by dichromate than AP in COD measurements. It is known that in COD analysis, aromatic hydrocarbons (e.g. AP) are not oxidized (by dichromate) to any appreciable extent, which usually results in underestimation of COD.

3.4.2. Effect of anode material on AP electro-oxidation/degradation

In this study, three different anodes (Pt/Ti, DSA, and PbO_2/Ti) were tested and compared at a galvanostatic condition (100 mA cm^{-2}) (initial AP concentration = 10 mg L^{-1}) for AP electro-oxidation/degradation. During electrolysis, the anode potentials using DSA, Pt, and PbO_2/Ti anodes were 1.76, 1.97 and 10.52 V (vs Ag/AgCl), respectively, and thus the overpotential for AP degradation on the PbO_2/Ti anode was significantly greater than those on the other two anodes. This phenomenon is responsible for the observation that among the tested electrodes, the PbO_2/Ti anode exhibited the best performance for AP degradation (Fig. 7). To achieve 90% AP degradation, the PbO_2/Ti anode needed 60 min which was only about one-third those required by the Pt/Ti and DSA anodes. The anodic activity to AP degradation is also associated with the overpotential of oxygen evolution. The potentials of oxygen evolution on Pt and IrO_2 anodes are 1.6 V vs SHE [37], while that on PbO_2 is higher (1.9 V vs SHE) [38]. Hence, when using Pt and IrO_2 anodes, a large amount of supplied current was wasted in production of oxygen, leading to a low current efficiency. For the destruction of organic compounds in aqueous solutions, lead dioxide electrodes usually have a very strong ability to generate hydroxyl radicals [39] which are favored for the electro-oxidation of AP. Ai *et al.* [36] indicated that hydroxyl radicals could be generated at 1.0−1.4 V on PbO_2, while this phenomenon was not obvious at Pt in phosphate buffer solution. Some researchers also reported that PbO_2 electrodes are superior to IrO_2 anodes for electrochemical oxidation of chloranilic acid [40], very efficient with reasonable current efficiencies for anodic oxidation of aniline [41], and relatively cheap/effective in oxidizing pollutants [42].

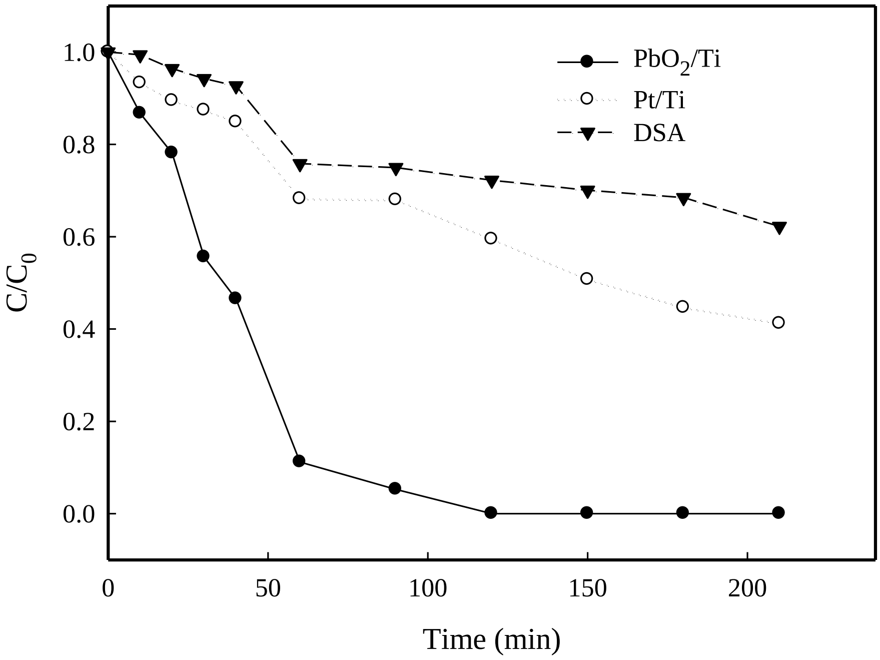


Figure 7. Variation of AP C/C_0 with time on different anodes (surface area =1cm^2) (AP = 10 mg L^{-1}, electrolyte: 1 M Na_2SO_4, temperature = 30 ^{o}C, and cathode: Ti 1cm^2).

3.4.3. Effect of pH on AP electro-oxidation/degradation

The degradation of aqueous AP (initial concentration = 10 mg L^{-1}) in pHs 3.1−10.4 was also tested at 100 mA cm^{-2}. The pHs of initial solutions were adjusted using sulfuric acid or sodium hydroxide solutions and the results are presented in Fig. 8. In the tested pH range, although the concentration of AP decreased with increasing electrolysis time, the degradation of AP was quicker at electrolysis time less than 60 min and approximately reached stable after 120-min electrolysis. Increasing pH from 3.1 to 6.4 noticeably enhanced the degradation of AP, but the increase of AP degradation was relatively lower when raising pH from 6.4 to 10.4. (About 90% AP degradation was accomplished within 60 min at pH = 10.4.) Nematollahi *et al.* [4] indicated that AP preferred to form NAPQI in pHs 1–4 and >9 via hydrolysis and hydroxylation, respectively, but underwent AP dimerization in pHs 5–9. It is inferred that the route of hydrolysis is inferior to those of hydroxylation and dimerization for AP degradation.

Nevertheless, the degradation of AP was slightly more favored in alkaline than in little acid medium. Noted that some AP molecules were present in an ionized form at pH 10.4 (pK_a = 9.4 [43]), and the negatively charged AP should be more readily attacked by the electrophilic ·OH. Lv *et al.* [44]

also observed that phenol removal efficiencies were 31.9, 69.3 and 69.3% at initial solution pH = 3.0, 5.9 and 9.4, respectively. (The chemical structure, functional group, and pK_a of phenol are similar to those of AP.)

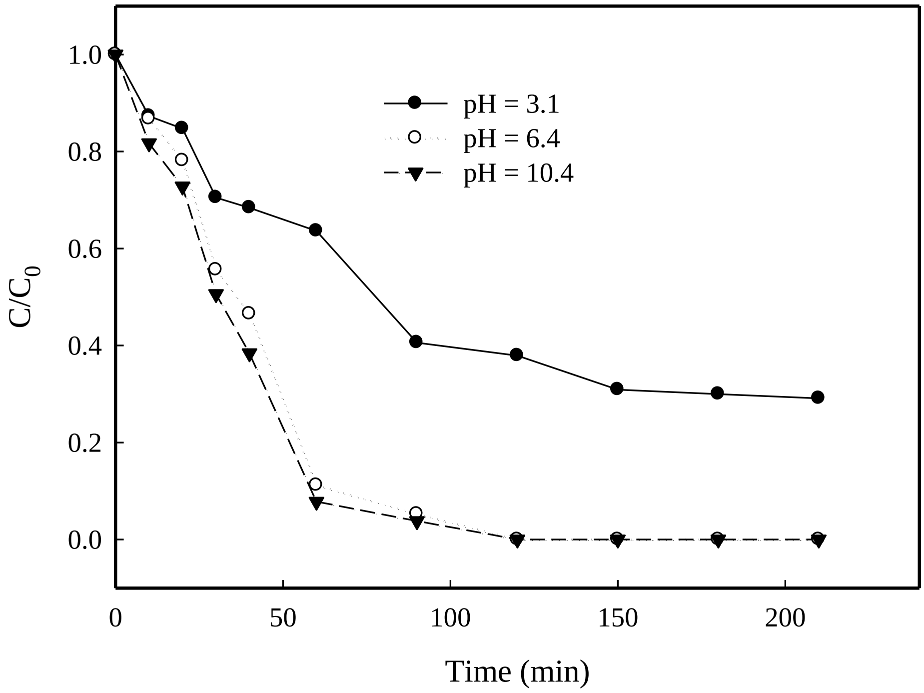


Figure 8. Effect of pH on AP electro-oxidation (AP = 10 mg L^{-1}, electrolyte: 1 M Na_2SO_4, temperature = 30 °C, anode: PbO_2/Ti 1cm^2, and cathode: Ti 1cm^2).

3.4.4. Comparison of two AP determination methods in AP electro-degradation

For comparison, the AP concentrations of samples taken from AP electro-degradation were analyzed using the PLS film modified GCE and an UV-visible spectrophotometer (at the maximum visible wavelength of 245 nm). Fig. 9 shows that when the electrolysis time was ~10 min, the AP concentration determined using the UV-visible spectrophotometric method was higher than the initial one, and thus the C/C_0 was greater than 1. This phenomenon is possibly attributable to the formation of intermediates such as *p*-benzoquinone which has a greater absorbance than AP at 245 nm. (The absorbance of *p*-benzoquinone is approximately 2.6-fold that of AP at 10 mg L^{-1} and 245 nm.) *P*-benzoquinone intermediates might be formed in the electro-oxidation of AP [4, 35]. Cui *et al.* [45] also indicated that some aromatic intermediates including benzoquinone were identified in the electrochemical oxidation of phenolic compounds. On the other hand, the C/C_0 >1 problem did not occur when the PLS film-modified GCE was used to detect AP. Therefore, the proposed electro-analytical approach (differential pulse voltammetric (DPV) technique) is more reliable and suitable than the UV-visible spectrophotometric method for the determination of AP concentration in AP electro-degradation.

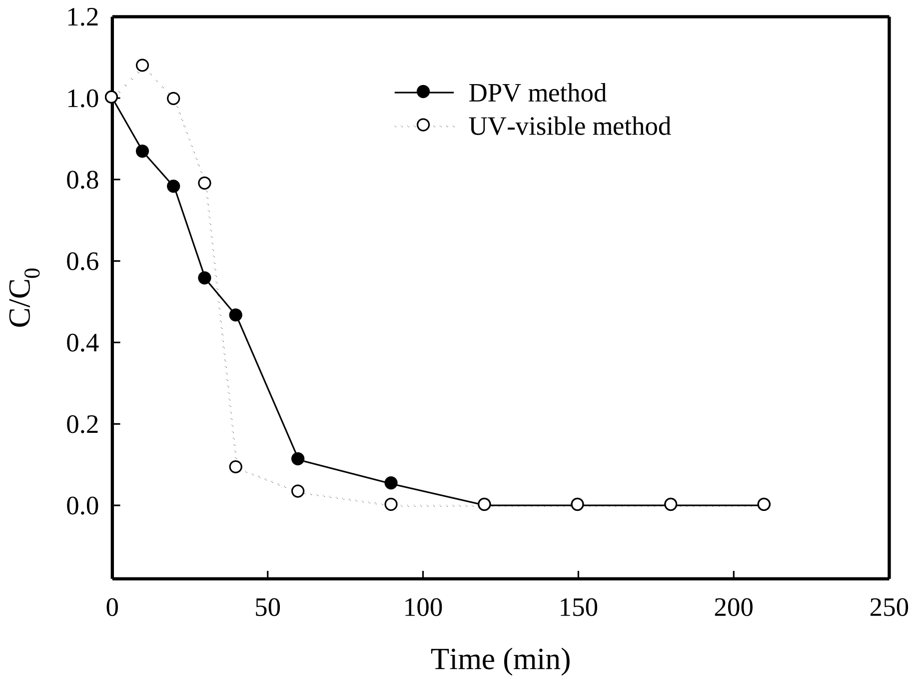


Figure 9. Comparison of two different methods for AP detection during AP electro-oxidation (AP = 10 mg L^{-1}, electrolyte: 1 M Na_2SO_4, applied current: 0.1 A, temperature = 30 ^oC, anode: PbO_2/Ti 1cm^2, and cathode: Ti 1cm^2).

4. CONCLUSIONS

In this study, a PLS film-modified GCE was prepared and it was applied for the detection of AP by DPV. The prepared electrode was found to significantly increase the electrochemical responses of AP, demonstrating an excellent electrocatalytic activity toward AP detection. The oxidation peak current of AP was linearly proportional to AP concentration over the range from 1×10^{-6} to 1.0×10^{-5} mol L^{-1} (correlation coefficient > 0.995). The detection limit (DL) of AP was determined as 1.0×10^{-7} mol L^{-1} and the average recoveries and relative standard deviation (RSD) were 97.5 and 2.8%, respectively, indicating that the prepared electrode has excellent accuracy and reproducibility for AP detection.

The removal efficiency of AP increased with an increasing current density. The degradation of AP was more favored in basic than in acidic solutions. The PbO_2/Ti anode was better for AP degradation than the Pt/Ti and DSA anodes. The proposed electroanalytic approach has the advantage of high sensitivity and is more suitable for AP detection than UV-visible spectrophotometry.

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