UV/H$_2$O$_2$ degradation of 4-aminoantipyrine: A voltammetric study

Xinyue Hu [a,b], Juan Yang [a], Changzhu Yang [b], Jingdong Zhang [a,*]

[a] College of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China
[b] College of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

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ABSTRACT

This work studied the degradation of 4-aminoantipyrine (4-AAP) by UV/H$_2$O$_2$ process and monitored the degradation process by an electroanalytical approach. Instead of traditional costly instrumental analysis, we developed a sensitive determination method for 4-AAP by utilizing a CNT film-modified glassy carbon electrode which showed dramatic promotion towards the electrochemical response of 4-AAP. On such a modified electrode, the peak current increased linearly with the concentration of 4-AAP in the range of 5.0×10^{-5}–2.0×10^{-3} mol/l with a detection limit of 2.6×10^{-5} mol/l. Based on this electroanalytical method, the photodegradation of 4-AAP was successfully monitored. The operation parameters of UV/H$_2$O$_2$ process such as the dosage of H$_2$O$_2$ and pH value were investigated systematically, which demonstrated that the electroanalytical approach was effective to study the photodegradation of organic compounds.

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1. Introduction

With the development of industry and agriculture, more and more pharmaceuticals have been manufactured and consumed by human beings and domestic animals. The occurrence of a variety of pharmaceuticals in surface, ground, and drinking water has attracted much attention in many countries [1,2]. In most cases, pharmaceuticals enter the waste water after being excreted in urine. Although a fraction of waste is eliminated through sorption and biological degradation in the municipal sewage treatment plant, the remaining part enters the water bodies with the effluent of treated waste water. Even though the concentration of pharmaceuticals appearing in the water environment is usually very low [3–5], they may cause detrimental risks on aquatic species and human health, due to their biologically active nature, and lipophilic and persistent physico-chemical properties [6]. Thus, pharmaceuticals must be degraded and removed from the water supplies.

Because many pharmaceuticals are difficult to be effectively degraded by the traditional biochemical treatment employed in the sewage plant, considerable attention to new techniques such as various advanced oxidation processes (AOPs) has been paid to explore the effective degradation approach. Among AOPs, the typical method can be represented by the photolysis of hydrogen peroxide (H$_2$O$_2$) by UV light to generate hydroxyl radicals that have strong oxidation ability to degrade various organic pollutants. Under the appropriate conditions, the organic carbon can be completely mineralized into CO$_2$ without introducing any secondary pollution. Such a UV/H$_2$O$_2$ process shows some advantages such as no phase transfer problems, no sludge formation, simplicity of operation, and low investment costs. The treatment of pharmaceuticals such as carbamazepine [7], diclofenac [8], pharmaceutical intermediates [9], and acetaminophen, antipyrine, bezafibrate, etc. [10] in water by utilizing UV/H$_2$O$_2$ has been extensively investigated.

In this work, we studied the UV/H$_2$O$_2$ degradation of 4-aminoantipyrine (4-AAP), one of new antipyrine derivatives (Fig. 1), used as an effective pharmaceutical for prophylactic and treatment of virus diseases [11]. Although 4-AAP could be effectively detected by some costly instrumental method such as LC–QTRAP-MS [12] and LC-electrospray tandem MS (LC–ES-MS–MS) [13], herein we would develop a novel convenient voltammetric method for the monitoring of the degradation process of 4-AAP based on its electrochemical activity. Moreover, considering that carbon nanotubes (CNTs), an important nanomaterials with unique properties, have shown effective promotion in the electrochemical detection of many pharmaceuticals such as acyclovir [14], celecoxib [15] and deferiprone [16], as well as phenolic estrogenic compounds [17], we prepared a CNT-modified electrode to improve the electrochemical response of 4-AAP. Thus, the photodegradation treatment of 4-AAP monitored with the electroanalytical approach was successfully demonstrated.

2. Experimental

2.1. Reagents and chemicals

Multi-walled CNTs were obtained from Nanjing University (Nanjing, China) (diameter 20–30 nm, length 1–10 μm). Prior to use, the CNTs were pretreated in concentrated nitric acid/sulfuric acid (1:3, v/v) with ultrasonication for 8 h. The obtained CNTs suspension was filtered and swilled to neutral, then dried at 60 °C.

4-AAP in analytical grade was obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Nafion (5 wt% in lower aliphatic alcohols) was obtained from Dupont Co Inc., USA. Hydrogen peroxide was obtained from Shanghai Experimental Reagent Co. (Shanghai, China). Other chemicals were of analytical grade and used as received. All solutions were prepared using doubly distilled water.

2.2. Electrode modification

One milligram of acid-treated CNTs was dispersed in 0.5% Nafion ethanol solution to give a 1.0 mg/ml black suspension with the aid of ultrasonic agitation. Prior to modification, the glassy carbon (GC) electrode surface was polished with emery papers, 0.5 μm diamond slurry and then ultrasonically washed with ethanol and distilled water for 5 min, respectively. After drying with nitrogen gas, the GC electrode was coated with 10 μl of 1.0 mg/ml CNTs suspension and dried in air.

2.3. Apparatus and procedure

A UNICO UV-2000 spectrometer (Shanghai Unico Instruments Co., China) was utilized for ultraviolet (UV) absorption spectroscopic measurements. The Raman spectra were measured with a VERTEX 70 FT-Raman spectrometer (Bruker Optics, Germany). Electrochemical measurements were carried out using a CHI660A electrochemical workstation (Shanghai Chenhua Instrument Co., China) using a conventional three-electrode cell. A CNT-modified GC electrode with a diameter of 3 mm, a platinum wire and a saturated calomel electrode (SCE) were used as the working, auxiliary and reference electrodes, respectively. All the potentials were versus SCE.

Cyclic voltammetric measurements were usually conducted in the potential window from 0 to 0.8 V in 0.1 mol/l hydrochloric acid unless otherwise indicated. The photodegradation of 4-AAP was performed in a photocatalytic reactor with a cylindrical quartz vessel (5 cm diameter × 12 cm depth). A 15-W low pressure UV lamp with a major emission wavelength of 253.7 nm was used as the illumination resource. Typically, 50 ml aqueous solution containing 4.0×10^{-3} mol/l 4-AAP was illuminated in the presence of H_2O_2 using the UV lamp. Every 20 min, 5 ml sample was taken out of the photoreactor and diluted with 4 ml doubly distilled water and 1 ml HCl (1 mol/l) and then analyzed by the electroanalytical method described above. The degradation efficiency was calculated from $(C_0 - C)/C_0 \times 100\%$ where C_0 was the initial concentration of 4-AAP and C was the concentration at degradation time t.

The chemical oxygen demand (COD) value was determined using the traditional dichromate method according to the standard methods issued by the China National Environmental Protection Agency [18]. 1 ml sample diluted with 1 ml doubly distilled
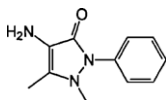

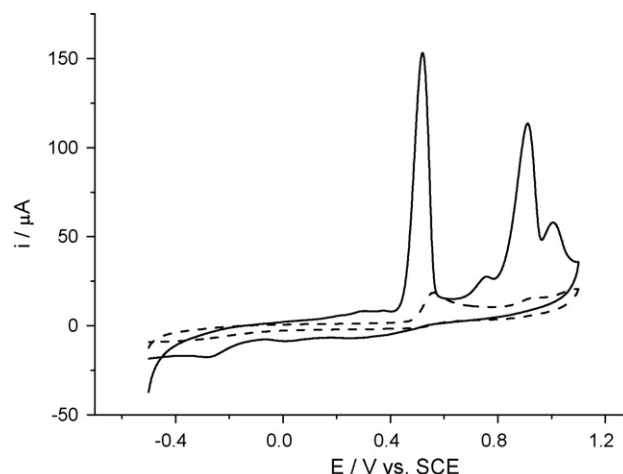**Fig. 1.** Molecular structure of 4-aminoantipyrine.

Fig. 2. Cyclic voltammograms of 1.0×10^{-3} mol/l 4-AAP in 0.1 mol/l HCl using CNT-modified (solid line) and bare glassy carbon electrodes (dashed line). Scan rate: 20 mV/s.

water and 2 ml COD digesting solution composed of $K_2Cr_2O_7$ and H_2SO_4–Ag_2SO_4 was mixed and shaken up in the Hach special digesting tube. Then the tube was put into the Hach DRB 200 COD digester for 2 h. The tube was taken out for cooling. The excess of $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate using the ferroin indicator.

3. Results and discussion

3.1. Electrochemical determination of 4-AAP based on CNT-modified electrode

3.1.1. Electrochemical behavior of 4-AAP at CNT-modified electrode

The electrochemical behavior of 4-AAP on bare and CNT-modified GC electrodes was studied and shown in Fig. 2. As can be seen, the cyclic voltammogram (CV) of 4-AAP on bare GC exhibits two anodic peaks at 0.56 V and 0.94 V, which could be respectively assigned to the oxidation of NH_2-group and antipyrine (AP) ring in 4-AAP molecule [11]. The electrochemical oxidation of NH_2-group in 4-AAP could be expressed as the following equation [19]:

$$AP\text{-}NH_2 \rightarrow AP\text{-}NH_2^{\bullet+} + e \tag{1}$$
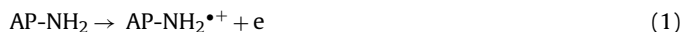
While the AP ring is oxidized at higher potential, the reaction proceeds via the following free radical cation formation [11,20]:

$$NH_2\text{-}AP \rightarrow NH_2\text{-}AP^{\bullet+} + e \tag{2}$$

When a CNT-modified GC electrode was employed, the oxidation peak potentials of NH_2-group and AP ring were shifted negatively to 0.52 V and 0.91 V, respectively. At the same time, the peak currents were significantly improved regardless of the slight shift of peak potentials. Compared with the bare GC electrode, the CNT-modified electrode increased the peak currents of NH_2-group and AP ring by 8.9 and 21.7 times, respectively. These results suggested that CNTs had obvious promotion to the oxidation of 4-AAP, which could be attributed to the large surface area and unique physiochemical and electronic properties of CNTs. Moreover, two weak peaks appeared around the main oxidation wave of AP ring, which was not observed on the bare GC electrode. However, it was noticed that multiple oxidation waves of AP ring also appeared in some AP derivatives such as 4-steroylaminoantipyrine, 4-(3-phenylacriloyl)-aminoantipyrine, 4-(8,9-dichlorstearoyl)-antipyrine [11] and 4-diethylaminoantipyrine [21], implying the complicated oxidation
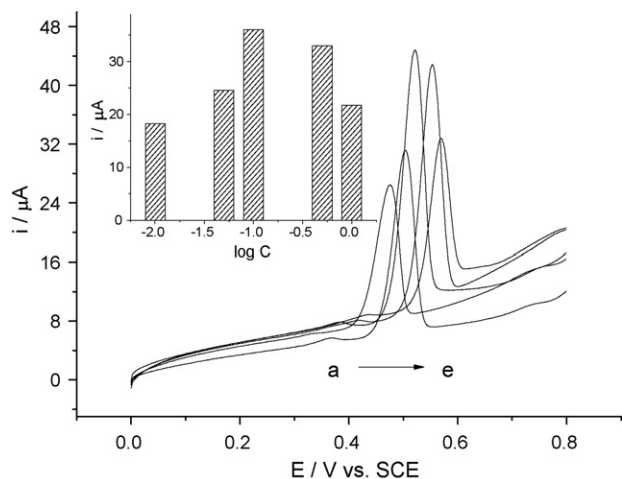
Fig. 3. Linear sweep voltammograms of 1.0×10^{-4} mol/l 4-AAP in (a) 0.01 mol/l, (b) 0.05 mol/l, (c) 0.1 mol/l, (d) 0.5 mol/l and (e) 1.0 mol/l HCl. Inset: variation of peak current with HCl concentration. Scan rate: 20 mV/s.

Fig. 5. Linear sweep voltammograms on CNT-modified electrode in 0.1 M HCl solution containing: (a) 2.0×10^{-3} mol/l, (b) 1.0×10^{-3} mol/l, (c) 7.0×10^{-4} mol/l, (d) 3.0×10^{-4} mol/l, (e) 1.0×10^{-4} mol/l, (f) 5.0×10^{-5} mol/l and (g) 1.0×10^{-5} mol/l 4-AAP. Inset: linear relationship between the concentration of 4-AAP and peak current. Scan rate: 20 mV/s. Accumulation time: 180 s.

mechanism of AP ring [11]. We speculated that some oxidation waves for AP ring in 4-AAP were too weak to be observed on bare GC electrode but displayed with the remarkable promotion of CNTs on the modified electrode. Since the peak current of NH_2-group was higher and simpler than that of AP ring, it was utilized as the analytical response signal in the following measurements.

3.1.2. Effects of supporting electrolyte and accumulation time

The influence of different supporting electrolytes including 0.1 mol/l acetate, phosphate buffer, HCl, H_2SO_4 and Na_2SO_4 solutions on the voltammetric response of 4-AAP was examined. The result indicated that the highest electrochemical response was obtained in HCl solution. Moreover, the concentration of HCl solution also shows obvious influence on the voltammetric response of 4-AAP (Fig. 3). As could be seen, with increasing the HCl concentration from 0.01 to 1 mol/l the peak potential was shifted to the negative direction while the highest peak current was observed in 0.1 mol/l HCl solution.

Fig. 4 illustrates the effect of accumulation time on the voltammetric response of 4-AAP. It was observed that the peak current increased dramatically with increasing the accumulation time up to 180 s. However, after the accumulation time was further increased only a slight enhancement in the response was observed. Accord-
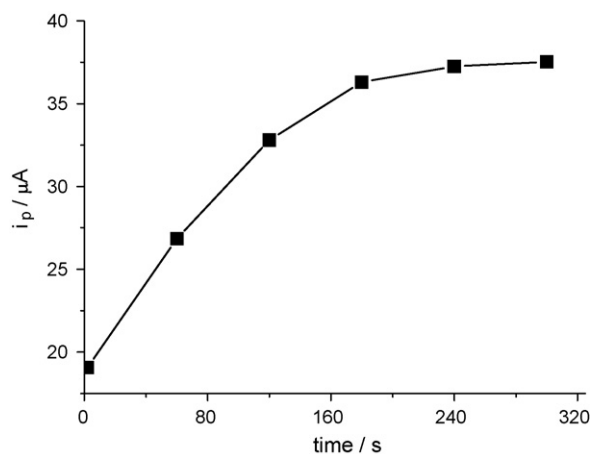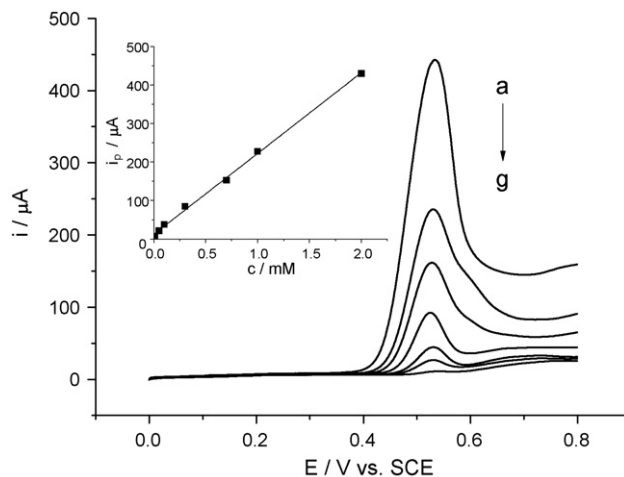
ingly, an optimum accumulation time of 180 s was selected for the analysis of 4-AAP.

3.1.3. Calibration curve

The linear sweep voltammograms of 4-AAP at various concentrations recorded on the CNT-modified electrode are shown in Fig. 5. It was found that the peak current increases linearly with the concentration of 4-AAP in the range of 5.0×10^{-5}–2.0×10^{-3} mol/l. The linear regression equation was expressed as I_p (μA) = $15.206 + 2.077 \times 10^2 c$ (mmol/l) with a correlation coefficient of 0.9984. The detection limit (3S/N) was estimated to be 2.6×10^{-5} mol/l.

To evaluate the feasibility of this voltammetric method, a water sample spiked with 4-AAP was analyzed respectively with the voltammetry using CNT-modified electrode and the traditional standard UV spectrometry using the maximum absorption of 4-AAP at 243 nm. The concentration of 4-AAP in this water sample was found to be 5.82×10^{-5} mol/l by voltammetry, close to 5.75×10^{-5} mol/l determined by UV spectrometry. This means that the proposed voltammetry using CNT-modified electrode is applicable for 4-AAP monitoring.

3.2. Voltammetric monitoring of the photodegradation of 4-AAP by UV/H_2O_2

3.2.1. UV degradation of 4-AAP and effect of H_2O_2

Fig. 6 shows the results of the degradation of 4-AAP by UV irradiation for 80 min. Compared with the peak current of 4-AAP before irradiation, there was a significant decrease in the peak current after the solution was irradiated by UV for 80 min. The result demonstrated that the electrochemical method could effectively monitor the change of the concentration of 4-AAP during the degradation process.

Fig. 7 illustrates the photodegradation of 4-AAP in the presence of H_2O_2 at concentrations ranging from 0 to 0.392 mol/l. As could be seen, the degradation efficiency for 4-AAP increased rapidly with increasing the H_2O_2 concentration up to 0.196 mol/l. However, when the H_2O_2 was further increased, the degradation efficiency of 4-AAP only increased slightly. Similar observations were also reported in previous studies where an increase in H_2O_2 level enhanced the destruction rate of humic acid up to an optimal point beyond which inhibition occurred [22]. This proved that

Fig. 4. Effect of accumulation time on the peak current of 1.0×10^{-4} mol/l 4-AAP in 0.1 mol/l HCl.
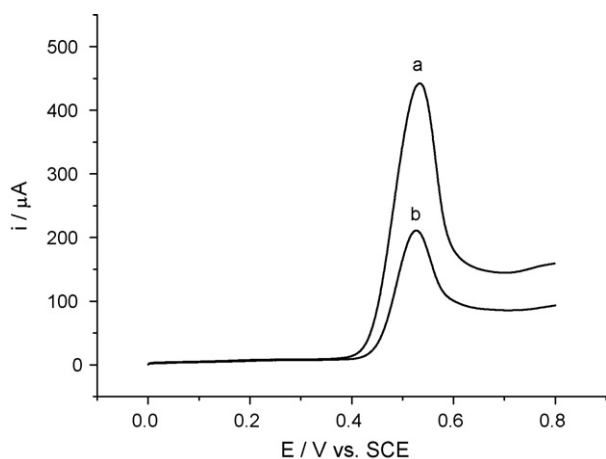
Fig. 6. Linear sweep voltammograms at 20 mV/s on CNT-modified electrode in 0.1 mol/l HCl containing 4-AAP before (a) and after (b) UV illumination for 80 min. The initial concentration of 4-AAP in the photoreactor was 4.0×10^{-3} mol/l.

Fig. 8. Linear sweep voltammograms at 20 mV/s on CNT-modified electrode in 0.1 mol/l HCl containing 4-AAP before (a) and after (b and c) adding H_2O_2 for 20 min (b) and 60 min (c). The initial concentration for 4-AAP in the photoreactor was 4.0×10^{-3} mol/l and 0.196 mol/l H_2O_2 was added into the photoreactor.

the effect of increasing H_2O_2 concentration was positive for the elimination of 4-AAP at first. However, there are two contradictory factors must be considered [23]. First, large amount of H_2O_2 can produce more hydroxyl radicals (Eq. (3)) for the oxidation of pollutant under UV radiation. Second, hydroxyl radical reacts with hydrogen peroxide to form hydroperoxyl radical ($HO_2^\bullet$) (Eq. (4)) which has lower oxidation capability compared with hydroxyl radical. Therefore, H_2O_2 in excess reduces the efficiency of pollutant degradation.

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \tag{3}$$

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \tag{4}$$

Interestingly, even without UV irradiation, a new voltammetric oxidation peak at 0.39 V appeared immediately accompanied by the decrease in the peak of 4-AAP at 0.56 V when H_2O_2 was added into the 4-AAP solution. This means that an electroactive intermediate is formed due to the interaction between 4-AAP and H_2O_2. However after a period of time, this intermediate peak was decreased and the 4-AAP peak was generally restored (Fig. 8). This phenomenon implies that the intermediate is not stable, which can easily convert to its original form. To elucidate the interaction between 4-AAP and H_2O_2, we measured the UV–vis and Raman spectra of 4-AAP solution before and after adding H_2O_2. However, neither UV–vis nor Raman spectrum of 4-AAP showed noticeable

variation after adding H_2O_2 (not shown). Accordingly, the intermediate should be the cation free radical $AP\text{-}NH_2^{\bullet+}$ generated by the following reaction:

$$2AP\text{-}NH_2 + H_2O_2 \rightarrow 2AP\text{-}NH_2^{\bullet+} + 2OH^- \tag{5}$$
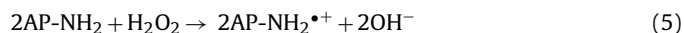
On the electrode, the cation free radical intermediate is readily oxidized which produces a new oxidation peak prior to the NH_2-group oxidation wave in the voltammetric curve. While the solution was illuminated with UV lamp, both peaks were reduced, indicating that 4-AAP and its intermediate were photodegradable.

3.2.2. Effect of pH

Fig. 9 shows the effect of the solution pH on the degradation of 4-AAP. The pH of the solution was adjusted with 1 mol/l HCl or NaOH. As can be seen, the degradation rate of 4-AAP increased to 86.63% with the increase of pH up to 6.80, after 80-min irradiation time. While the pH value was further increased, the degradation efficiency was reduced. Similar phenomena have been reported by Xu et al. for dimethyl phthalate, whose degradation rate was increased with increasing pH in the range of 2.5–4 but started to decrease at higher pH [24]. Although the increase of pH can improve the formation of hydroxyl radical from the reaction of H_2O_2, the ionic form
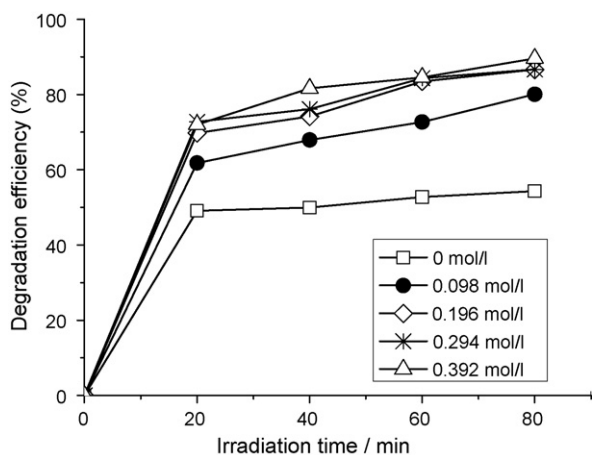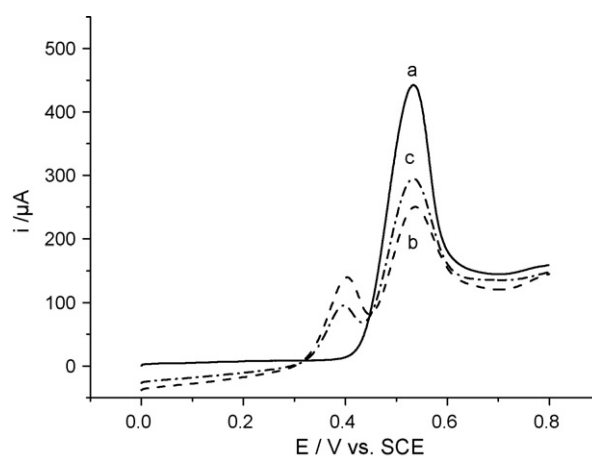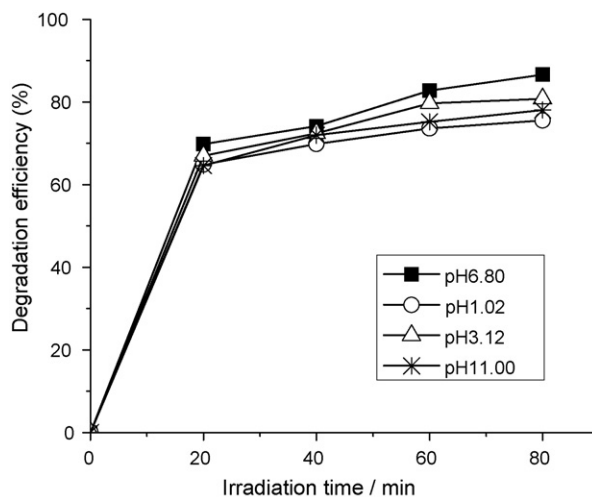

Fig. 7. Influence of the initial concentration of H_2O_2 on the photodegradation efficiency of 4-AAP. The initial concentration of 4-AAP in the photoreactor was 4.0×10^{-3} mol/l.

Fig. 9. Influence of pH on the photodegradation efficiency of 4-AAP. The initial concentrations for 4-AAP and H_2O_2 in the photoreactor were 4.0×10^{-3} mol/l and 0.196 mol/l, respectively.

of H_2O_2 at high pH namely HO_2^-, can also scavenge the hydroxyl radicals (Eq. (6)). The reaction rate of HO_2^- with $HO^\bullet$ is faster than that of H_2O_2 [25].

$$HO_2^- + HO^\bullet \rightarrow HO_2^\bullet + OH^- \qquad (6)$$

That is, the scavenging rate of hydroxyl radicals is increased with pH which results in the decreased degradation efficiency at high pH.

3.3. COD analysis of 4-AAP removal under optimal conditions

Based on the above optimal condition for the photodegradation of 4-AAP, the mineralization of 4-AAP was studied by COD analysis. The result showed that the COD removal efficiency for 4-AAP solution was only reduced 64.30% after 80-min treatment, less than the high degradation efficiency evaluated with the electroanalytical method. The difference implied that many 4-AAP molecules were actually degraded to some intermediates instead of complete mineralization under such UV/H_2O_2 treatment.

4. Conclusions

In this work, we prepared a CNT-modified electrode, which significantly promoted the electrochemical oxidation of 4-AAP. Using such a CNT-modified electrode, an electroanalytical method for 4-AAP was developed. Under optimal conditions, the voltammetric response of 4-AAP was found to be increased linearly with the concentration of 4-AAP in the range of 5.0×10^{-5}–2.0×10^{-3} mol/l. Based on this electroanalytical method, the photodegradation of 4-AAP with UV/H_2O_2 was studied. Moreover, the voltammetric response also showed an unstable intermediate formed due to the reaction of 4-AAP and H_2O_2. Our study successfully demonstrated that the electroanalytical method based on nanomaterial-modified electrode could be applied to monitor the photodegradation study of organic electroactive pollutant, which provided a cheap but effective approach to the pollution control.

Acknowledgements

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