Voltammetric monitoring photodegradation of EDTA based on carbon nanotubes-modified electrode

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ARTICLE INFO

ABSTRACT

This work described a fast and sensitive voltammetric method developed for monitoring the photodegradation of ethylenediaminetetraacetic acid (EDTA). Due to the unique properties of carbon nanotubes (CNTs) such as negative charges, large surface area and excellent electron transfer ability, metal ion namely Fe^{3+} showed a pair of well-defined redox response peaks on the CNTs-modified electrode. When EDTA was present in the solution, the voltammetric response of Fe^{3+} was suppressed due to the chelating interaction between Fe^{3+} and EDTA. In acetate buffer solution, the concentration of EDTA was found to be inversely proportional to the decreased cathodic peak current in the range of 1.0×10^{-6} to 1.0×10^{-4} mol/L with a detection limit (3S/N) of 6.5×10^{-7} mol/L. While EDTA was degraded by UV irradiation, the voltammetric response on the CNTs-modified electrode was enhanced due to the reduced amount of EDTA species chelating with Fe^{3+}. Accordingly, the concentration variation of EDTA during the photodegradation was analyzed. The effects of H_2O_2 and pH on the photodegradation of EDTA were investigated. Thus, the proposed CNTs-based voltammetry provided a useful analytical tool for studying the degradation of EDTA.

1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is a well-known chelating reagent, which has been widely used in medicine, chemical industry, food technology, agriculture and pharmaceutical manufacture. However, EDTA is not easily biodegradable [1] and thus it presents widely in the sewage effluents, rivers, lakes and groundwater [2]. Although EDTA is not considered as a toxic pollutant, it can form stable complexes with heavy metals and enable them to re-dissolve in water from sediments, which reduces the treatment efficiency for heavy metals in the water treatment plant. Thus, controlling the effluent of EDTA waste has become an emerging task in the environmental protection. Some advanced oxidation processes such as UV/H_2O_2 [3–5], photocatalysis [6], Fenton's reagent [7], ultrasound [8], chemical oxidation [9], Fe–M catalyst [10] and permanganate [11] have been considered as the clean and ecologically safe treatment methods for the effective degradation of EDTA.

On the other hand, a fast and sensitive determination method is pivotal to the evaluation of the degradation efficiency of EDTA. There have been various analytical methods developed for EDTA detection, such as titrimetry, spectrophotometry, polarography and chromatography [12]. Among these, chromatography has been the prevailing analytical approach due to its excellent analytical performance. A HPLC method for the quantification of EDTA in commercially available non-alcoholic drinks has been developed and validated [13]. Using ion chromatography, EDTA in pharmaceutical formulations and canned foods has been successfully determined [14]. However, chromatography is expensive in terms of cost of instrumentation and reagent consumption, which usually generates a mass of organic solvent waste. In comparison, electrochemical analysis uses inexpensive instrumentation but could provide a fast and sensitive determination method. Nevertheless, because the oxidation potential of EDTA is high (1.25 V vs. SCE) and the sensitivity of the direct electrochemical analysis of EDTA is low [15], most studies on the electroanalysis of EDTA are based on the complexes of metal–EDTA. Belal et al. [16] have used a dropping mercury electrode and Eu(III) to realize the detection of EDTA by polarography. Ciszkowska and Stojek [17] have utilized the strong adsorption of the Hg(II)–EDTA complex on a hanging mercury-drop electrode to detect EDTA by differential pulse cathodic stripping voltammetry. However, these reports are based on cumbersome toxic mercury electrode. To avoid this problem, the electrochemical detection of EDTA based on the adsorption of Fe(EDTA)$^-$ on a positively charged chitosan-coated glassy carbon (GC) electrode has been developed [18], which has paved a way for the analysis of EDTA using modified electrode.

Carbon nanotubes (CNTs) have been extensively demonstrated as one of the most important advanced nanomaterials with unique

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chemical, physical, electronic and mechanical properties [19]. Due to the surface total acidity (including carboxyls, lactones and phenols) presenting on the surface sites of CNTs, CNTs can adsorb various metal ions such as Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from aqueous solution [20], thus providing an effective way to the detection of trace metals. A solid phase extraction method for selective separation/preconcentration of Cu^{2+} on CNTs [21] and simultaneous enrichment-separation of metal ions from environmental samples using CNTs [22] have been investigated and applied to the determination of metal ions in real water samples. An on-line separation/preconcentration of Cu, Zn, Mn and Pb using microcolumn packed with oxidized CNTs prior to their determination by the flame atomic absorption spectrometry has been evaluated [23]. When CNTs are employed as electrode material, trace metal ions could be facilely detected using the electrochemical measurements. Tarley et al. [24] have reported an electrochemical method for Zn^{2+}, Cd^{2+} and Pb^{2+} monitoring in water samples based on simultaneous preconcentration/reduction of metal ions onto the CNTs electrode. The remarkable role of CNTs in the sensitive electroanalysis of Cd^{2+} has been described [25]. Using the CNTs-modified electrode, simultaneous determination of trace levels of Cd^{2+} and Pb^{2+} with improved sensitivity has been achieved by the anodic stripping voltammetry [26]. Moreover, the CNTs-modified electrode has been demonstrated as a Cr^{3+} sensor with a good selectivity [27].

In this work, we developed a novel electrochemical method for the determination of EDTA, based on the voltammetric response of Fe^{3+} which was significantly improved by CNTs on the modified electrode. The aim of this proposed electroanalytical method was to provide a fast and sensitive approach to the study of the photodegradation treatment of EDTA. Due to the chelating interaction between EDTA and Fe^{3+}, the voltammetric response of Fe^{3+} on the CNTs-modified electrode was suppressed linearly with increasing the concentration of EDTA. While EDTA was degraded, the voltammetric response was increased since the amount of EDTA species chelating with Fe^{3+} was reduced. Using this CNTs-based voltammetry, the photodegradation of EDTA by UV/H_2O_2 process was assessed and some influence factors such as the dosage of H_2O_2 and pH value were investigated.

2. Experimental

2.1. Reagents

Multi-walled CNTs were provided by 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.

Iron(III) chloride hexahydrate and EDTA in analytical grade were obtained from Sinopharm Chemical Regent Co. (Shanghai, China). Anhydrous ethanol (99.9%) was purchased from Chemical Reagent Factory of Tianjin University (Tianjin, China). Nafion (5 wt% in lower aliphatic alcohols) was obtained from Dupont Company (Wilmington, DE, USA). Other solvents and chemicals were of analytical grade.

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 30-min ultrasonic agitation. Prior to modification, the GC electrode surface was polished with emery papers and then ultrasonically washed in ethanol and distilled water for 5 min, respectively. After drying with nitrogen gas, the GC surface was
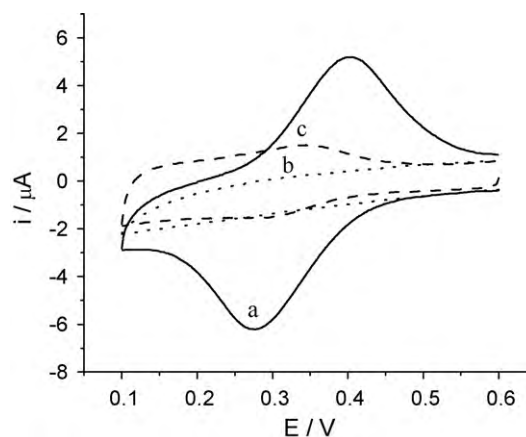
Fig. 1. CVs recorded on CNTs-modified (a, c) and bare (b) GC electrodes in acetate buffer solution (pH 3.6) with (a, b) and without (c) 1.0×10^{-4} mol/L Fe^{3+} at 40 mV/s.

coated with 1.5 μL of 1.0 mg/mL CNTs suspension and dried in air.

2.3. Apparatus and procedure

All electrochemical experiments were performed with a CHI 660A electrochemical workstation (Chenhua Instrument Co., Shanghai, China). The experiments were carried out at the ambient temperature with a conventional three-electrode system. A CNTs-modified GC electrode with an exposed geometric area of $0.0314 cm^2$ was used as the working electrode. A platinum plate and a saturated calomel electrode (SCE) were employed as the auxiliary and reference electrodes, respectively. The voltammetric analysis of EDTA was carried out in the electrolyte which was prepared by adding 1 mL of EDTA stock solution into 9 mL of 0.1 mol/L acetate buffer solution (pH 3.6) containing 1.0×10^{-4} mol/L Fe^{3+}.

The photodegradation experiments were carried out in a quartz tube containing 100 mL of 1.0×10^{-3} mol/L EDTA aqueous solution irradiated by a 15-W UV lamp with a major emission wavelength of 253.7 nm. After irradiating for appropriate time, 1 mL of sample was taken out of the photoreactor and then analyzed using the above-mentioned voltammetric method.

3. Results and discussion

3.1. Voltammetric determination of EDTA using Fe^{3+} as indicator

3.1.1. Electrochemical behavior of Fe^{3+} on CNTs-modified electrode

The cyclic voltammograms (CVs) of Fe^{3+} in acetate buffer solution (pH 3.6) on bare and CNTs-modified GC electrodes are shown in Fig. 1. As could be seen, Fe^{3+} did not show any faradeic response on the bare GC electrode but it exhibited a pair of well-defined redox peaks on the CNTs-modified electrode, demonstrating that CNTs effectively improved the electrochemical response of Fe^{3+}. There are three possible explanations for the promotion of CNTs towards the voltammetric response of Fe^{3+}. First, the negative charged groups of acid-treated CNTs could feasibly adsorb and accumulate cationic Fe^{3+} on the electrode surface via the electrostatic interaction. Second, the large surface area of CNTs is advantageous to increase the amount of reaction species on the electrode surface and improve the electrochemical response. Third, the excellent electron transfer ability of CNTs could effectively promote the electrochemical reaction kinetics [28].
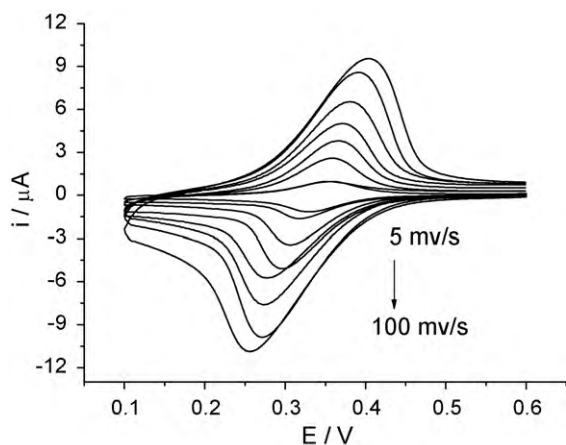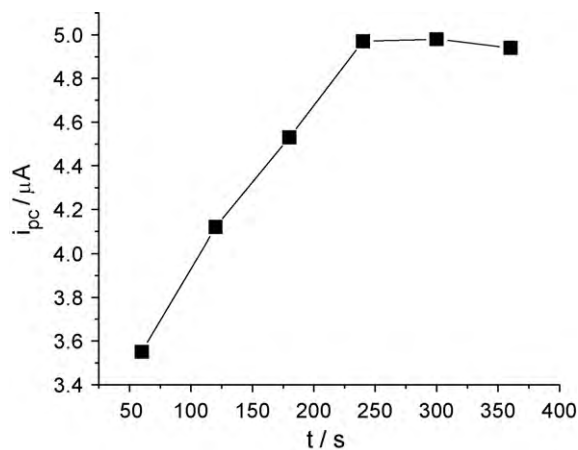
Fig. 2. CVs of 1.0×10^{-4} mol/L Fe^{3+} in acetate buffer solution (pH 3.6) on CNTs-modified electrode at different scan rates.
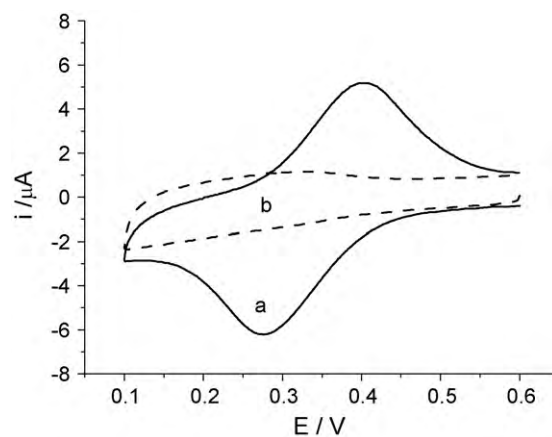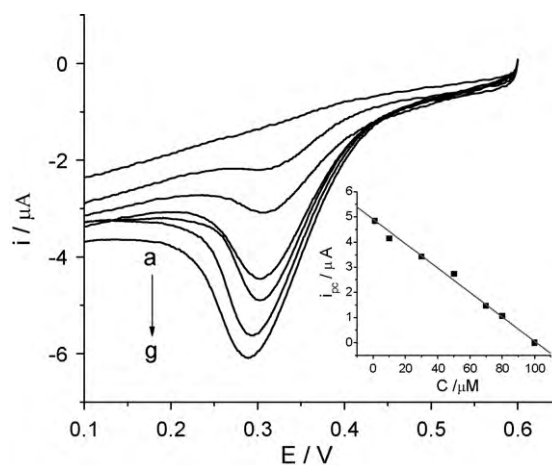

Fig. 4. CVs recorded on CNTs-modified electrode in acetate buffer solution (pH 3.6) containing 1.0×10^{-4} mol/L Fe^{3+} before (a) and after (b) adding 1.0×10^{-4} mol/L EDTA. Scan rate: 40 mV/s.

### 3.1.2. Influences of scan rate and accumulation time on the voltammetric response of Fe^{3+}

Fig. 2 shows the CVs of Fe^{3+} on the CNTs-modified electrode recorded at different scan rates. It was observed that the potential difference between the cathodic and anodic peaks was obviously increased with increasing the scan rate from 5 to 100 mV/s, indicating a quasi-reversible redox behavior of Fe^{3+}. At the same time, the cathodic peak current was linearly increased with increasing the square root of scan rate, meaning that the electrochemical reaction of Fe^{3+} on the CNTs-modified electrode was a diffusion-controlled process.

On the other hand, the voltammetric response of Fe^{3+} on the CNTs-modified electrode was obviously influenced by the accumulation time (Fig. 3). With increasing the accumulation time from 60 to 240 s, the cathodic peak current of Fe^{3+} was increased rapidly, implying the adsorption of Fe^{3+} on the CNTs-modified electrode. However, when the accumulation time was further increased to more than 240 s, the peak current did not show obvious enhancement, indicating that the adsorption of Fe^{3+} on the CNTs reached saturation. Accordingly, 240 s was considered as the optimal accumulation time in the following measurements.

3.1.3. Interaction between Fe^{3+} and EDTA and voltammetric determination of EDTA

Fig. 4 compares the CVs of Fe^{3+} on the CNTs-modified electrode before and after adding EDTA. As could be seen, the well-defined response of Fe^{3+} on the CNTs-modified electrode was completely suppressed when 1.0×10^{-4} mol/L EDTA was added into the solution. This result was attributed to the strong chelating interaction between EDTA and Fe^{3+} which led to the formation of the complex of $Fe(EDTA)^-$ but reduced the amount of free Fe^{3+} ions. Although $Fe(EDTA)^-$ could show a pair of redox peaks after adsorbed on the positively charged chitosan-modified electrode [18], it was repelled by the anionic groups of CNTs and did not exhibit any faradeic response on the CNTs-modified electrode.

Based on the interaction between EDTA and Fe^{3+} which suppressed the response of Fe^{3+} on the CNTs-modified electrode, the voltammetric determination of EDTA was tested by adding different amounts of EDTA in the acetate buffer solution containing 1.0×10^{-4} mol/L Fe^{3+} (Fig. 5). It was observed that the peak current of Fe^{3+} was decreased with increasing the concentration of EDTA. In the range from 1.0×10^{-6} to 1.0×10^{-4} mol/L, the concentration of EDTA was inversely proportional to the decreased cathodic peak current. The linear regression equation was expressed as i_{pc} (μA) = 4.83 − 0.047c (μmol/L) with a correla-

Fig. 3. Influence of accumulation time (t) on peak current (i_{pc}) of 1.0×10^{-4} mol/L Fe^{3+} in acetate buffer solution (pH 3.6) on CNTs-modified electrode. Scan rate: 40 mV/s.

Fig. 5. LSVs recorded on CNTs-modified electrode in acetate buffer solution (pH 3.6) containing 1.0×10^{-4} mol/L Fe^{3+} and different concentrations of EDTA (mol/L): (a) 1.0×10^{-4}, (b) 8.0×10^{-5}, (c) 7.0×10^{-5}, (d) 5.0×10^{-5}, (e) 3.0×10^{-5}, (f) 1.0×10^{-5}, and (g) 1.0×10^{-6}. Scan rate: 40 mV/s. Inset: linear relationship between peak current and EDTA concentration.
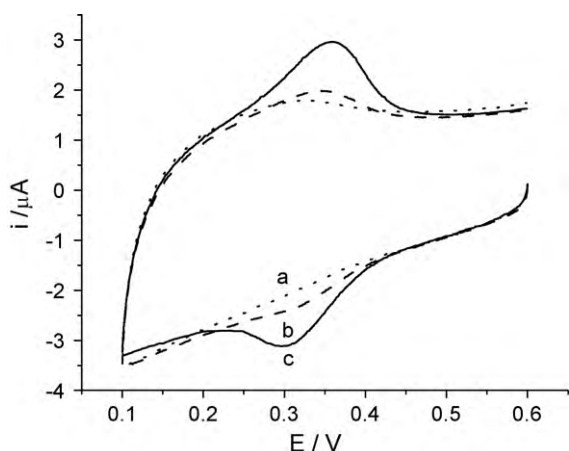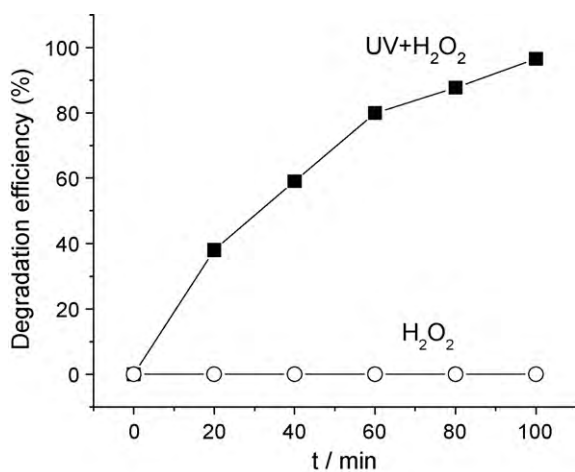
Fig. 6. CVs of 1.0×10^{-4} mol/L Fe^{3+} in acetate buffer solution (pH 3.6) on CNTs-modified electrode in the presence of EDTA irradiated by UV for 60 min (a), 120 min (b) and 180 min (c). Scan rate: 40 mV/s.
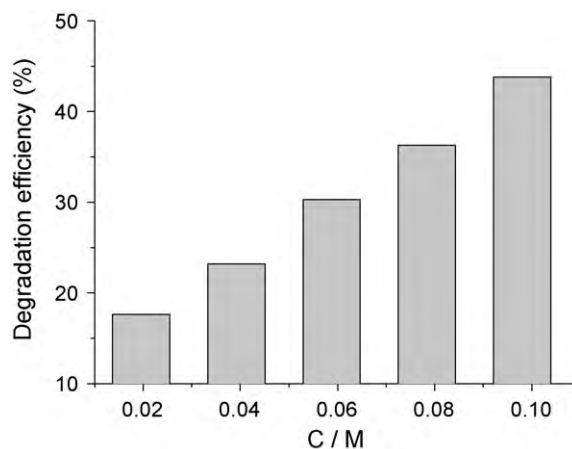

Fig. 8. Influence of initial concentration of H_2O_2 on the photodegradation of EDTA. Initial concentration of EDTA: 1.0×10^{-3} mol/L. Treatment time: 20 min.

tion coefficient of 0.9963. The detection limit (3S/N) was estimated to be 6.5×10^{-7} mol/L. Compared with the previously reported determination of EDTA based on the voltammetric response of Fe(EDTA)$^-$ on a chitosan-modified electrode [18], the present CNTs-based voltammetry provided a wider linear concentration range. Moreover, the voltammetric response of Fe(EDTA)$^-$ on the chitosan-modified electrode appeared at -0.095 V (vs. Ag/AgCl), close to the reduction of oxygen. Therefore, in order to avoid the interference of the dissolved oxygen, the electrolyte solution needed to be deaerated prior to the measurement. In contrast, the CNTs-based method did not require time-consuming deaeration since the response of Fe^{3+} on the CNTs-modified electrode appearing at ca. $+0.28$ V (vs. SCE) was much more positive than the reduction wave of oxygen.

3.2. Photodegradation of EDTA monitored with voltammetry

To study the degradation of EDTA, 1.0×10^{-3} mol/L EDTA solution was irradiated with a UV lamp and the concentration of EDTA was analyzed with the above-mentioned CNTs-based voltammetry. As could be seen, with the photodegradation of EDTA, the voltammetric response on the CNTs-modified electrode was increased (Fig. 6) due to the reduced amount of EDTA species chelating with Fe^{3+} in the detection solution. Accordingly, the degradation effi-
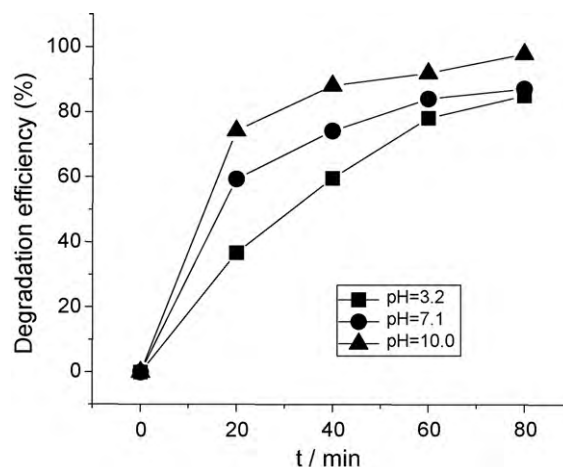
ciency for EDTA was evaluated by comparing the concentration corresponding to the cathodic peak current before and after degradation. The voltammetric measurements indicated that the direct photolysis of EDTA by UV was very slow. Even after 3-h irradiation, only 22.8% EDTA was degraded. While 9.8×10^{-2} mol/L H_2O_2 was added into the EDTA solution, the degradation rate of EDTA was dramatically improved. The degradation efficiency for EDTA reached 96.58% after 100-min treatment with UV/H_2O_2. In contrast, under dark conditions, almost no EDTA was decomposed after adding 9.8×10^{-2} mol/L H_2O_2 in the solution for 100 min (Fig. 7). Accordingly, UV irradiation and H_2O_2 showed a synergetic effect on the degradation of EDTA, which was well known as the result of the strong oxidation of hydroxyl radicals ($^\bullet$OH) formed from the decomposition of H_2O_2 by UV irradiation [5]. Moreover, the concentration of H_2O_2 obviously influenced the photodegradation of EDTA as illustrated in Fig. 8. When the concentration of H_2O_2 was increased from 1.96×10^{-2} to 9.8×10^{-2} mol/L, the photodegradation efficiency for EDTA was almost linearly increased due to more $^\bullet$OH formed in the solution. However, when the concentration of H_2O_2 was further increased to 0.196 mol/L, the voltammetric response of Fe^{3+} on CNTs-modified electrode was obviously influenced, thereby limiting the applicability of such a voltammetric evaluation method.

On the other hand, the effect of the initial pH of solution on the photodegradation of EDTA was also clarified by the voltammetric

Fig. 7. Comparison for degradation efficiency of EDTA in the presence of 9.8×10^{-2} mol/L H_2O_2 with and without UV irradiation. Initial concentration of EDTA: 1.0×10^{-3} mol/L.

Fig. 9. Effect of pH on the UV/H_2O_2 photodegradation of EDTA. Initial concentration of EDTA: 1.0×10^{-3} mol/L. Initial concentration of H_2O_2: 9.8×10^{-2} mol/L.

analysis. Fig. 9 shows the degradation curves for EDTA by adjusting the pH of solution with minute volume of high-concentrated H_2SO_4 or NaOH. It was observed that the photocatalytic degradation efficiency of EDTA in acidic solution was the lowest among acidic, neutral and alkaline conditions. This result might be attributed to the fact that H^+ ions blocked the electron pairs at the O and N atoms and thus the efficiency of electronic excitation of the organic molecules as well as the probability of their decomposition were reduced [5].

4. Conclusions

In this work, a CNTs-based voltammetry was developed to study the photodegradation of EDTA. The determination of EDTA was based on the chelating interaction between EDTA and Fe^{3+} which suppressed the voltammetric response of Fe^{3+} on the CNTs-modified electrode. The linear relationship existed between the voltammetric response and the concentration of EDTA in the range of 1.0×10^{-6} to 1.0×10^{-4} mol/L. Compared with the conventional method, the convenience of voltammetry, low cost of electrochemical instrumentation and unique features of CNTs-modified electrode provided a superior analytical approach to the study of EDTA. Based on this electrochemical method, the photodegradation of EDTA by UV/H_2O_2 process under different conditions was successfully investigated, demonstrating the feasibility of the proposed voltammetric analysis for studying the pollution control.

Acknowledgement

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