



Degradation of EDTA in aqueous solution by using ozonolysis and ozonolysis combined with sonolysis

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ABSTRACT

Degradation of ethylenediaminetetraacetic acid (EDTA) in aqueous solution by means of ozonolysis or ozonolysis combined with sonolysis was investigated for a variety of operating conditions. Synergistic effects can be observed when ozonolysis was combined with sonolysis because additional $\cdot\text{OH}$ was produced. It was found that the degradation of EDTA in aqueous solution follows the pseudo-first-order reaction kinetics and the degradation rate depends on the initial concentration of EDTA, the temperature and the acidity of the aqueous medium. The main degradation products of EDTA, such as amino acid and nitrate were tentatively identified by using GC–MS and ion chromatogram techniques.

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1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is widely used in industrial, pharmaceutical and agricultural applications, and wastewaters containing EDTA have become an environmental concern [1]. One of the reasons for this alarm is the possibility of toxic heavy metal mobilization, extended biological availability to aquatic life, and the subsequent risks these metals pose to groundwater and drinking water. When the metallic complexes were formed, such as Pb–EDTA, it is difficult to remove Pb ion by general methods and the metallic species can be released into the environment.

EDTA is stable and has low biodegradability, therefore effective methods to remove it are necessary. Several attempts have been made to develop techniques for EDTA removal from waters, principally using advanced oxidation processes, such as oxygen activation [2], photooxidation [3], H_2O_2 /UV oxidation [4,5], ozonation [6–9] and ultrasonication [10,11]. Microbial degradation is also mentioned [12–15].

Ozone is well known to act as a powerful oxidizing agent of organic water pollutants because of its excellent oxidation ability [16–18]. The combined use of ozone and other advanced oxida-

tion processes such as ultraviolet radiation [19], hydrogen peroxide [20] and γ -irradiation [21] for degradations of various pollutants in aqueous solution has been successfully applied and a synergistic effect was usually obtained.

Sonochemistry has been demonstrated as a promising method for the destruction of aqueous pollutants. During the collapse of cavitation bubbles, high temperatures (5000 K) and pressures (100 MPa) are obtained, leading to the formation of chemical species such as $\cdot\text{H}$, $\cdot\text{OH}$, $\cdot\text{O}$ and H_2O_2 [22]. Those high energy phenomena can cause degradation of various organic pollutants in aqueous solutions, and numerous studies have investigated a wide range of systems for the sonolysis of organic pollutants in water [23–27]. Beside such works, many approaches are concentrated on the potential use of the combination of sonolysis with other advanced oxidation process. Sonolysis/photocatalysis [28,29], sonolysis/hydrogen peroxide [30] and sonolysis/Fenton's reagent [31,32] were reported for use in water treatment.

It was reported that EDTA is difficult to eliminate by O_3 alone [33], however, it can be effectively removed by O_3 /UV process [33,34] and ozonolysis/photocatalysis [35]. Ozonolysis/sonolysis process has been widely used to eliminate organic water pollutants [36–38], however, the use of this technique for the degradation of EDTA has not yet been reported. In this work, the degradation of EDTA by ozonolysis/sonolysis was studied. The effect of EDTA concentration, pH of the solution and temperature of the medium were investigated. The degradation products of EDTA were also tentatively identified.

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2. Experimental

2.1. Sonolysis/ozonolysis

EDTA solution was prepared by dissolving $\text{Na}_2\text{H}_2\text{EDTA}$ (analytical grade, Sinopharm Chemical Reagent Co., Ltd.) in deionized water. 100 mL EDTA aqueous solution was sonicated in a 150 mL glass reactor with a 20 kHz Model JCS-204 Ultrasonic Reactor at a power of 150 W (Jining Ultrasonic Instruments Factory). O_3 was produced by the SK-CFG-1C ozone generator (Jinan Sanhang Envi-tech Co., Ltd.), and bubbled in the solution through an inert polytetrafluoroethylene tubing. The flow rate of O_3 maintains 0.5 g h^{-1} . The pH of solutions was adjusted to the desired value by using either NaOH or HCl. The reaction temperature was kept constant with the help of condensation water surrounding the reactor cell.

2.2. Analytical procedure

The concentration of EDTA was measured by HPLC method according to the procedure reported by Nowack et al. [39]. EDTA solution was diluted with deionized water and ferric chloride solution before the chromatographic analysis. The mobile phase consisted of methanol and 0.02 M formate buffer (90:10, v/v). The pH was adjusted to 3.5. The EDTA–iron complex was detected using UV–vis detector at a wavelength of 258 nm.

The degradation products of EDTA were analysed by a combination of gas chromatograph with mass spectrometer (GC–MS) as ethylic ester derivatives. For this analysis, the pH of the sample was adjusted to 7 with 1 M NaOH, 100 mL solution was concentrated to 2 mL in rotary evaporator at the temperature 70°C . And then, the sample was esterified with ethanol under catalysis of oil of vitriol (H_2SO_4 , 98%). The esterification products were dried with sodium sulfate and then 1 μL sample was injected to the sample container of PerkinElmer/Clarus 500 for GC–MS analysis. The GC oven temperature programme was as follows: initial temperature 50°C held for 5 min, then increased at 5°C min^{-1} to 250°C . Helium was used as a carrier gas at a constant flow rate of 2.0 mL min^{-1} . The degradation products were identified by comparison with the mass spectra of the pure samples obtained from a mass spectra database.

The inorganic anions of EDTA degradation products such as nitrate ion were detected by using Dionex ICS2000 ion chromatograph with Dionex IonPac AS19 analytical column (250 mm \times 4 mm i.d.). The mobile phase was 0.8 mM sodium carbonate–1.0 mM sodium bicarbonate with flow rate 1.0 mL min^{-1} . The injection volume was 50 μL .

3. Results and discussion

3.1. The ozonolysis process

3.1.1. Effects of EDTA concentrations

The effect of EDTA concentrations on the ozonolysis of EDTA was investigated at the temperature of 293 K and pH 5.2 (the original pH of EDTA aqueous solution). The degradation of EDTA in aqueous solution can be described by the first-order kinetics and the degradation kinetics of EDTA for different initial concentrations are shown in Fig. 1. It was found that with increasing initial concentrations, the degradation rate constants were decreased. The degradation rate constants of EDTA were 10.8×10^{-3} , 5.91×10^{-3} , 4.51×10^{-3} , 3.95×10^{-3} or $0.76 \times 10^{-3} \text{ min}^{-1}$ at initial concentrations of 0.25, 0.50, 0.75, 1.0 or 5.0 mM, respectively. This result was similar to the ozonolysis of pentachlorophenol [40] and dye ozonolysis [41].

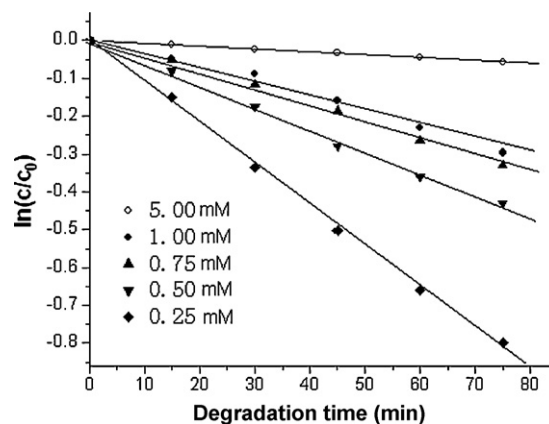


Fig. 1. The effect of initial concentrations on the degradation rate of EDTA at temperature 293 K and pH 5.2.

The reactions of ozone with organic substances follow two ways [42–45]: (1) molecules of organic substances were cleaved by ozone molecules at unsaturated linkages; (2) organic substances were oxidized by OH radicals (the decomposition products of ozone in water). The forming of OH radicals can be described simply as follows [45]:



When the temperature and pH of the medium are constant, the solubility of ozone in water and the amount of OH radicals produced from ozone decomposition in water would be constant. So when the initial concentration of EDTA was increased, which meant that the total amount of EDTA was increased, the EDTA removal ratio must be reduced, and the degradation rate constants of EDTA were decreased.

3.1.2. Effects of temperature of aqueous medium

The effect of temperature on the ozonolysis of EDTA was investigated at the initial concentrations of 0.25 mM and pH 5.2 and the results were shown in Fig. 2. It was found that the degradation rate constants of EDTA were 1.62×10^{-2} , 1.08×10^{-2} , $0.64 \times 10^{-2} \text{ min}^{-1}$ at temperature 273, 293 or 313 K, respectively. The result showed that with increasing of reaction temperatures, degradation rate of EDTA was decreased. Because higher temperature can decrease the solubility of ozone in aqueous solution, the degradation rate of EDTA decreased accordingly. However, it was found that the

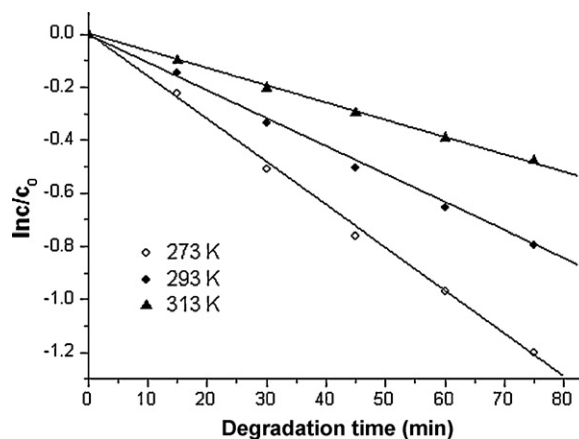


Fig. 2. The effect of temperature on the degradation rate of EDTA at initial concentration 0.25 mM and pH 5.2.

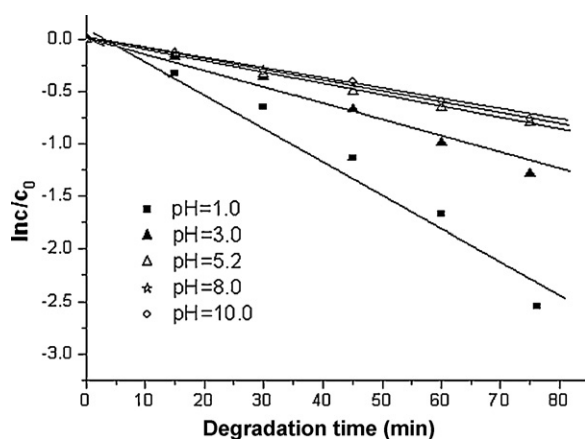


Fig. 3. The effect of pH value on the degradation rate of EDTA at initial concentration 0.25 mM and temperature 293 K.

decrease of degradation rate was less than the decrease of solubility of ozone which was shown in Table 1. It could be explained in two ways: (1) higher temperature is beneficial to the rising of chemical reaction; (2) the decomposition of ozone is much faster at higher temperature and more OH radicals can be produced [45].

3.1.3. Effects of medium pH values

The effect of initial pH values of the aqueous solution on the ozonolysis of EDTA was investigated at different pH in the range of 1.0–10.0 with EDTA initial concentration of 0.25 mM and temperature of 293 K. The results were shown in Fig. 3. The degradation rate constants of EDTA were 2.77×10^{-2} , 1.75×10^{-2} , 1.08×10^{-2} , 1.02×10^{-2} , $1.00 \times 10^{-2} \text{ min}^{-1}$ at pH 1.0, 3.0, 5.2, 8.0, 10.0 respectively. The results indicate that the degradation rate constants in acidic medium are higher than those in neutral and basic medium, and the degradation rate constants are almost constant after pH > 7.0. This result was similar to the $\text{H}_2\text{O}_2/\text{UV}$ degradation of Pb–EDTA [5].

The results may be related to the state of EDTA at different pH. It seems that molecule state of EDTA is easier to oxidize. As we know when the solution is acidic, namely $\text{pH} < \text{pK}_a$ of EDTA, the EDTA presents the molecule state basically, furthermore, with decreasing solution pH, the amount of molecule state of EDTA increases. In addition, the increase of the oxidation potential of ozone in the acidic medium might be another reason for the increase of the degradation rate. On the other hand, a high pH value may create more free radical scavengers (i.e. CO_3^{2-} , HCO_3^-) and results in the decrease in the concentration of $\bullet\text{OH}$ [46]. It can decrease the degradation rate of EDTA.

3.2. The ozonolysis/sonolysis process

3.2.1. Synergistic effect between ozonolysis and sonolysis

The degradation of aqueous solutions of EDTA with concentration of 0.25 mM at temperature of 293 K and pH of 5.2 was carried out through three approaches as follows: (1) using O_3 (0.5 g h^{-1}) alone, (2) using ultrasonic cavitation (with power of 88 W) alone

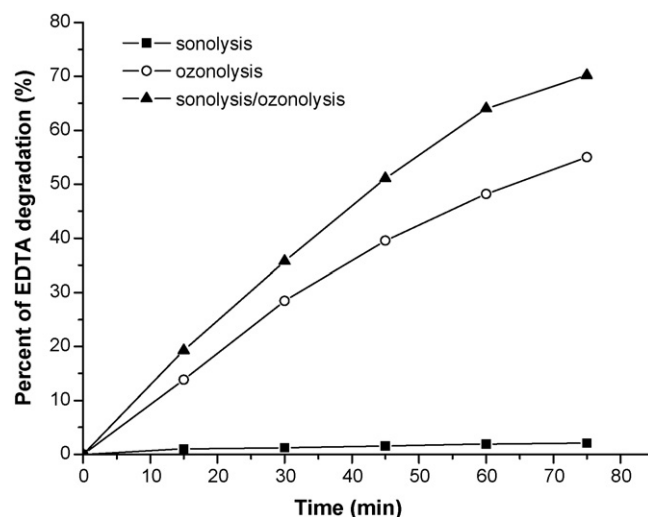
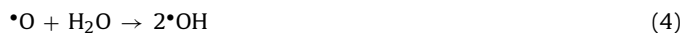
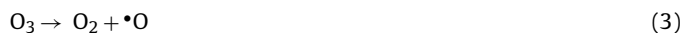


Fig. 4. Contrast of EDTA degradation under the process of sonolysis, ozonolysis and sonolysis combined with ozonolysis at initial concentration 0.25 mM, temperature 293 K, pH 5.2.

and (3) using O_3 (0.5 g h^{-1}) combined with ultrasonic cavitation (power 88 W). The results were shown in Fig. 4. It can be seen from the results that although the sonolysis of EDTA could be ignored but the ozonolysis of EDTA were enhanced obviously by ultrasonic cavitation.

Ozone reacts with various organic contaminants in water. Mainly depending of the conditions, O_3 can react directly on its molecular form or indirectly through hydroxyl radical generated by its decomposition in water. The synergic effects observed here seem to be the result of two effects: i.e. the increase of the O_3 dissolution rate caused by the ultrasound gas–liquid mass transfer enhancement [47], and additional source of hydroxyl radicals from the ozone activation. In addition to water and oxygen splitting, ultrasonic cavitation can induce ozone decomposition and then provides additional source of hydroxyl radicals [48].



Since reaction rate constants of ozone (10^{-2} – $10^3 \text{ M}^{-1} \text{ s}^{-1}$) are much more lower than reaction rate constants of HO radical (10^6 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [49], the most of the synergic effects would be from additional source of hydroxyl radicals.

It is difficult to determine the yield of OH radical because of its high reactivity, short half-life and very low concentration. Some of trapping agents such as salicylic acid [50], phenylalanine [51] and 5,5-dimethyl-1-pyrroline-N-oxide [52] were used for the detection of OH radical, but their hydroxylated derivatives are either unstable, produced endogenously, or difficult to measure. Terephthalic acid dianion (TA) has proven to be an especially convenient OH radical trap, which can be used to estimate relative amounts of OH radicals produced by γ -irradiation [53] and ultraviolet irradiation [54]. In the terephthalate analysis, TA reacts with OH radicals to form hydroxyterephthalate

Table 1

Contrast of decreasing percent of ozone solubility in aqueous solution and degradation rate constant of EDTA with the increase of temperature.

Temperature (K)	Solubility of ozone in aqueous solution (g L^{-1})	Decrease of solubility according to the value of 273 K (%)	Degradation rate constant of EDTA (min^{-1})	Decrease of rate constant according to the value of 273 K (%)
273	1.13		0.0162	
293	0.57	50	0.0108	31
313	0.28	75	0.00641	60

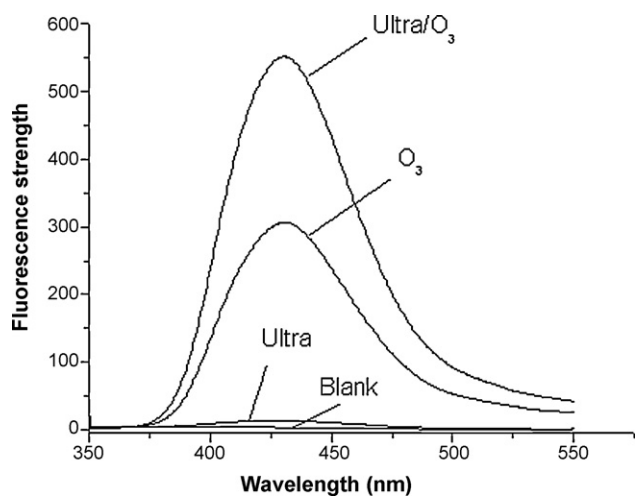


Fig. 5. Fluorescence strength of terephthalic acid solution after 10 min treatment by ultrasound, ozone and ultrasound/ozone.

(HTA). This results in a fluorescent molecule HTA that is a stable and highly fluorometric isomer (excitation, $\lambda_{\text{EX}} = 322$ nm; emission, $\lambda_{\text{EM}} = 427$ nm). Reaction of TA to form HTA is highly specific towards HO^\bullet ; other common oxygen radical species such as superoxide anion and organic hydroperoxides have failed to produce HTA fluorescence directly [55]. Since TA is non-fluorescent, eliminating the problem of a high initial background. Moreover, because of TA has four identical ring hydrogens, there is only one form of the monohydroxylated adduct. Here we determined the relative amounts of OH radicals produced by ozonolysis, sonolysis and ozonolysis combined sonolysis respectively, by using TA as a fluorescent probe. The results were shown in Fig. 5. From the results it can be seen that very low fluorescence spectrum was observed with sonolysis, but strong fluorescence spectrum was displayed in the ozonolysis and much stronger fluorescence spectrum was observed when ozonolysis was combined with sonolysis. The evidence of OH radicals production in ozonolysis is well known and the production of OH radicals in ozonolysis can be remarkably enhanced by sonolysis. So a remarkable synergic effect for the degradation of EDTA in ozonolysis/sonolysis process was observed.

3.2.2. Effects of EDTA concentrations

The effect of EDTA concentrations on the degradation rates in the ozonolysis/sonolysis process was investigated at ultrasonic power 88 W (the other conditions were as same as the process in Section 3.1.1). It indicates that the degradation of EDTA can also be described by the first-order kinetics. The degradation rate constants of EDTA were 17.2×10^{-3} , 9.90×10^{-3} , 5.71×10^{-3} , 4.74×10^{-3} or $0.93 \times 10^{-3} \text{ min}^{-1}$ at initial concentrations 0.25, 0.50, 0.75, 1.0 or 5.0 mM respectively. Compared with ozonic oxidation, the degradation rate of EDTA was increased obviously with the ozonolysis/sonolysis process. An interesting result was observed after comparing the amount of EDTA decomposed after 75 min using ozonolysis/sonolysis process to that using ozonolysis process alone at different initial EDTA concentrations. The amounts of decomposed EDTA after 75 min were all increased with ozonolysis/sonolysis process compared to those with ozonolysis process. And with varied initial EDTA concentrations of 0.25, 0.50, 0.75, 1.0 or 5.0 mM (the volume of solution was 100 mL), the increase of the amount of EDTA decomposed was 4.4×10^{-3} , 4.7×10^{-3} , 4.6×10^{-3} , 4.3×10^{-3} or $5.0 \times 10^{-3} \text{ mM}$, respectively. These results indicate that the increase of decomposed EDTA by the enhancement of sonolysis was almost the same regardless of the variation

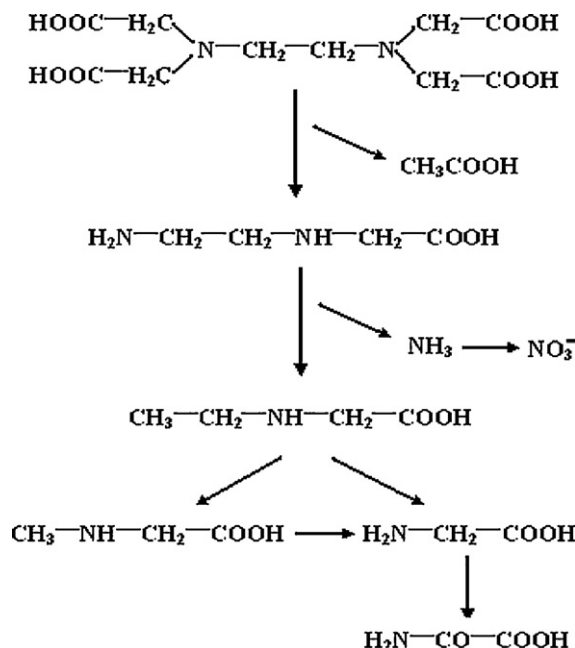


Fig. 6. The proposed degradation pathway of EDTA.

of initial EDTA concentration. This implies that a same amount of OH radicals was added by the enhancement of sonolysis.

3.2.3. Effects of medium temperature

The effect of temperature on the degradation of EDTA with ozonolysis/sonolysis process was also investigated at ultrasonic power 88 W, and other conditions were in accord with that described in Section 3.1.2. The degradation rate constants of EDTA were 20.7×10^{-3} , 16.5×10^{-3} , $9.81 \times 10^{-3} \text{ min}^{-1}$ at temperature of 273, 293 or 313 K. This result was similar to that obtained in ozonolysis process that the degradation rate of EDTA was decreased as the increase of reaction temperatures. However, the range of degradation rate was reduced. This result indicates two opposite effects: (1) as mentioned above, the solubility of ozone in aqueous solution is reduced at higher temperature, the degradation rate of EDTA was decreased; (2) the presence of ultrasonic cavitation accelerated the dissolution rate of O_3 and the gas–liquid mass transfer [47], and the degradation rate of EDTA was increased.

3.2.4. Effects of medium pH

The effect of medium pH value on the degradation of EDTA with ozonolysis/sonolysis process was investigated at ultrasonic power 88 W, and other conditions were in accord with that described in Section 3.1.3. The degradation rate constants of EDTA were 6.13×10^{-2} , 2.34×10^{-2} , 1.82×10^{-2} , 1.64×10^{-2} , $1.60 \times 10^{-2} \text{ min}^{-1}$ at pH of 1.0, 3.0, 5.2, 8.0, 10.0, respectively. It can be seen that the degradation rates of EDTA under ozonolysis/sonolysis process were much higher than those in ozonolysis process, especially under acidic condition. It has been reported that three different regions are formed in the aqueous sonochemical process [56], i.e. the gas phase within the cavitation bubble, the interfacial zone between the bubble and the bulk solution. As mentioned above, EDTA presents a molecule state in more acidic solution. The molecule state of EDTA enters the cavitation bubbles easily and degrades directly. Because of the additional degradation of EDTA in cavitation bubbles, the degradation rate of EDTA under ozonolysis/sonolysis process was higher than that in ozonolysis process under acidic condition.

Table 2

The ethylic ester derivatives of EDTA degradation products identified by GC–MS.

Peak	T_R (min)	M_W	Molecular formula	Compound	Characteristic peaks of the mass spectrum
1	2.26	117	$C_5H_{11}O_2N$	N-methylamino acetic acid ethyl ester	61, 73, 88, 103, 117
2	3.11	103	$C_4H_8O_2N$	Amido acetic acid ethyl ester	57, 73, 87, 103
3	3.79	131	$C_6H_{12}O_2N$	N-ethylamino acetic acid ethyl ester	57, 72, 100, 131
4	4.91	117	$C_5H_{10}O_2N$	Ethanedioic acid monoamide ethyl ester	71, 88, 101, 117
5	6.49	147	$C_7H_{14}O_2N_2$	N-(2-aminoethyl)amino acetic acid ethyl ester	57, 87, 102, 130, 147
6	7.90	138		Unknown	59, 93, 110, 138

3.3. Identification of the degradation products of EDTA

Some of degradation products of EDTA were tentatively identified by GC–MS and ion chromatograph. The mass spectral data of the degradation products are listed in Table 2. Previous studies showed that different degradation products were found in different oxidation processes [3,57,58]. Some low molecular weight oxidation intermediates with functional groups such as amines, carbonyl and carboxylic acids have been reported. In the current study the main oxidation intermediates of EDTA were amino acid, including amido acetic acid, N-methylamino acetic acid, N-ethylamino acetic acid, N-(2-aminoethyl)amino acetic acid, etc. Some of the compounds such as amino acetic acid and ethanedioic acid monoamide have been reported as degradation products of EDTA in the photocatalytic degradation [3] and Fenton oxidation [57]. Furthermore, nitrate ion as another degradation product of EDTA was also measured by ion chromatograph. It was found that the concentration of nitrate in solution was 5.46×10^{-3} mM after 1 h degradation, and 1.13×10^{-2} mM nitrate was tested after 2 h treatment. The results showed that some of nitrogen in EDTA have been oxidized to nitrate by ozonolysis/sonolysis. From the information obtained so far, a possible degradation pathway of EDTA may be proposed as Fig. 6.

4. Conclusions

EDTA can be decomposed by means of ozonolysis and a synergistic effect can be observed by using ozonolysis combined with sonolysis because additional $\cdot OH$ was produced. The degradation of EDTA in aqueous solution by using ozonolysis or ozonolysis combined with sonolysis follows a pseudo-first-order reaction kinetics. It was found that the degradation rate of EDTA increased with the decrease of EDTA concentration, medium pH and reaction temperature. The main degradation products of EDTA were tentatively identified by GC–MS and IC.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.11.032.

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