



Decomposition of EDTA in aqueous solution by UV/H₂O₂ process

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Received 17 July 1997; received in revised form 31 October 1997; accepted 1 November 1997

Abstract

The decomposition of EDTA in aqueous solution by UV/H₂O₂ process was studied under various solution pH values, H₂O₂ dosages, UV light intensities, temperatures and concentrations of Cu²⁺ in order to determine the completeness of decomposition. The removal and mineralization rates of EDTA by UV/H₂O₂ process increased with increasing light intensity possibly due to the increased generation rate of hydroxyl free radicals. Free copper ions might serve as catalysts to accelerate the reaction rate, except in alkaline conditions, where copper ion would precipitate as hydroxide. The increase of solution temperature slightly increased the reaction rate because of the low activation energy of the reactions. An optimum solution pH value and H₂O₂ dosage existed

Abbreviations: *A* Light absorbance; *C_a* Initial concentration of EDTA as carbon (mg l⁻¹); *C_{a,n}* (EDTA)_n, concentration of EDTA as nitrogen at time *t* (mg l⁻¹); *C_{ao}* (EDTA)_c, concentration of EDTA as carbon at time *t* (mg l⁻¹); *C_{ao,n}* Initial concentration of EDTA as nitrogen (mg l⁻¹); *C_b* Concentration of organic intermediates as carbon at time *t* (mg l⁻¹); *C_{b,n}* Concentration of intermediate as nitrogen at time *t* (mg l⁻¹); *C_c* Concentration of CO₂ as carbon at time *t* (mg l⁻¹); *C_{c,n}* Concentration of nitrate as nitrogen at time *t* (mg l⁻¹); (CO₂)_c Concentration of CO₂ as carbon (mg l⁻¹); (EDTA)_c Concentration of EDTA as carbon (mg l⁻¹); (EDTA)_n Concentration of EDTA as nitrogen (mg l⁻¹); (Interme)_c Concentration of organic intermediates as carbon (mg l⁻¹); (Interme)_n Concentration of intermediate as nitrogen (mg l⁻¹); *k₁* Pseudo-first order rate constant for the decomposition of EDTA (min⁻¹); *k_{2c}* Pseudo-first order rate constant for the mineralization of intermediates based on carbon (min⁻¹); *k_{2n}* Pseudo-first order rate constant for the mineralization of intermediates based on nitrogen (min⁻¹); *k_{1,OH}* Pseudo-first order rate constant for the decomposition of EDTA by indirect oxidation (min⁻¹); *k_{1,UV}* Pseudo-first order rate constant for the decomposition of EDTA by direct photolysis (min⁻¹); *k_{1,UV/H₂O₂}* Pseudo-first order rate constant for the decomposition of EDTA by the UV/H₂O₂ process (min⁻¹); *k_{2,OH}* Pseudo-first order rate constant for the mineralization of intermediates based on carbon by indirect oxidation (min⁻¹); *k_{2,UV}* Pseudo-first order rate constant for the mineralization of intermediates based on carbon by direct photolysis (min⁻¹); *k_{2,UV/H₂O₂}* Pseudo-first order rate constant for the mineralization of intermediates based on carbon by the UV/H₂O₂ process (min⁻¹); (NO₃⁻)_n Concentration of nitrogen as nitrate (mg l⁻¹)

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for the degradation of EDTA. Excessive H_2O_2 species may scavenge hydroxyl radicals and impede the decomposition rate of EDTA. NTA and ammonia were detected as decomposition products of EDTA. Ammonia was slowly oxidized at alkaline solutions by the UV/ H_2O_2 process. A simplified two-step kinetic model was found to describe the concentrations of reactants and products of EDTA in aqueous solution by UV/ H_2O_2 process. © 1998 Elsevier Science B.V.

Keywords: EDTA; UV/ H_2O_2 process; Copper species

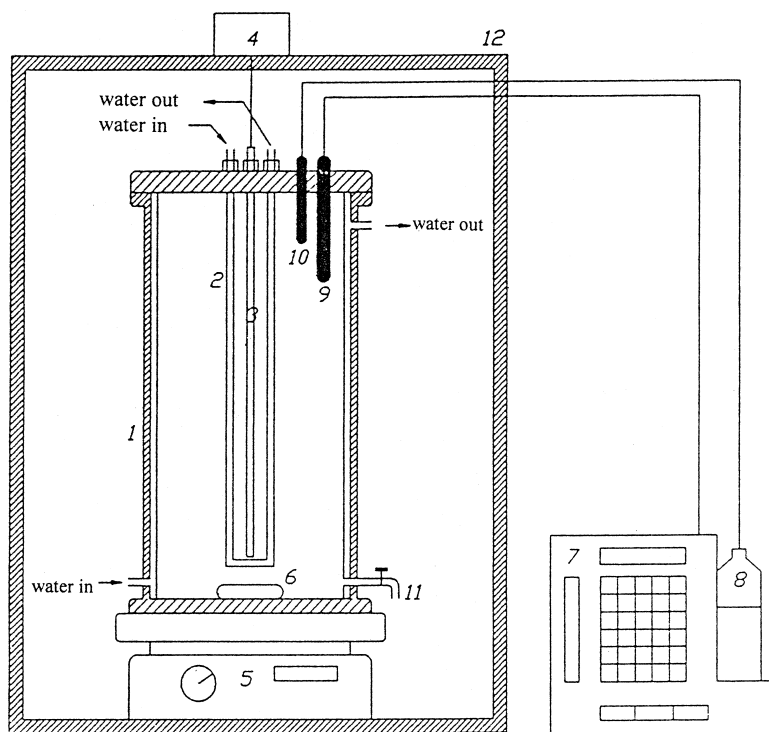
1. Introduction

The presence of heavy metals in water and wastewater is a subject of increasing importance. Depending on the origin of this wastewater, various complexing agents such as ammonia, citrate, tartrate, EDTA, etc. may also be present. The presence of complexing agents in wastewater is believed to play an important role in transporting the heavy metals into the environment. They can prevent the removal of heavy metals by conventional precipitation processes mainly because of the dramatic increase in the solubility of the heavy metal ion, especially in the presence of strong chelating agents like EDTA. In addition, the presence of organic chelating agents may also cause problems for some metal-laden wastewater discharges to violate the COD requirement for effluent discharge, because the toxicity of heavy metal prevents the removal of COD by most biological treatment processes.

Previous researches indicate that carbon adsorption, membrane processes, ion exchange, and oxidation were all possible treatment techniques for metal chelates [1]. Many advanced oxidation processes (AOPs) were reported to effectively mineralize various refractory organics into carbon dioxide, water and anions. This is a potential advantage of oxidation over other treatment methods that simply transfer the pollutants from aqueous phase to another phase. AOPs involve the generation of highly reactive free radicals, especially the hydroxyl radicals (OH^\cdot), to oxidize the organics in aqueous solution and are found to be several-order of magnitudes faster than oxidation by O_3 or H_2O_2 molecules [2–7]. Formation of OH^\cdot radicals by the decomposition of hydrogen peroxide can be initiated by ultraviolet (UV) light irradiation and ozone (O_3). The goal of the present study is to investigate the decomposition rate and applicability of the UV/ H_2O_2 process for treating EDTA in aqueous solutions.

2. Experimental

The schematic representation of the experimental apparatus employed in this work is shown in Fig. 1. The outer tube of the annular photoreactor was made entirely of Pyrex glass with an effective volume of 2.5 l and was water-jacketed to maintain constant solution temperature at 25°C. The inner tube of the reactor consisted of one 1.5 cm inner diameter quartz tube housing a UVP-XX-15S 254 nm low-pressure mercury UV lamp with approximately 5.3 W maximum output. The light intensity of the UV lamp was adjusted by a variable voltage transformer and detected by a Spectroline model DRC-100X digital radiometer combining with a DIX-254 radiation sensor. The solution



- | | |
|-------------------------|---------------------------------------|
| 1. Annular Photoreactor | 7. pH Controller |
| 2. Quartz Tube | 8. NaOH (HClO ₄) Solution |
| 3. UV Lamp | 9. pH Meter |
| 4. UV Lamp Set | 10. Dosage Unit |
| 5. Magnetic Stirrer | 11. Sampling Port |
| 6. Stir Bar | 12. Stainless Box |

Fig. 1. The schematic representation of the experimental apparatus employed in this work.

pH value was kept constant at desired levels with NaOH and HClO₄ solutions by a Kyoto APB-118-20B autotitrator. The EDTA, H₂O₂, CuSO₄ and other chemicals used were reagent grade, and all experimental solutions were prepared with deionized water. The EDTA solution was added to the reactor with a predetermined amount of H₂O₂ solution. Typical reaction runs lasted 5 h. At desired time intervals, aliquots of solution were withdrawn from the sampling port, which was located at the bottom of the reactor, and analyzed for EDTA, TOC, H₂O₂ and various anion concentrations. Total sample volumes were kept below 3% of the total reactor volume. Each run of the experiments in this work was replicated twice. The total organic carbon was analyzed by an OIC model 700 TOC analyzer. The EDTA and anion concentrations, including nitrite and nitrate,

were analyzed by a Dionex model DX-100 ion chromatograph with a conductivity detector and an IonPacR AS5 (10-32) P/N 35395 column. The mobile phase was a mixture of 1.6 mM Na₂CO₃ and 0.72 mM NaHCO₃ flowing at 2 ml min⁻¹. The standard deviations of the concentrations of EDTA and anions determined by ionic chromatograph and of total organic carbon were analyzed to be ±0.1 mg l⁻¹ and ±1.0 mg l⁻¹, respectively. The concentration of H₂O₂ in the aqueous solution was determined by the KI titration method [8]. The concentration of ammonia was analyzed by Nesslerization [9]. The identification of NTA was determined by comparing with the retention time of an available chemical standard. The UV light absorbance of reacting solutions were detected by a Shimadzu model UV-160A UV/Visible spectrophotometer.

3. Results and discussion

3.1. The decomposition of H₂O₂ in aqueous solution

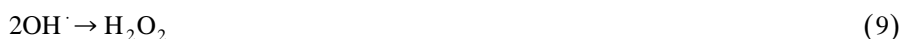
Hydrogen peroxide (H₂O₂) dissociates in aqueous solutions of which the pK_a values is reported to be 11.6 [10]. The dissociation of H₂O₂ in aqueous solution can be described as follows:



In alkaline conditions, the deprotonated HO₂⁻ species can be further consumed by the H₂O₂ molecules [11] and OH⁻ ions [12]:



The above reactions were studied in this research by examining the stability of H₂O₂ in aqueous solutions at solution pH 3 and 11. The experimental results shown in Fig. 2 indicate that H₂O₂ is very steady at pH 3, but about 7% of H₂O₂ disappeared at pH 11 after 5 h of reaction time. The experimental results shown in Fig. 2 also indicate that the disappearance rates of H₂O₂ were markedly increased by UV irradiation at both pH 3 and 11. The mechanism for photolytic decomposition of H₂O₂ by UV irradiation proposed by Venkatadri and Peters [12] as follows:



Similar experiments were conducted with the presence of Cu²⁺ ions in the absence of UV irradiation. No variation of H₂O₂ concentration was found at pH 3 as shown in Fig.

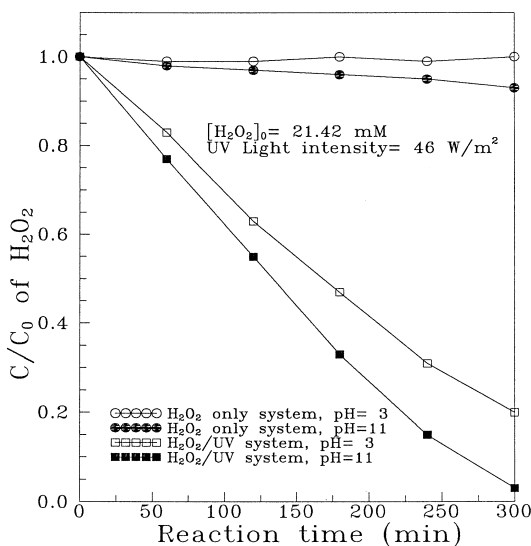


Fig. 2. The stability of H_2O_2 in aqueous solutions at solution pH 3 and pH 11.

3, but significant enhancements of H_2O_2 decomposition were observed at pH 11 with the presence of Cu^{2+} ions, similar to the results reported by Parker [13]. It was possibly because that Cu^{2+} ions would consume OH^- to form hydroxyl complexes or hydroxide precipitates and accelerate reaction (2). Fig. 3 also reveal that the presence of Cu^{2+} ions increased the photolytic rates of H_2O_2 in aqueous solutions by UV irradiation possibly

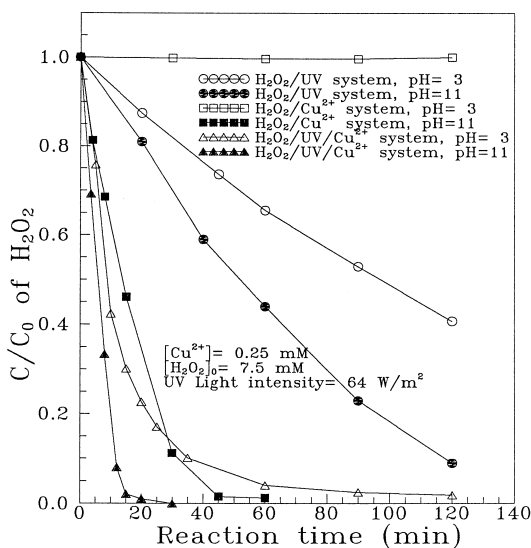


Fig. 3. The concentration variations for H_2O_2 in aqueous solutions in presence of Cu^{2+} and UV irradiation at solution pH 3 and pH 11.

Table 1

The pseudo-first order rate constants of H₂O₂ in various reaction system

	pH = 3		pH = 11	
	$k_{\text{H}_2\text{O}_2}$ (min ⁻¹)	r^2	$k_{\text{H}_2\text{O}_2}$ (min ⁻¹)	r^2
H ₂ O ₂	ND	–	0.00024	0.98
UV/H ₂ O ₂	0.00706	1.0	0.0159	0.98
H ₂ O ₂ /Cu ²⁺	ND	–	0.0918	0.97
UV/H ₂ O ₂ /Cu ²⁺	0.0669	0.98	0.249	0.96

UV light intensity = 64 W m⁻²; [EDTA]₀ = 0.25 mM; [H₂O₂]₀ = 7.5 mM; [Cu²⁺]₀ = 0.25 mM.
 ND = nondetectable.

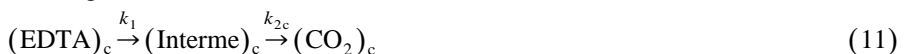
because the quantum yield of H₂O₂ at 254 nm UV light could be raised by the addition of Cu²⁺ ions. The disappearance of H₂O₂ is found to be highly dependent on the solution conditions and can be adequately described by pseudo-first-order irreversible kinetics; the observed rate constants are shown in Table 1.

3.2. The decomposition of EDTA by UV/H₂O₂ process

The decomposition of organics in aqueous solution by UV/H₂O₂ process involves a complex combination of cyclic and linear reactions. The free radicals formed by the decomposition of H₂O₂ may enter into chain reactions with other H₂O₂ molecules to perpetuate H₂O₂ decomposition. Then, they react with organics to form oxidized species and secondary radicals that also participate in chain reaction with H₂O₂; or react with scavengers in aqueous solution (such as HO₂, carbonate and bicarbonate) and effectively interfere with radical chain reactions [14].

Morooka et al. [15] have found that the major intermediates generated during the decomposition of EDTA in aqueous solution by ozonation is nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), and glycine. Gilbert and Glewe [16] indicated that, in addition to the compounds mentioned above, ethylenediaminediacetic acid (EDDA), glyoxylic acid, oxalic acid, formic acid were also detected from the ozonation of EDTA. For the decomposition of EDTA by UV/H₂O₂ process, NTA, ammonia and nitrate were detected in this research. The possible decomposition pathway of EDTA is then suggested to start with the breakage of C–N bonds of EDTA by OH· radical attack to form EDDA, NTA and IDA. The C–N bonds on these compounds are further attacked by OH· to form glycine, ammonia, oxalic acid and formic acid. Finally, the intermediates are oxidized and mineralized into carbonate and nitrate. The proposed reaction scheme for the decomposition of EDTA is shown as Fig. 4.

Owing to the complexity of the decomposition schemes of EDTA in advanced oxidation processes, a simplified two-step kinetic model based on the elemental mass balances of carbon and nitrogen was used to describe the temporal behaviors of reacting species during the reaction:



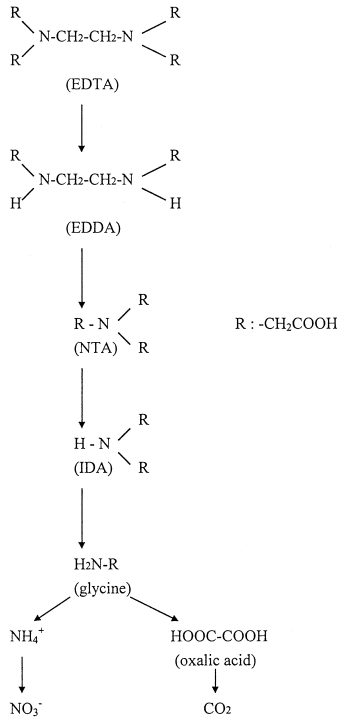


Fig. 4. The proposed simplified reaction scheme for the decomposition of EDTA by UV/H₂O₂ process.

Each step of the reaction was assumed to be irreversible and first order with respect to the reactant. The concentrations of EDTA, organic intermediates, carbonates, and nitrates were used to establish the elemental mass balance of carbon and nitrogen during the reaction:

$$(EDTA)_{o,c} = (EDTA)_c + (Interme)_c + (CO_2)_c \tag{13}$$

$$(EDTA)_{o,n} = (EDTA)_n + (Interme)_n + (NO_3^-)_n \tag{14}$$

The profiles of all reacting species are given by Shen et al. [7].

$$C_a = C_{ao} e^{-k_1 t} \tag{15}$$

$$C_b = C_{ao} (e^{-k_1 t} - e^{-k_{2c} t}) / (k_{2c} - k_1) \tag{16}$$

$$C_c = C_{ao} - C_a - C_b \tag{17}$$

$$C_{a,n} = C_{ao,n} e^{-k_1 t} \tag{18}$$

$$C_{b,n} = C_{ao,n} (e^{-k_1 t} - e^{-k_{2n} t}) / (k_{2n} - k_1) \tag{19}$$

$$C_{c,n} = C_{ao,n} - C_{a,n} - C_{b,n} \tag{20}$$

where C_{ao} is the initial concentration of EDTA as carbon; C_a is $(EDTA)_c$, concentration of EDTA as carbon at time t ; C_b is $(Interme)_c$, concentration of organic intermediates as

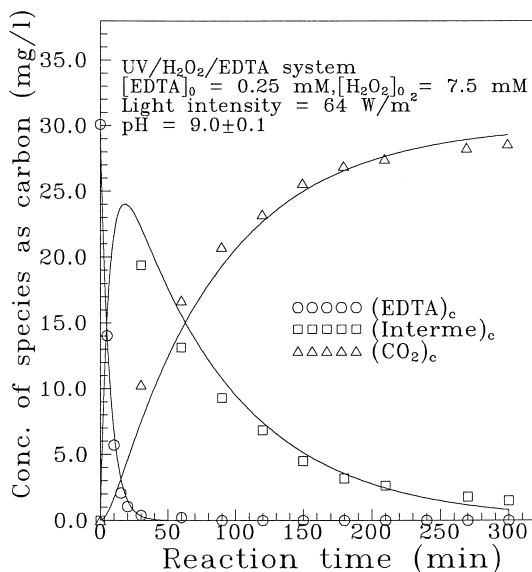


Fig. 5. The temporal distribution of the carbon-containing species of the decomposition of EDTA in aqueous solution at pH 9 by UV/H₂O₂ process.

carbon at time t ; C_c is $(\text{CO}_2)_c$, concentration of CO_2 as carbon at time t ; $C_{\text{ao},n}$ is the initial concentration of EDTA as nitrogen; $C_{\text{a},n}$ is $(\text{EDTA})_n$, concentration of EDTA as nitrogen at time t ; $C_{\text{b},n}$ is $(\text{Interme})_n$, concentration of intermediate as nitrogen at time t ; $C_{\text{c},n}$ is $(\text{NO}_3^-)_n$, concentration of nitrate as nitrogen at time t ; k_1 is the pseudo-first order rate constant for the decomposition of EDTA; k_{2c} is the pseudo-first order rate constant for the mineralization of intermediates based on carbon; k_{2n} is the pseudo-first order rate constant for the mineralization of intermediates based on nitrogen.

Using the reaction rate equations proposed above, the rate constants were determined by regressing the experimental data. The simplified kinetic model was found to fit well with experimental results as shown in Figs. 5 and 6 for carbon and nitrogen species, respectively, on the EDTA decomposition by the UV/H₂O₂ process at pH 9. EDTA was decomposed almost completely within 1 h and the organic intermediates are mineralized to form CO_2 within 5 h. The decomposition of the nitrogen-containing species was much more difficult. Less than 20% of the organic nitrogen initially present was converted to nitrate within 5 h of reaction time.

EDTA and H_2O_2 dissociate in aqueous solutions. Thus, the light absorbance and UV photolytic rate constant ($k_{1,\text{uv}}$) of EDTA were found to be highly dependent on the solution pH as shown in Table 2. It was found that both the light absorbance (A) and photolytic decomposition rates of EDTA were increased with increasing solution pH. The photolytic mineralization rate constants ($k_{2,\text{uv}}$) were relatively small indicating that almost no mineralization of intermediates occurred during the photolysis of EDTA, especially for acidic conditions. The reaction rates by UV/H₂O₂ process were much higher than those for the UV photolysis process. The rate difference between the rates of these two processes indicates that the free radical attack would be the dominant

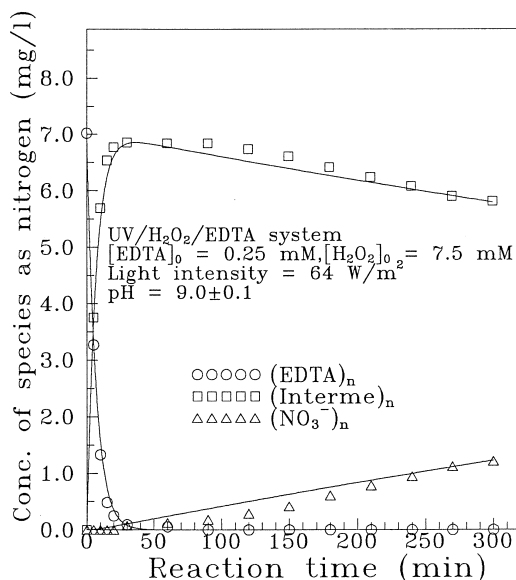


Fig. 6. The temporal distribution of the nitrogen-containing species of the decomposition of EDTA in aqueous solution at pH 9 by UV/H₂O₂ process.

mechanism for the decomposition of EDTA by the UV/H₂O₂ process. The total contribution ($k_{1,UV/H_2O_2}$) to the decomposition of EDTA was assumed to be the linear summation of those by the UV photolysis ($k_{1,UV}$) and the attack by free radical ($k_{1,OH}$):

$$k_{1,UV/H_2O_2} = k_{1,UV} + k_{1,OH} \quad (21)$$

where $k_{1,OH}$ is the pseudo-first order rate constant for the decomposition of EDTA by indirect oxidation; $k_{1,UV}$ is the pseudo-first order rate constant for the decomposition of

Table 2

The decomposition rate constants of EDTA in aqueous solution by the direct photolysis and the UV/H₂O₂ process at various solution pH

	pH = 3	pH = 7	pH = 9	pH = 11
Absorbance	0.00400	0.01000	0.01300	0.02400
$k_{1,uv}$	0.00027	0.00572	0.00739	0.01233
$k_{2,uv}$	ND	0.00063	0.00072	0.00084
$k_{1,UV/H_2O_2}$	0.12060	0.12473	0.14985	0.03140
$k_{2,UV/H_2O_2}$	0.00464	0.00636	0.01236	0.00470
$k_{1,uv} / k_{1,UV/H_2O_2}$	0.02%	4.6%	4.9%	39.3%
$k_{1,OH}^a$	0.12033	0.11901	0.14246	0.01907
$k_{1,OH} / k_{1,UV/H_2O_2}$	99.8%	95.4%	95.1%	60.7%
$k_{2,OH}^b$	0.00464	0.00573	0.01164	0.00386
$k_{2,OH} / k_{2,UV/H_2O_2}$	100%	90.1%	82.1%	82.1%

UV light intensity = 64 W m⁻²; [EDTA]₀ = 0.25 mM; [H₂O₂]₀ = 7.5 mM.

^a $k_{1,OH} = k_{1,UV/H_2O_2} - k_{1,UV}$ (min⁻¹).

^b $k_{2,OH} = k_{2,UV/H_2O_2} - k_{2,UV}$ (min⁻¹).

ND = nondetectable.

Table 3

The formation rate constants of CO_2 and NO_3^- for the decomposition of EDTA in aqueous solution by the UV/ H_2O_2 process

pH	CO_2 formation rate constant		NO_3^- formation rate constant		k_{2c} / k_{2n}
	k_{2c} (min^{-1}) ^a	r^2	k_{2n} (min^{-1})	r^2	
3	0.00464	0.96	0	—	—
5	0.00411	0.97	0	—	—
7	0.00636	0.89	0.00027	0.98	23.6
9	0.01236	1.00	0.00066	0.97	18.7
11	0.00470	0.99	0.00023	0.97	20.4

UV light intensity = 64 W m^{-2} ; $[\text{EDTA}]_0 = 0.25 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 7.5 \text{ mM}$.

^a $k_{2c} = k_{2,\text{UV}/\text{H}_2\text{O}_2}$.

EDTA by direct photolysis; $k_{1,\text{UV}/\text{H}_2\text{O}_2}$ is the pseudo-first order rate constant for the decomposition of EDTA by UV/ H_2O_2 process.

The contribution by direct photolysis gradually was found to increase with solution pH. For instance, about 40% of the EDTA decomposed by the UV/ H_2O_2 process may be attributed to direct photolysis at pH 11 as shown in Table 2. The decomposition and mineralization rate constants of EDTA by the UV/ H_2O_2 process, $k_{1,\text{UV}/\text{H}_2\text{O}_2}$ and $k_{2,\text{UV}/\text{H}_2\text{O}_2}$, respectively, were increased with increasing solution pH values, but decreased significantly at pH 11. It was suggested that the species distribution of EDTA and H_2O_2 plays an important role on the decomposition of EDTA by the UV/ H_2O_2 process. Even though the major EDTA species is negatively charged HEDTA^{3-} at pH 11 which is favorably attacked by OH^\cdot radicals [17], the OH^\cdot radicals are also readily scavenged by the HO_2^- species dominant in alkaline solutions. The oxidation of organic nitrogen was found to be much slower than that of organic carbon during the UV/ H_2O_2 treatment of EDTA-containing solutions as shown in Table 3; no indications of NO_3^- formation were noticed for acidic solutions.

The presence of H_2O_2 significantly enhanced the photodecomposition of EDTA until a H_2O_2 :EDTA molar ratio up to 30 as shown in Fig. 7 (where the solid lines do not mean to be described from the kinetic model). Excessive H_2O_2 might compete for OH^\cdot radicals with EDTA as indicated by reaction (6). Similar experimental results were reported by Ogata et al. [18], Ho [19] and Schulte et al. [20]. Fig. 8 depicts that the decomposition rate constant, $k_{1,\text{UV}/\text{H}_2\text{O}_2}$, linearly increased with UV light intensity (I) at fixed H_2O_2 dosage and can be expressed as:

$$\text{at pH 3, } k_{1,\text{UV}/\text{H}_2\text{O}_2} = 0.039I \quad (r^2 = 0.98) \quad (22)$$

$$\text{at pH 11, } k_{1,\text{UV}/\text{H}_2\text{O}_2} = 0.151I \quad (r^2 = 0.99) \quad (23)$$

The effect of UV light intensity on the mineralization rate constant, $k_{2,\text{UV}/\text{H}_2\text{O}_2}$, of organic intermediates is shown in Fig. 9, and can be expressed as:

$$\text{at pH 3, } k_{2,\text{UV}/\text{H}_2\text{O}_2} = 0.0000624I / (1 + 0.00315I) \quad (24)$$

$$\text{at pH 11, } k_{2,\text{UV}/\text{H}_2\text{O}_2} = 0.0000897I / (1 + 0.00488I) \quad (25)$$

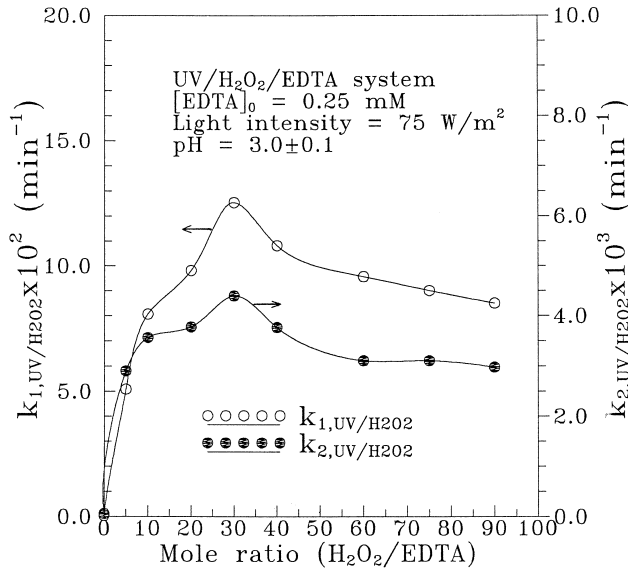


Fig. 7. The effect of H₂O₂ dosage on the decomposition of EDTA in aqueous solution by UV/H₂O₂ process.

It was found that the UV light intensity effect on increasing the decomposition rate of EDTA at pH 3 and pH 11 was contrary to that of the mineralization rate constant of organic intermediates. The orders of UV light intensity in Eqs. (22)–(25) were similar to the previous studies of Ku and Ho [21] and Shen et al. [22].

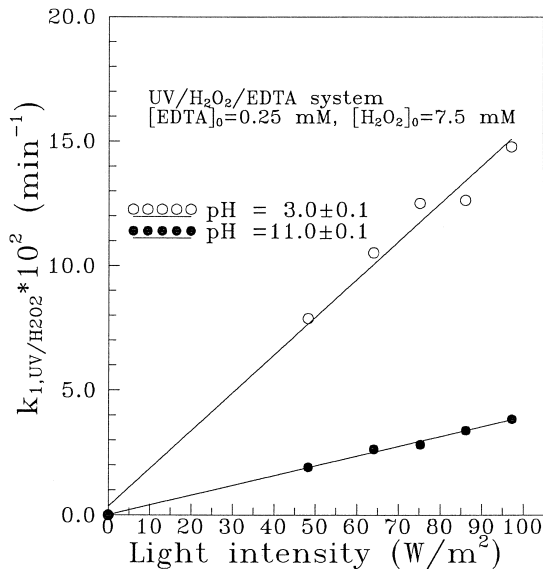


Fig. 8. The effect of UV light intensity on the decomposition of EDTA in aqueous solution at pH 3 and pH 11 by UV/H₂O₂ process.

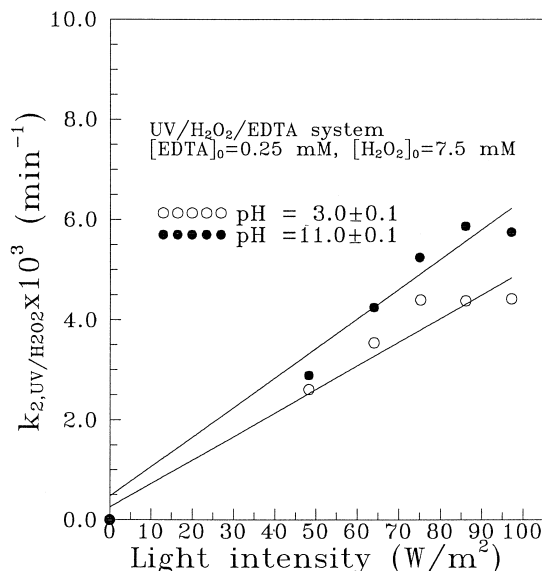


Fig. 9. The effect of UV light intensity on the mineralization rates of EDTA in aqueous solution at pH 3 and pH 11 by UV/H₂O₂ process.

The effect of the presence of copper ion (Cu²⁺) on the photooxidation of EDTA by the UV/H₂O₂ process was studied at pH 3 and 11. For the cases where the molar concentration of copper species were less than those of EDTA, most copper species are present as CuEDTA form at pH 3. It was found that the CuEDTA species compete favorably for UV light than H₂O₂ (the absorbance of CuEDTA and H₂O₂ at 254 nm were determined to be 0.72 and 0.141 at pH 3, respectively), thus retarded the generation of OH[·] from the photolysis of H₂O₂ to decompose EDTA as shown in Table 4. The presence of free copper species (Cu²⁺), when the molar concentration of copper species exceeded that of EDTA, was found to accelerate the decomposition rate EDTA at pH 3, indicating the formation of OH[·] by the photolytic decomposition of H₂O₂ was catalyzed by free copper ions. As depicted in Table 4, the presence of copper species

Table 4

The effect of copper on the decomposition of EDTA in aqueous solution by UV/H₂O₂ process

	Cu ²⁺ (mM)				
	0	0.050	0.125	0.250	0.500
pH = 3					
$k_{1,UV/H_2O_2}$ (min ⁻¹)	0.1210	0.1030	0.0713	0.1490	0.3600
r^2	1.00	1.00	0.99	0.99	0.99
pH = 11					
$k_{1,UV/H_2O_2}$ (min ⁻¹)	0.0314	—	0.0349	0.0077	0.0121
r^2	1.00	—	0.94	0.99	0.81

UV light intensity = 64 W m⁻²; [EDTA]₀ = 0.25 mM; [H₂O₂]₀ = 7.5 mM.

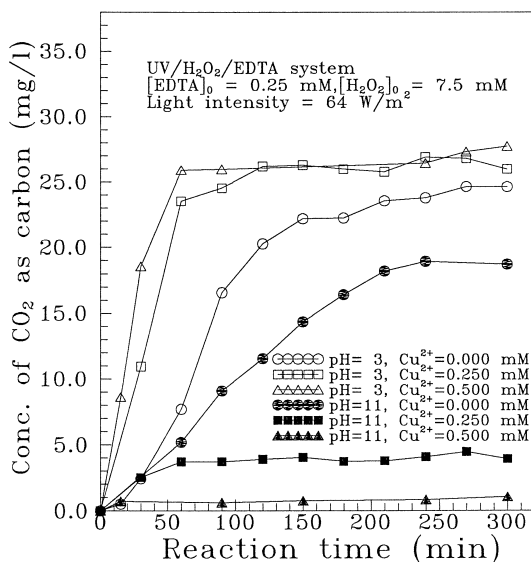


Fig. 10. The effect of copper ion on the mineralization rates of EDTA in aqueous solution at pH 3 and pH 11 by UV/H₂O₂ process.

inhibited the decomposition of EDTA by UV/H₂O₂ process at pH 11 possibly because the formation of copper hydroxide and hydroxyl complexes might inhibit the decomposition of H₂O₂ to generate effective OH[•] radicals. The effect of copper species on the mineralization rates of EDTA by UV/H₂O₂ process shown in Fig. 10 also indicates that copper may play different roles at various solutions and pH conditions.

The experimental results conducted at different solution temperatures indicate that the reaction rates increased slightly with increasing solution temperature and can be correlated by Arrhenius' Law. The activation energies for $k_{1,UV/H_2O_2}$ and $k_{2,UV/H_2O_2}$ were determined to be 6.75 and 3.72 kcal mol⁻¹, respectively. The low activation energies found in this research were similar to the experimental results reported by Li et al. [23] and Weir and Sundstrom [24] for various photocatalytic systems.

4. Conclusion

The stability of H₂O₂ in aqueous solutions were studied and found to be influenced by solution pH, the presence of UV light, and copper ion. Almost complete decomposition of EDTA in aqueous solution by UV/H₂O₂ can be accomplished in 1 h. The decomposition rates of EDTA by UV/H₂O₂ were fairly dependent of the solution pH value, light intensity and H₂O₂ dosage. The breakage of C–N bonds on EDTA was found to occur at very early periods of the reaction. Mineralization of organic intermediates to form NTA, ammonia and nitrate ions was observed. A two-step kinetic model could adequately describe the temporal behavior of the decomposition of EDTA in aqueous solution by UV/H₂O₂ process.

Acknowledgements

This research was supported in part by Grant EPA-85-E3J1-09-03 from the Environment Protection Administration, Republic of China.

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