Photodegradation of EDTA and NTA in the UV/H₂O₂ Process

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Dedicated to Prof. H. P. Fritz on the occasion of his retirement

Z. Naturforsch. **50b**, 1845–1853 (1995); received May 4, 1995

EDTA, NTA, UV/H₂O₂, Photochemical Degradation

The influence of H₂O₂ on the UV degradation of the broadly used aminopolycarboxylates EDTA and NTA in aqueous solution was investigated. The photochemical degradation in the UV/H₂O₂ process was compared with classical oxidative treatment of potable water. The German drinking water regulation (Trinkwasserverordnung) was the orientation for all experiments. The Advanced Oxidation Process (AOP) turned out to be superior to the classical oxidation processes.

The photochemical degradation of EDTA and NTA by UV irradiation could be significantly stimulated in the presence of H₂O₂. There was a strong increase in the degradation rate and a decrease in the quantum yield of the aminopolycarboxylates. Experiments with butyl chloride as radical scavenger proved the photolytically generated hydroxyl radicals to be responsible for the increase in the degradation rates.

The effect of increasing the degradation rate at higher concentrations of H₂O₂ was limited, because the steady-state concentrations of the hydroxyl radicals as reactive species, did not increase at the same rate as the initial concentration of H₂O₂.

Low amounts of iron dissolved from the high-grade steel photoreactor walls had a significant catalytic effect on the degradation.

1. Introduction

In the past few years there has been increasing interest in advanced oxidation processes (AOPs) for water treatment [1]. One of these AOPs, the combination of H₂O₂ and ultraviolet irradiation, is known to have a high potential for the degradation of organic matter of natural and anthropogenic origin. To date only the degradation of some anthropogenic water contaminants, mostly of non-ionic character like halogenated hydrocarbons and pesticides, has been investigated. This study focusses on the behavior of the chelating agents EDTA and NTA.

There is great environmental interest in these substances because they are found in nearly all German rivers and lakes that are close to human habitation or receive industrial waste water. In lake Constance water concentrations range from 1.3 to 4.9 µg/L EDTA and 0.5 to 0.6 µg/L NTA. The tributaries show about the tenfold concentrations and in the river Rhine average values up to 50 µg/L EDTA have been found [2, 3].

The microbial degradation of EDTA obtained by Alder *et al.* was relatively poor and took place only under very special conditions [4]. Brauch and Schullerer observed fast breakthrough of EDTA and NTA in activated carbon filters. They also found that treatment with chlorine or other disinfectants did not result in any significant degradation of EDTA [5]. Only with ozone there was significant EDTA and NTA degradation measured by Gilbert and Beyerle [6].

As a consequence, there is great interest in studying the ability of AOPs to degrade this class of organic substances. The free uncomplexed forms of EDTA and NTA used in the experiments reflect the situation in aquatic systems in a much better way than the rapidly decomposing iron-complexes. It was found by others that the predominant complexes of EDTA and NTA in surface waters are those of Ca²⁺, Zn²⁺ and Cu²⁺ [7].

The objectives of this work were: (1) to investigate the possibility of degrading EDTA and NTA photochemically in the UV/H₂O₂-process, (2) to determine the rate constants for the reactions and (3) to calculate the steady state concentrations of the OH-radicals under water treatment-oriented conditions.

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2. Experimental methods and calculation

2.1 Analysis

EDTA and NTA concentrations were measured using reversed-phase HPLC [8]. Before passing the column (Merck LiChrospher 100 RP C 18, 5 μ m 250 $\times$ 4) the aminopolycarboxylates were converted to their iron(III) complexes with ferric nitrate. For the mobile phase 100 mg Fe(NO₃)₃, 0.5 g tetrabutylammonium nitrate and 8.5 mL 1 N nitric acid were dissolved in bidistilled water to one liter.

The concentration of H₂O₂ was determined using the method of Eisenberg [9]: 5 mL of the sample were acidified with hydrochloric acid, and 1 mL of titaniumtetrachloride dissolved in concentrated hydrochloric acid was added. These samples were filled up to 25 mL with bidistilled water. The spectral absorption of the formed titanium peroxo complex was quantified in a photometer at $\lambda = 415$ nm. The extinction coefficient of the titanium peroxo complex was measured to be $\epsilon(\lambda = 415 \text{ nm}) = 723 \pm 18 \text{ L (mol cm)}^{-1}$. Absolute concentrations of H₂O₂ were calculated according to the law of Lambert and Beer.

The oxygen concentration was measured electronically by oxygen electrodes (WTW, OXI 530).

The pH value was measured with a glass electrode (WTW, pH 521).

The flux of photons was estimated by uranyl oxalate actinometry. This actinometer was prepared according to the method of Braun *et al.* [10].

A Milton Roy Spectronic 1201 UV/vis spectral photometer was used for measuring the spectral absorption of the solutions at the irradiation wavelength. Solutions containing no H₂O₂ were measured in a quartz cell with 10 cm pathlength and at somewhat higher EDTA and NTA concentrations than used in the experiments. This procedure was necessary to measure in a useful range of the spectrometer.

2.2 Chemicals

EDTA: Disodium salt, Fluka No. 03679, Micro Select; NTA: Fluka No. 72559, Micro Select; H₂O₂: Riedel-de Haen No. 31624, pro analysi; TiCl₄: Fluka No. 89545, purissima; butyl chloride: Fluka No. 19750, purissima; UO₂SO₄ was prepared by dissolving UO(OH)₂ in H₂SO₄ (Riedel-de Haen, No. 30743, pro analysi). For purification it was recrystallised three times. UO(OH)₂ was made by treating a saturated solution of uranyl acetate (Riedel-de Haen, No. 31636, pro analysi) with so-

dium hydroxide (Riedel-de Haen, No. 30620, pro analysi); Na₂C₂O₄: Merck, No. 6557, pro analysi.

2.3 Reactor system

The system used is given in Fig. 1. The solution was thoroughly stirred in the reservoir from which the samples were taken. A rotary pump (PTFE type) was used to transport the solution into the photoreactor. Oxygen concentration, pH value and flow were measured by continuously working meters. The reactor (high-grade steel tube) had a low-pressure mercury vapor lamp (Katadyn) axially arranged. The optical path length for the solution passing through the reactor tube was 0.75 cm. The power output at $\lambda = 254$ nm (measured by actinometry) was 14.5 W or 47.6 μ Einstein (L s)⁻¹. The emission of the lamp at $\lambda = 185$ nm was absorbed in the quartz tube separating the lamp from the solution. The solution was equilibrated with filtered air to achieve oxygen saturation. The model water used was unbuffered and demineralized.

The glasreactors, a "Merry-Go-Round" photo reactor and a tube photo reactor used for comparing experiments were described elsewhere [11, 12].

Fig. 1. Experimental setup for the investigation of photodegradations in an open reactor system.

2.4 Calculation

Symbols used

A: spectral absorption; $A_{(0.75\text{cm}, 254\text{nm})}$: spectral absorption in the photoreactor; AOP: advanced oxidation process; a: exponent; b: exponent; C: concentration (mol L⁻¹); C₀: initial concentration (mol L⁻¹); d: effective length of the light path in the photoreactor (cm); EDTA: ethylenediaminetetraacetate; k₁: constant; k₂: constant; k_{sys}: measured rate constant in the used system (first order, s⁻¹); k_{eff}: effective rate constant of degradation in the irradiated volume (first order, s⁻¹); k_{EDTA}:

second order rate constant of the reaction of EDTA with OH[•] (L mol⁻¹ s⁻¹); k_{NTA} : second order rate constant of the reaction of NTA with OH[•] (L mol⁻¹ s⁻¹); NTA: nitrilotriacetate; OH[•]: hydroxyl radicals; P_o : radiation flux density (Einstein L⁻¹ s⁻¹); P_{abs} : radiation flux density absorbed in the irradiated solution (Einstein L⁻¹ s⁻¹); V_{PR} : volume of the photoreactor (mL); R_v : ratio $V_{\text{tot}}/V_{\text{ir}}$; t_{sys} : time when the sample was taken (s); t_{eff} : effective time of irradiation (s); V_{tot} : total volume of the solution (mL); V_{ir} : irradiated volume of the solution (mL); ϵ : extinction coefficient (L mol⁻¹ cm⁻¹); λ : wavelength (nm); Φ : quantum yield.

In the through-flow reactor used (Fig. 1), only a fraction of the whole solution was irradiated. The other part was stirred in the nonirradiated reservoir. As a consequence, the total volume (V_{tot}) of the solution had an influence on the measured rate of degradation (k_{sys}). Of special interest was the effective kinetics (k_{eff}) of the reaction taking place in the photoreactive zone (the irradiated volume, V_{ir}). The hypothesis was used that the photochemical reaction only takes place in the irradiated zone and that dark reactions in the reservoir play no significant role. To derive k_{eff} from k_{sys} , k_{sys} was multiplied with the ratio R_v which was 4.5 for the system applied (1):

$$3000 \text{ mL}/667 \text{ mL} = V_{\text{tot}}/V_{\text{ir}} = 4.5 = R_v \quad (1)$$

The validity of this approach was proven by a set of experiments using different total volumes of solution. The results are shown in Fig. 3. The calculated R_v value of that correlation is 4.4 ± 0.1 .

In the following diagrams the concentrations of the aminopolycarboxylates are shown as a function of t_{eff} . These results turned out to be valid for degradation yields <80% during one run through the irradiated zone.

Fig 2. Experimentally determined rate constants (k_{sys}) for the photodegradation of EDTA as function of the total volume of the solution (V_{tot}).

Fig. 3. Degradation of EDTA in the UV/H₂O₂ process compared with UV photolysis alone and thermal degradation with H₂O₂ under matching conditions.

To determine the rate constant for higher conversions, it is necessary to know the extinction coefficients and quantum yields of the organic products. Usually these data are not available. Using the method of small amounts of conversion has the advantage that the influence of the degradation products can be ignored. When the light absorption in the photoreactor is smaller than 0.1, Equations (2) to (4) can be applied:

$$\frac{dC_i}{dt} = P_o \Phi f_i \left(1 - e^{-2.3 d \sum_{j=1}^n \epsilon_j C_j} \right) \quad (2)$$

$$f_i = \frac{\epsilon_j C_j}{\sum_{j=1}^n \epsilon_j C_j} \quad (3)$$

$$\ln \frac{C_t}{C_o} = -k_{\text{eff}} t \quad (4)$$

All of our experiments were carried out in the absorption range $A < 0.1$, so that the quantum yields were not affected by spectral absorption effects resulting from the algorithm chosen. For higher spectral absorbances ($A > 2$) the degradation rate becomes independent of the concentration of the aminopolycarboxylates in the solution. In the range $2 > A > 0.1$ the mathematical description of the reaction is rather complex.

The rate constant of degradation was calculated by fitting a linear regression for the logarithm of the concentration ratio versus the effective irradiation time ($t_{\text{eff}} = t/R_v$) (Eq. (4)). The value of the slope is k_{eff} . In all cases the assumed level of confidence was higher than 97%.

For technical application of a photoreactor, the quantum yield of the degradation is informative. It can be calculated according to Eq. (5), which can be

derived from Eq. (2). It has to be kept in mind that at high spectral absorbances the concentrations of the dissolved substances are of influence on the values of the quantum yield.

$$\Phi = \frac{k_{\text{eff}} C_o}{P_{\text{abs}}} \quad (5)$$

The initial concentrations of the polycarboxylates (C_o) were determined by HPLC as described above. The absorbance (A) at the initial concentrations were measured to estimate the number of the absorbed photons (P_{abs}) according to Eq. (6).

$$P_{\text{abs}} = P_o (1 - 10^{-A_{(0.75 \text{ cm}, 254 \text{ nm})}}) \quad (6)$$

3. Results and Discussion

3.1 General considerations

Photolysis was performed at different initial concentrations of EDTA and NTA. Table Ia, b shows that there was no clear change in the quantum yield for the applied concentration range (6.8–102 $\mu\text{mol/L}$ EDTA and 20–103 $\mu\text{mol/L}$ NTA).

Figure 3 shows a significant synergistic photochemical effect for the EDTA degradation at the initial concentration of 0.5 mmol/L H₂O₂. This is the maximum H₂O₂ concentration allowed by German law for treatment of potable water [13]. For comparison the thermal (dark) reaction with H₂O₂ alone and the irradiation of EDTA in the

C_o (EDTA) in $\mu\text{mol L}^{-1}$	Φ
6.8	0.47
10.2	0.47
20.4	0.41
34	0.43
51	0.49
68	0.43
85	0.44
102	0.41

Table Ia. Quantum yields of the photolytic degradation of EDTA for different EDTA concentrations at pH = 6. Emitted photon rate $P_o = 46.7 \mu\text{Einstein (L s)}^{-1}$.

C_o (NTA) in $\mu\text{mol L}^{-1}$	Φ
20	1.26
32	1.66
54	1.51
86	1.28
103	1.70

Table Ib. Quantum yields of the photolytic degradation of NTA for different NTA concentrations at pH = 6. Emitted photon rate $P_o = 46.7 \mu\text{Einstein (L s)}^{-1}$.

Fig. 4. The chemical degradation of EDTA by ozone and chlorine compared with the UV/H₂O₂ process under the conditions of the German drinking water regulation (Trinkwasserverordnung, TVO).

absence of H₂O₂ are also given. The rate constant of the combined oxidation reaction (AOP) is nine times higher than the sum of the single processes.

This supports the use of AOPs in potable water treatment. Fig. 4 compares the results for the application of the UV stimulated oxidation of EDTA with H₂O₂ with the classical oxidants Cl₂ and O₃ used in water treatment. All concentrations of the oxidants were chosen according to the maximum allowed values of the German drinking water regulation [13]. The comparison shows that the degradation with UV/H₂O₂ is by far the fastest one.

In Fig. 5, the effect of the H₂O₂ initial concentration on the degradation is given. The degradation rate increases with increasing concentration of H₂O₂. All degradations are of pseudo first-order kinetics.

The comparison of the degradation rates of the photolysis of EDTA and its oxidation by UV/H₂O₂ leads to the conclusion that the photolysis

Fig. 5. Effect of initial concentration of H₂O₂ for the photochemical degradation of EDTA.

can be ignored in the photochemical degradation using high concentrations of H₂O₂. This can be explained by the following facts:

The number of photons absorbed by the chemicals is related to their spectral absorption (A). Comparing the absorption of H₂O₂ and EDTA the product of C_0 and ε of each substance is the determining value. Because the optical path length is equal for both substances, $(C_0\varepsilon)_{\text{H}_2\text{O}_2} \gg (C_0\varepsilon)_{\text{EDTA}}$. Therefore, the light-induced reaction pathway leading to OH-radicals accounts for a higher degradation of the aminopolycarboxylates than the photolysis, especially for $C_0(\text{H}_2\text{O}_2) > 0.3 \text{ mmol/L}$.

3.2 Model kinetics

It is reasonable to assume that the degradation of EDTA depends on the concentration of the oxidants in the solution. Therefore Eq. (7) can be used:

$$\frac{dC(\text{EDTA})}{dt} = -k_2 C(\text{O}_2)^c C(\text{H}_2\text{O}_2)^b C(\text{EDTA})^a \quad (7)$$

For the experiments with different initial concentrations of H₂O₂:

$C(\text{O}_2) = \text{const.}$ and for each specific reaction holds:

$$C(\text{H}_2\text{O}_2) = C_0(\text{H}_2\text{O}_2) = \text{const.}$$

Therefore Eq. (7) can be transformed by the use of Eq. (8) into Eq. (9)

$$k_{\text{eff}} = k_2 C(\text{O}_2)^c C_0(\text{H}_2\text{O}_2)^b = k_1 C_0(\text{H}_2\text{O}_2)^b \quad (8)$$

$$\frac{dC(\text{EDTA})}{dt} = -k(\text{eff}) C(\text{EDTA})^a \quad (9)$$

$$\ln k_{\text{eff}} = \ln k_1 + b \ln C_0(\text{H}_2\text{O}_2) \quad (10)$$

In the logarithmic form of (Eq. (10)) a linear correlation of k_{eff} and $C_0(\text{H}_2\text{O}_2)$ becomes evident. Using $k_1 = 0.72 (\text{L/mol})^{0.55} \text{s}^{-1}$, $a = 1$, and $b = 0.55$, Eq. (11) can be obtained:

$$\frac{dC(\text{EDTA})}{dt} = -0.72 \text{ s}^{-1} (\text{L/mol})^{0.55} C(\text{H}_2\text{O}_2)^{0.55} C(\text{EDTA})^1 \quad (11)$$

In case of NTA, the equation reads:

$$\frac{dC(\text{NTA})}{dt} = -0.02 \text{ s}^{-1} (\text{L/mol})^{0.25} C(\text{H}_2\text{O}_2)^{0.25} C(\text{NTA})^1 \quad (12)$$

Figure 6 shows the comparison of the calculated curve and the experimental data. Even though it is not possible to obtain information on the reaction

Fig. 6. The degradation rate constants for the aminopolycarboxylates in the UV/H₂O₂ process as a function of the initial H₂O₂ concentration for NTA(■) and EDTA(□) and the calculated model kinetics.

mechanisms with this model, it is useful to predict the kinetics of the degradation in a photoreactor using similar aqueous solutions and a low-pressure mercury lamp of known photon flux.

3.3 Calculation of the OH-radical concentration

The acceleration of the degradation processes decreases with increasing H₂O₂ concentration. The reason for this phenomenon is the generation of hydroxyl radicals by the photolysis of H₂O₂. If these radicals are produced in higher concentrations, they tend to recombine or to react according to the scheme of Haber and Willstätter [14]. This is especially favorable for concentrations of the aminopolycarboxylates ($\leq 3 \cdot 10^{-5} \text{ mol L}^{-1}$) lower than the lowest concentration of hydrogen peroxide ($1 \cdot 10^{-4} \text{ mol L}^{-1}$). It is possible to calculate the hydroxyl radical concentration for the experiments described ($\varepsilon(\text{H}_2\text{O}_2, 254 \text{ nm}) = 18.6 \text{ L mol}^{-1} \text{ cm}^{-1}$, $\Phi(\text{H}_2\text{O}_2, 254 \text{ nm}) = 1$ [15]) using the recombination of OH-radicals and the Haber-Willstätter scheme.

The presence of high concentrations of radical scavengers (butyl chloride) led to degradation rate

Table II. Influence of butyl chloride (BuCl) as a radical scavenger on the degradation of EDTA in the UV/H₂O₂ process at pH = 6. C₀(EDTA) = 30 μmol L⁻¹.

C ₀ (H ₂ O ₂) [mmol L ⁻¹]	BuCl [mmol L ⁻¹]	k _{eff} [s ⁻¹]
0	0	0.00055
0.5	0	0.0122
0.5	10	0.0061
1.0	0	0.0167
1.0	20	0.0073

constants of EDTA similar to those without H₂O₂ (Table II). Therefore, it can be deduced, that the hydroxyl radicals were the reactive species, in the UV/H₂O₂ process.

Two different degradation pathways for the aminopolycarboxylates (R) in the UV/H₂O₂ process have to be considered:

1. Photolysis: $R \xrightarrow{h\nu, O_2} R^* \rightarrow CO_2 + H_2O + NH_3 + NO_3^-$
2. Light-induced degradation:

The dominating kinetics for the degradation of EDTA with the hydroxyl radicals generated from the photolysis of hydrogen peroxide can be described by Eq. (13):

$$dC(EDTA)/dt = k_{EDTA} C(OH^\cdot) C(EDTA) \quad (13)$$

In this case, the observed rate constant can be given by Eq. (14)

$$k_{eff} = k_{EDTA} C(OH^\cdot) \quad (14)$$

As a consequence a differential equation can describe the photochemical formation of hydroxyl radicals and their consumption through chemical reactions in the investigated system Eq. (15):

$$\begin{aligned}
 dC(OH^\cdot)/dt = & (\Phi_{H_2O_2} P_{abs}/V_{PR}) - (k_{EDTA} C(OH^\cdot) C(EDTA)) - \\
 & (k_{OH^\cdot} C(OH^\cdot)^2) - (k_{H_2O_2} C(OH^\cdot) C(H_2O_2)) \quad (15)
 \end{aligned}$$

The assumption of a steady-state concentration of the hydroxyl radicals in the irradiated zone is reflected in Eq. (16):

$$dC(OH^\cdot)/dt = 0 \quad (16)$$

For $t \Rightarrow t(=0)$, and with the assumption that $C(OH^\cdot) \cong 0$, Eq. (15) can be written as Eq. (17):

$$\begin{aligned}
 C(OH^\cdot) = & \frac{(\Phi_{H_2O_2} P_{abs})}{(k_{EDTA} C(EDTA)) + (k_{H_2O_2} C(H_2O_2)) V_{PR}} \quad (17)
 \end{aligned}$$

Combining Eq. (17) with Eq. (14) leads to Eq. (18):

$$\begin{aligned}
 k_{EDTA} = & \frac{k_{H_2O_2}}{(\Phi_{H_2O_2} P_{abs}) / (C(H_2O_2) k_{eff} V_{PR}) - (C(EDTA) / C(H_2O_2))} \quad (18)
 \end{aligned}$$

The same calculation can be done for NTA. The results for the observed data are given in Table IIIa and IIIb.

C ₀ (EDTA) [μmol L ⁻¹]	C ₀ (H ₂ O ₂) [mmol L ⁻¹]	k _{eff} [1/s]	A(254) measured	Φ	C(OH [·]) [mmol L ⁻¹]
32	0	0.00045 ± 0.0002	0.00023	0.47 ± 0.17	—
31	0.1	0.0045 ± 0.0001	0.0021	0.56 ± 0.06	8.5 · 10 ⁻¹²
32	0.2	0.0068 ± 0.0001	0.004	0.48 ± 0.05	9.9 · 10 ⁻¹²
29	0.3	0.0095 ± 0.0003	0.006	0.42 ± 0.05	1.2 · 10 ⁻¹¹
29	0.5	0.0122 ± 0.0004	0.009	0.34 ± 0.3	1.4 · 10 ⁻¹¹
31	0.7	0.0139 ± 0.0006	0.013	0.29 ± 0.02	1.6 · 10 ⁻¹¹
30	1	0.0167 ± 0.0006	0.018	0.24 ± 0.02	1.8 · 10 ⁻¹¹
29	1.5	0.0211 ± 0.0007	0.027	0.20 ± 0.02	2.2 · 10 ⁻¹¹
31	2	0.0257 ± 0.001	0.036	0.19 ± 0.02	2.2 · 10 ⁻¹¹
32	2.5	0.027 ± 0.00095	0.044	0.17 ± 0.02	2.3 · 10 ⁻¹¹
25	3	0.0293 ± 0.001	0.055	0.12 ± 0.01	3.0 · 10 ⁻¹¹
27	4	0.0338 ± 0.0014	0.074	0.11 ± 0.01	3.2 · 10 ⁻¹¹

Table IIIa. Rate constants k_{eff} and quantum yields Φ of the photochemical degradation rate of EDTA in the UV/H₂O₂ process at pH = 6, and steady-state concentrations of hydroxyl radicals. Emitted photon rate P₀ = 47.6 μEinstein (L s)⁻¹.

$C_0(\text{NTA})$ [$\mu\text{mol L}^{-1}$]	$C_0(\text{H}_2\text{O}_2)$ [mmol L ⁻¹]	k_{eff} [1/s]	A(254) measured	Φ	$C(\text{OH})$ [mmol L ⁻¹]
53	0	0.00135 ± 0.001	0.00039	1.5 ± 0.56	–
52	0.07	0.00176 ± 0.0001	0.0016	0.48 ± 0.05	$1.8 \cdot 10^{-11}$
52	0.15	0.0021 ± 0.0001	0.0028	0.33 ± 0.03	$1.7 \cdot 10^{-11}$
52	0.3	0.0026 ± 0.0001	0.0052	0.21 ± 0.02	$1.9 \cdot 10^{-11}$
53	0.4	0.0027 ± 0.0001	0.0068	0.18 ± 0.01	$2.0 \cdot 10^{-11}$
53	0.5	0.003 ± 0.0002	0.0084	0.16 ± 0.01	$2.1 \cdot 10^{-11}$
51	0.7	0.0031 ± 0.0001	0.012	0.12 ± 0.01	$2.2 \cdot 10^{-11}$
52	1	0.0032 ± 0.0002	0.017	0.09 ± 0.07	$2.5 \cdot 10^{-11}$
50	1.5	0.0034 ± 0.0005	0.025	0.07 ± 0.9	$2.7 \cdot 10^{-11}$
48	2	0.0035 ± 0.0004	0.033	0.05 ± 0.06	$2.8 \cdot 10^{-11}$

Table IIIb. Rate constants k_{eff} and quantum yields Φ of the photochemical degradation rate of NTA in the UV/H₂O₂ process at pH = 6, and steady-state concentrations of hydroxyl radicals. Emitted photon rate $\dot{P}_0 = 46.7 \mu\text{Einstein (L s)}^{-1}$.

Fig. 7. The second-order rate constant of the reaction of EDTA with hydroxyl radicals as a function of the steady state concentration of the hydroxyl radicals.

Fig. 8. The second-order rate constant of the reaction of NTA with hydroxyl radicals as a function of the steady state concentration of the hydroxyl radicals.

The degradation rate (k_{eff}) versus the concentration of the hydroxyl radicals is shown in Fig. 7 for EDTA and in Fig. 8 for NTA and seems to be a linear correlation. However it has to be kept in

mind, that an additional increase of the hydroxyl radical concentration by the increase of hydrogen peroxide initial concentration is limited for reasons described above (Fig. 6).

4. Influence of the Iron(III) Ions on the Photodegradation

The quantum yields of combined oxidative degradations (AOP) of the chelators are shown in Table IIIa and IIIb. For low concentrations, quantum yields higher than 1 were obtained. This is usually explained by a chain reaction. Regarding the experimental data for the photolysis in the absence of H₂O₂ in Fig. 5, it can be seen that the gradient of the curve increases steadily. This autocatalytic effect can only be observed at very low concentrations of H₂O₂ ($C_0(\text{H}_2\text{O}_2) < 0.1 \text{ mmol/L}$). To prove the autocatalytic effect, experiments were done with two all glass laboratory scale reactors as system controll: (a) a "merry-go-round" type and (b) a photo reactor tube with circulating solution. No quantum yields larger than 1 were observed (Table IV) in the lower concentration range of H₂O₂. At higher H₂O₂ initial concentrations, the same results as in the technical scale reactor were obtained. In the technical scale reactor the solution was in contact with high-grade steel. To check a possible dissolution, the iron concentrations were measured in the experiments. There was a clear increase with increasing reaction time, which can be explained by corrosion processes (Table V). The same tendency was observed for the photodegradation reactions of NTA as was expected. As a consequence a new experiment was carried out. EDTA was decomposed photolytically

Table IV. Comparing quantum yields Φ of photochemical degradation of EDTA obtained in the different photoreactors at pH = 6.

H ₂ O ₂ [mmol L ⁻¹]	Φ tech. reactor	Φ glass reactor I	Φ glass reactor II
0	1.1*	0.54	0.50
0	0.47**	0.54	0.50
1	0.24	0.20	0.20
2	0.19	0.17	0.16
3	0.12	0.11	0.11

* k_{eff} was calculated from data observed for long irradiations times; ** k_{eff} was calculated from data observed for short irradiation times.

t_{sys} [s]	Fe [$\mu\text{g L}^{-1}$]
0	–
300	4.9
600	10.8
900	14.7
1200	21.1
1500	23.4

Table V. Concentration of iron in a UV irradiated solution of EDTA at pH = 6 as a function of time.

and the samples were taken in very short intervals. The quantum yield calculated from this experiment was in the same range as the quantum yields calculated from the experiments carried out in the two laboratory glass reactors. This leads to the conclusion that the observed quantum yields higher than 1 were very likely artifacts caused by iron ions. In this context it should be kept in mind, that the influence of iron is not caused by a Fenton-type-reaction but by a intracomplex photodecarboxylation of Fe(III)EDTA. The molar extinction coefficient of the ferric aminopolycarboxylate complexes ($\epsilon(\text{FeEDTA}, 254 \text{ nm}) = 7890 \text{ L mol}^{-1} \text{ cm}^{-1}$; $\epsilon(\text{FeNTA}, 254 \text{ nm}) = 4590 \text{ L mol}^{-1} \text{ cm}^{-1}$) is nearly 1000 times higher than that of the aminopolycarboxylates ($\epsilon(\text{EDTA}, 254 \text{ nm}) = 10 \text{ L mol}^{-1} \text{ cm}^{-1}$; $\epsilon(\text{NTA}, 254 \text{ nm}) = 10 \text{ L mol}^{-1} \text{ cm}^{-1}$). Therefore the observed iron concentrations have a great influence, especially in reactions with long degradation times. The data obtained in the different reactor types (Table IV) are in good agreement for the all-glass reactors and for the reactions with high initial concentrations of H₂O₂, which all had a small sojourn time, and as a consequence no significant increase of iron(III)ions. The reactions with NTA lead to the same results. More details

on the degradation of EDTA by the combination of UV-light and H₂O₂ in the presence of iron will be presented in our next publication.

5. Conclusions

Combination of the application of photoreactors specially designed for potable water disinfection with a chemical oxidant proved to be a useful tool for water treatment. The method applied in our system worked very well for the degradation of aminopolycarboxylates in a concentration range between $5 \cdot 10^{-5}$ and $1.25 \cdot 10^{-6} \text{ mol L}^{-1}$. This holds also for many other organic pollutants which cannot easily be eliminated with classical treatment steps. However, the mechanisms of the degradation are not totally known. For model solutions with only a limited and well defined number of reactants the experimental results can be explained by the known principles of photochemistry. Due to the more complex mixture of raw water photooxidative treatment in water plants has to face a broad variety of parallel reactions. Further investigations on the mechanisms involved and on the influence of aquatic background substances will improve the understanding of the UV/H₂O₂ combination and will add prognostic power to the interpretation of the results. The addition of the chemical oxidants has to be optimized with the aim of high reaction efficiency and with respect to maximum allowed concentrations in drinking water treatment. Problems have to be expected from poorly designed reactors. This calls for critical selection of the materials used. The variety of natural water contaminants and pollutants also includes inorganic species. This means there is potential for a broad spectrum of competing reactions, which was clearly demonstrated by the example of the iron.

Acknowledgements

Financial support was provided by DVGW-Forschungsmittel, Deutscher Verein des Gas- und Wasserfachs e.V., Eschborn. The authors thank G. Bürkle and T. Stöhr for running most of the experiments and E. Miller for help in HPLC troubleshooting.

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