

**Effect of Oxygen Partial Pressure and Catalysts on the Rate of UV irradiated
Oxidation of EDTA**

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Abstract

Oxidative degradation of Ethylenediaminetetraacetic acid (EDTA) under UV irradiation can be carried out with oxygen absorbed from ambient air. This degradation process is a dual phase multi step process. In the first phase rapid cleavage of the substance is observed. At ambient temperature the intermediates slowly oxidize by forming carbon dioxide and water in a second phase, which is rate controlling.

Oxidation of intermediates with oxygen dissolved from ambient air is controlled by the oxygen concentration, the formation of oxidizers through irradiation and the rate of oxidation.

Investigation of catalytic acceleration of oxidation with heavy metal ions showed a negative impact on oxidation due to interaction of catalysts and oxidizers [Kracker-Semler, 2004]. Instead of promoting the oxidation of intermediates the catalysts consumed oxidizer themselves.

In a next step the role of oxygen concentration on the rate of oxidation was investigated. Partial pressure of oxygen was varied to produce an oxygen concentration in the feed solution of as much as 30 mg/l prior to irradiation.

To overcome this limitation several oxidation resistant catalysts have been investigated in the ongoing project.

1 Introduction

Ethylenediaminetetraacetic acid (EDTA) as well as other aminopolycarboxylic acids are strong chelating agents, applied to enforce the solubility of metal cations by forming strong metal complexes. EDTA is widely used in industrial and private applications for preventing formation of scales and for increasing the solubility of heavy metal cations (conductor board industry). Through the intensive use of EDTA, it is the organic chemical with probably the highest concentration found in European rivers and lakes [Sørensen *et al.*, 1998]. Due to its complexation properties, EDTA has a negative effect on the separation of several heavy metal ions from aqueous effluents. Depending on the chemical nature of the metal cation and the applied precipitation or separation route, precipitation can be suppressed [Vohra and Davis, 1999].

Above that there is a long standing concern that chelators such as EDTA may not only carry toxic metal species such as lead into the environment, but that they may also mobilize toxic heavy metals from sediments [Frimmel *et al.*, 2000]. Therefore problem specific water treatment processes – advanced oxidation processes – for the degradation of EDTA were suggested [Tucker *et al.*, 1999; Sørensen *et al.*, 1998].

Anodic oxidation of EDTA and several influence parameters on the degradation were proved by several authors [Johnson *et al.*, 1972; Hartinger, 1991]. A Combination of anodic oxidation with UV irradiation was also topic of a research activity [Letonja *et al.*, 2003].

Several authors published the degradation of EDTA by adding strong oxidizers such as H_2O_2 , O_3 or photocatalysts (TiO_2) to the effluent combined with UV-irradiation [Gilbert and Hoffmann-Glewe, 1995; Sørensen *et al.*, 1998; Babay *et al.*, 2001]. A first industrial realisation of a photochemical copper loaded EDTA degradation was published by Sørensen *et al.*, (2002). The reaction of oxidizers with organic compounds such as EDTA produces various organic intermediates, which may be eventually mineralized to CO_2 , water, NO_3^- and NH_4^+ , depending on the substance degraded [Vohra and Davis, 1999]. Destruction of the metal complex is the major benefit of photochemical oxidation with H_2O_2 under UV-irradiation.

The chelating agent is finally oxidized to CO_2 or organic substances with low molecular weight. These organic substances are biodegradable and the remaining toxic heavy metal ions can be precipitated. The disadvantage of EDTA degradation with H_2O_2 and UV irradiation is the high amount of H_2O_2 required [Tucker *et al.*, 1999].

Therefore an EDTA degradation method without addition of auxiliary oxidizers except oxygen was investigated. Oxidation parameters such as pH-value and oxidation catalysts without addition of chemical oxidizers to the EDTA solution were investigated [Kracker-Semler, 2004]. During UV irradiation strong oxidizers such as ozone, hydrogen peroxide and OH-radicals are generated from dissolved oxygen, which was absorbed from ambient air in a bubble column.

Target of this project was to investigate the oxygen partial pressure on the rate of degradation of the EDTA. A Hg medium pressure lamp was used for generating oxidizers from oxygen absorbed from ambient air. Acceleration of EDTA degradation with photocatalysis was considered.

2 Experimental Setup and Analysis

For the experiments a Hg medium pressure lamp TQ 150 (150 W) applicable to the UV reactor system II from Heraeus Noblelight was used.

2.1 Experimental Setup

The UV reactor system shown in Figure 2-1 consists of a reactor with five flanges and a socket for insertion of the cooling tube and the UV irradiation lamp. The double wall cooling tube is made of quartz glass which can be penetrated by irradiation wavelengths above 190 nm. The reaction vessel is made of Borosilicate glass and can not be penetrated by irradiation below 350 nm. For cooling the UV lamp and for keeping the reaction temperature constant, the cooling circuit was operated with distilled water. On the flanges of the reactor different measurement devices, a pH meter with an integrated temperature meter (WTW, type 197-S with SenTix41 electrode) and an oxygen meter (WTW, type Oxi 630) were installed. At the bottom a diffuser stone was assembled to aerate the effluent for keeping the oxygen concentration at a constant level. The effluent was mixed with a magnetic stirrer. Depending on the scheduled experiment, ambient air and nitrogen (quality 5.0) were mixed in a T-type mixer to provide less oxygen concentration in the EDTA

solution. Prior to absorption in the reactor the oxidation gas was water saturated. Thus no change of the EDTA concentration in the reactor occurred by mass transfer of water from the EDTA solution into the oxidation gas. Gas flow rate was held constant at $0.1 \text{ m}^3_{\text{STP/h}}$.

A PTFE tube with an inner diameter of 6 mm, which inhibited an inflow of ambient air into the EDTA solution, was connected to the second flange on top of the reactor. In particular this PTFE tube was important when performing oxygen free experiments. The investigation of the influence of oxygen partial pressure on the rate of degradation of EDTA was accomplished with the experimental setup and for the investigation of the effect of photo catalysts.

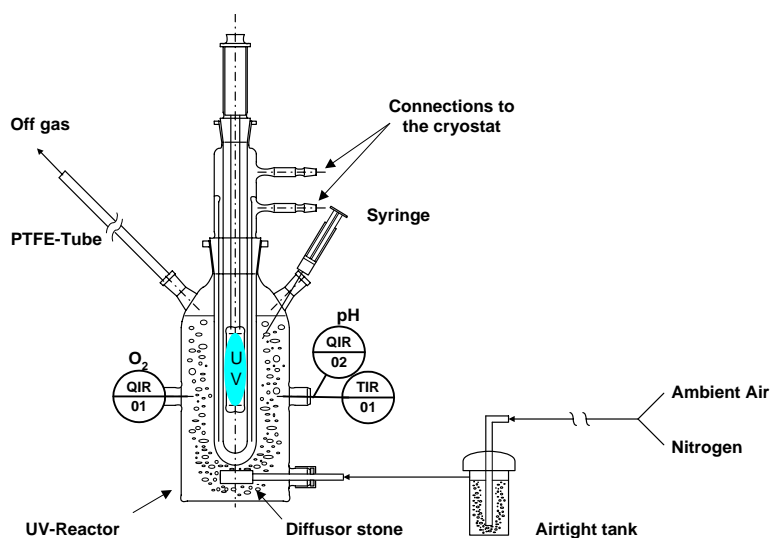


Figure 2-1: Experimental setup - UV reactor

2.2 Analysis

During experiments samples of the EDTA solution for analytical purpose were taken with a syringe at the sealed top of the reactor. The concentration of EDTA was measured with an ion pair chromatographic method [German standard methods for water control, waste water and sludge analysis] employing a Dionex DX500 HPLC system with a Lee Scientific Series 600 UV/Vis detector. A reversed phase analytical column (Agilent C12) served as the stationary phase. The mobile phase was a solution of Tetrabutylammonium-hydrogensulfate and Tetrabutylammoniumhydroxide. Prior to analysis the EDTA samples were chelated with Fe(III)-ions and the absorption was measured at a wavelength of 260 nm.

For COD (Chemical Oxygen Demand) analysis of the samples a quick test based on the German standard method DIN ISO 15705:2003-09 was applied.

3 Results and discussion

3.1 Investigation of the role of oxygen partial pressure

The experiments were carried out at constant temperature of $21 \pm 2^\circ\text{C}$ and a start pH 5.1 ± 0.1 . For investigating the influence of the oxygen partial pressure on EDTA degradation the Hg medium pressure lamp was assembled. For all experiments a 1.34 mM EDTA solution ($\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$, Fluka Chemika 03685) was prepared. The reactor was filled with 800 ml of the solution and then aerated with different nitrogen/ambient air mixtures to reach an oxygen concentration of 1 mg O_2/l , 5 mg O_2/l and 9 mg O_2/l . The results are shown in Figure 3-1.

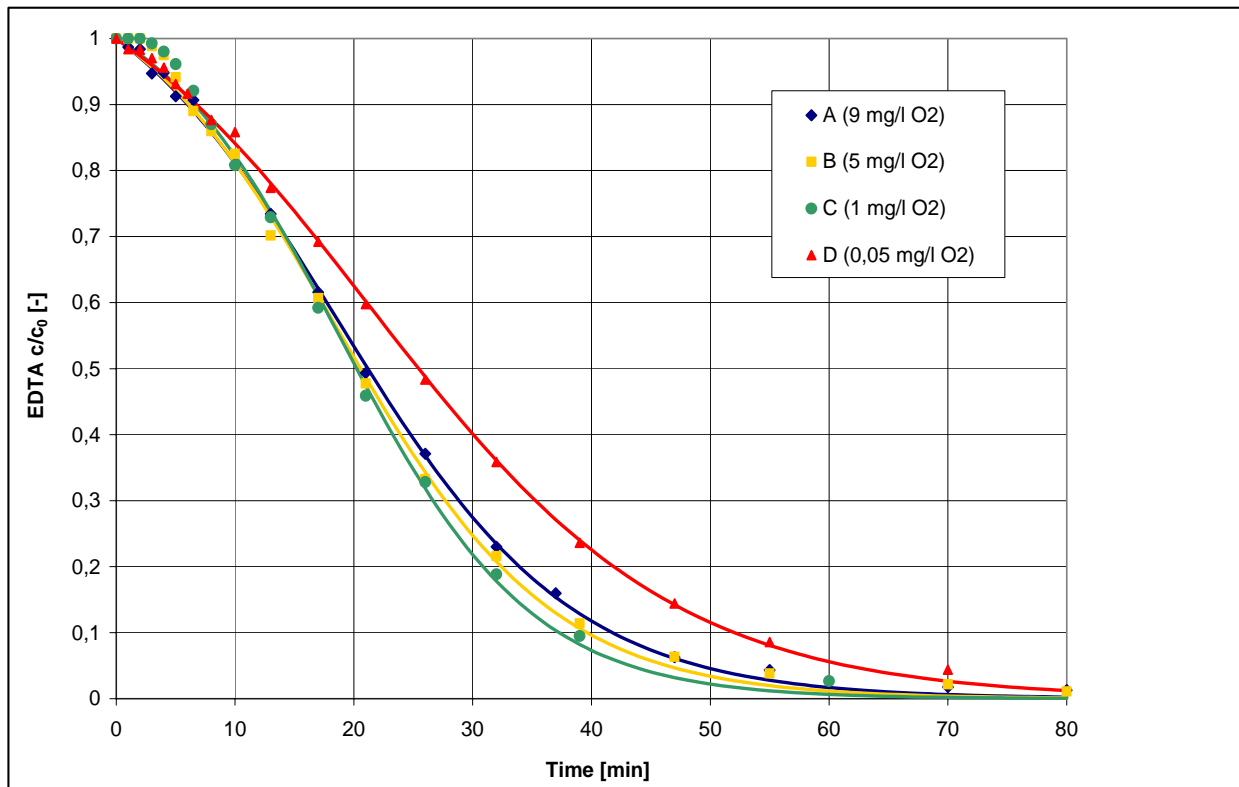


Figure 3-1: Effect of oxygen partial pressure (dissolved oxygen) on the rate of EDTA degradation. Operation parameters: A: oxygen concentration at saturation level by aerating with ambient air; B, C: oxygen concentration at saturation level by aerating with an mixture of ambient air and nitrogen; D: aerated only with nitrogen.

EDTA degradation by UV irradiation showed a dependence on the pH value. During EDTA degradation the pH increased from pH 5 up to pH 7. Between the three experiments (A, B, C) only a small deviation in degradation rate was found. This deviation was caused by a slight deviation of the start pH value.

In experiment D the dissolved oxygen concentration was reduced to 0.05 mg O_2/l by aerating the solution for 10 h with pure nitrogen (quality 5.0) at a temperature of 60°C . EDTA degradation under oxygen free conditions was dropped by 20 %.

Experiment E was carried out in a sealed UV reactor without aeration. The EDTA solution was stirred with a magnetic stirrer. The PTFE tube was exchanged with a sealed screw plug. For the generation of oxidizers a total amount of dissolved oxygen of 7 mg was available in the EDTA solution.

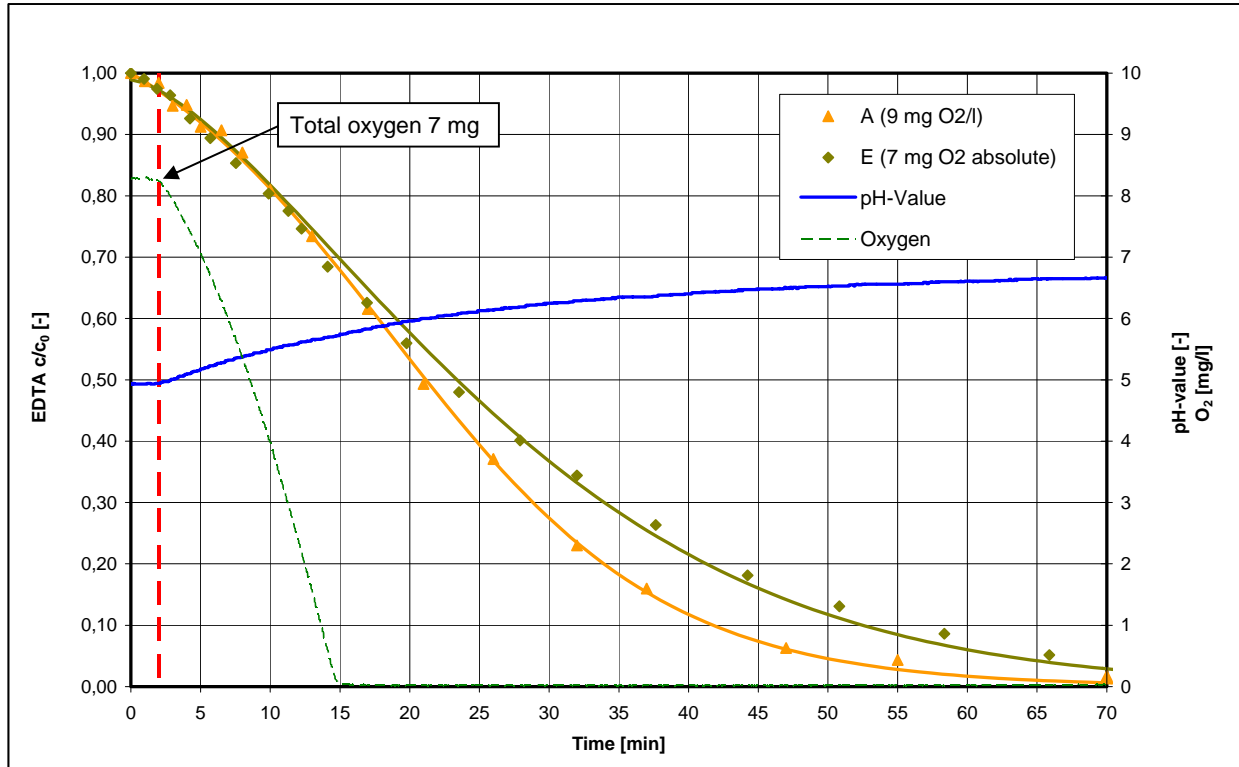


Figure 3-2: Determination of the decrease of the oxygen and EDTA

As shown in Figure 3-2 no change of the pH and oxygen concentration was detected within the first minutes because of the retarded start up of the UV lamp. Then an oxygen concentration dropped within 15 min. from 8.3 mg O_2/l to 0.03 mg O_2/l . Compared with the results of experiment A, which was carried out under complete oxygen saturation within the whole experiment, no significant difference between the two degradation experiments was obtained. The rate of oxygen free EDTA degradation retarded after that period.

In principle degradation of EDTA under UV irradiation is possible without dissolved oxygen, but oxygen increases the rate of degradation. The chemical oxygen demand (COD) does not change. Degradation of EDTA under UV irradiation is therefore limited to cleavage the molecule. Photochemical oxidation of EDTA is limited by the generation of oxidizers from absorbed oxygen.

3.2 Influence of photocatalysts

For photocatalytic acceleration of the EDTA 1 g/l of zinc sulphide (ZnS, Riedl de Haën) respectively powdered TiO₂ (P25, Degussa) was added to the reaction solution. Titanium dioxide was needed for reference purposes.

As shown in Figure 3-3 TiO₂ raised degradation of EDTA in comparison with oxygen saturated feed solution (A). ZnS retarded degradation by about 50-60 %. During the experiment the initial pH-value decreased and hydrogen sulphide was detected qualitatively (odour). The photocatalyst was destroyed by conversion into Zn²⁺-ions and H₂S. As a consequence the rate of EDTA degradation was reduced.

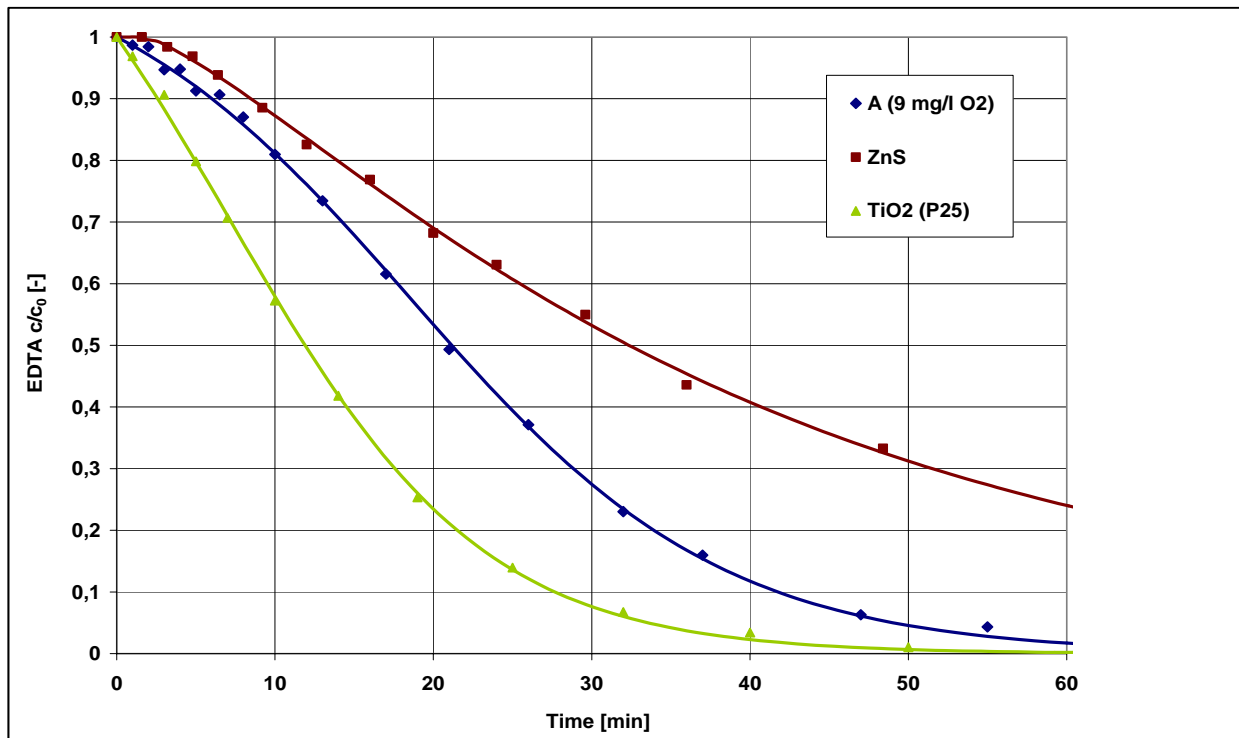


Figure 3-3: Comparison of the effect of photocatalysts on the degradation of EDTA

4 Summary

Target of the project was to investigate the influence of dissolved oxygen and catalysts on the rate of EDTA degradation under UV irradiation.

Degradation of EDTA under UV irradiation with oxygen is controlled by the formation of oxidizers. Even at low oxygen concentration of 1 mg/l the rate of degradation does not differ from experiments with complete oxygen saturation. The generation of oxidizers is not limited by mass transfer of the oxygen from the gas to the liquid phase. Retarded degradation was only observed for oxygen free operation.

The photocatalyst ZnS did not contribute to acceleration of EDTA destruction but was subject of chemical conversion itself.

References

- Babay P.A., Emilio C.A., Ferreyra R.E., Gautier E.A., Gettar R.T., Litter M.I.: Kinetics and mechanisms of EDTA photocatalytic degradation with TiO₂, *Water Science and Technology* Vol. 44 No 5, 179-185, (2001)
- Frimmel F. H., Gräbe G., Schmitt D., ATV-DVWK-Schriftenreihe 22, Tagungsband Wasser Berlin, Teil1, (2000).
- German standard methods for the examination of water, waste water and sludge, Single components (group P) – part 8: Determination of nitrilotriacetic acid (NTA), ethylenedinitrilotetraacetic acid (EDTA) and diethylenetrinitrilopentaacetic acid (DTPA) by liquid chromatography) Band VII, Wiley-VCH, Weinheim, (2003)
- Gilbert, E., Hoffmann-Glewe, S.: Ozonierung von Nitrilotriessigsäure in Gegenwart anorganischer und organischer Wasserinhaltsstoffe, *Vom Wasser*, Band 62, 11-23, (1984)
- Hartinger, L.; *Handbuch der Abwasser- und Recyclingtechnik für die metallverarbeitende Industrie*, Carl Hanser Verlag, München, (1991)
- Johnson, J. W., Jiang, H. W., Hanna, S. B., James, W. J: Anodic Oxidation of Ethylenediaminetetraacetic Acid on Pt in Acid Sulfate Solutions, *Electrochemical Science and Technology* 119 (12), 574-580, (1972)
- Kracker-Semler, G.: Katalytische und photokatalytische Beschleunigung der Reaktivabsorption von Sauerstoff - Experimentelle Untersuchung und Modellierung, Dissertation, TU-Graz, (2004)
- Letonja P., Marr R., Siebenhofer M.: Anodic oxidation of Ethylendiaminetetraacetic acid (EDTA), Poster session Gatlingburg (2003)
- Sörensen, M., Zurell, S., Frimmel, F. H.: Degradation Pathway of the Photochemical Oxidation of Ethylenediaminetetraacetic Acid in the UV/H₂O₂-process, *Acta hydrochim. Hydrobiol.* 26, 109-115, (1998)
- Sörensen, M., Weckenmann, J., Hofmann, R., Pagel, J., Weber, A., Harder, F.: Zerstörung von komplexem Cu-EDTA – Konzept, Technologie und Praxisbericht der Referenzkunden Multek und Shipley, *Galvanotechnik* 8, 2127-2133, (2002)
- Tucker, M. D., Barton, L. L., Thomson, B. M., Wagener, B. M., Aragon, A.: Treatment of waste containing EDTA by chemical oxidation, *Waste Management* 19, 477-482, (1999)
- Vohra, M. S., Davis, A. P.: TiO₂-Assisted Photocatalysis of Lead-EDTA, *Wat. Res.* 3, 952-964, (1999)