Electrochemical and photochemical Oxidation of Ethylendiaminetetraacetic acid (EDTA)

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Abstract

Advanced oxidation processes will increasingly contribute to wastewater treatment in the near future. Advanced oxidation processes focus on persistent, poorly biodegradable substances and substances with mutagenic or carcinogenic properties.

Ethylendiamintetraacetic acid (EDTA) is widely used in both industrial as well as consumer application. It has well known complexing properties and it is poorly biodegradable. On this account EDTA was chosen as a representative persistent organic pollutant for investigation of degradation and mineralization by chemical, electrochemical and photochemical techniques. On the other hand the chemical composition and properties of the substance EDTA itself have been major reason for its choice.

Chemical oxidation treatment with H_2O_2 was investigated for comparison purposes with photochemical and electrochemical treatment.

The effect of pH, heavy metal ion load and photocatalysts on degradation under UV-irradiation and air saturation of the effluent has been reported elsewhere [Gangl *et al.*, 2004]. Extinction is pH-dependent. The impact and interaction of heavy metal ions depends on the element properties. As a consequence heavy metal ions may undergo oxidation or precipitation or may retard or accelerate degradation under air saturated oxygen load and varying pH. Photocatalysts may contribute to degradation (e.g. anatas) but also undergo chemical reaction (e.g. zinc sulphide).

Rate and mechanism of electrochemical degradation differs from photochemical treatment [Letonja, 2004; Kracker-Semler, 2003]. In this research project the effect of the electrolyte composition (e.g. waste water) and the operation conditions on rate and mechanism of degradation and mineralization has been investigated. Subject of present investigation has been the optimization of treatment and the correlation of degradation, mineralization and specific energy consumption. Photochemical treatment has been carried out with a Hg low pressure and a Hg medium pressure UV-lamp.

Electrochemical treatment results in similar observation but differs in detail. Beside pH and heavy metal ion load the properties of the anode and the current density strongly affect the process.

Experimental investigation of electrochemical treatment was carried out in a membrane cell with the basic electrolyte sodium sulphate and a DSA (IrO_2-doped titanium grid). While cleavage and mineralization are favoured at low current density oxygen evolution controls the mid current density ranges without significant improvement of both degradation and mineralization. Finally at elevated current density both processes will improve. For application reasons the specific energy consumption and as a consequence the current density are important design boundaries.

1 Introduction

Research in wastewater treatment has a focus on investigation of Advanced Oxidation Processes (AOP) and Advanced Electrochemical Oxidation Processes (AEOP). With AOP's or AEOP's persistent organic substances can be degraded and/or mineralized. The OH radical is therefore a preferred oxidizer. OH-radicals can be generated by irradiation of photocatalysts (e.g. TiO_2), photolysis of H_2O_2 or O_3 and by the Fenton process (Fe^{2+}/H_2O_2) [Andreozzi *et al*. 1999].

Faust and Hoigné (1990) reported the generation of OH radicals from Fe(III)-hydroxycomplex $Fe(OH)^{2+}$. In latter process Fe^{3+} is reduced to Fe^{2+} which is inactive in OH-radical production.

Ethylendiaminetetraacetic 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 consumer applications for preventing formation of scales and for increasing the solubility of heavy metal cations. It was chosen as a model substance, because of its properties and certainly due its persistent character.

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 respectively artificial solar radiation [Gilbert and Hoffmann-Glewe, 1995; Sörensen *et al.*, 1998; Babay *et al.*, 2001]. 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].

The photochemical degradation mechanism of Fe^{3+} chelated EDTA was investigated by Lockhart and Blakeley (1975). They found two main degradation pathways of Fe(III)EDTA which are pH dependent. Cleavage of the acetic acid group is favoured at pH 4.5 whereas at pH 7–8 EDTA is degraded by cleavage of the ethylene group.

The effect of pH, heavy metal ion load and photocatalysts (TiO_2) on degradation of EDTA (Na_2EDTA) under UV-irradiation and air saturation of the effluent has been reported [Babay *et al.*, 2001; Gangl *et al.*, 2005].

Subject of present investigation has been the optimization of photochemical and/or electrochemical treatment and the correlation of degradation, mineralization (TOC depletion) and specific energy consumption. In electrochemical oxidation pH and heavy metal ion load (e.g. Fe-ions), the properties of the anode and the current density strongly affect the process.

2 Experimental Setup and Analysis

Investigation was accomplished in an aerated UV reactor system (800 ml) equipped with a Hg low pressure lamp TNN 15/32 (15 W). All experiments were carried out with 1.34 mM/l EDTA solution at pH 3 ± 0.3 and 298 ± 2 K.

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. For complete data record several measurement devices, such as 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.

For UV/O_2 and UV/O_2/Fe-ions experiments a sparger was assembled at the bottom of the reactor for aeration to provide sufficient oxygen for mineralization of the constituent. Electrochemical experiments were carried out without sparger due to anodic oxygen evolution.

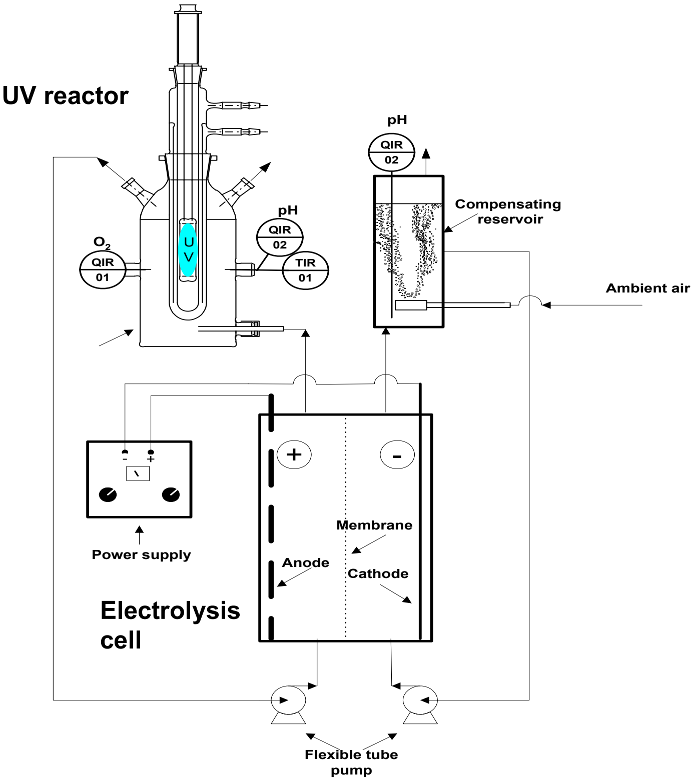

Figure 2-1: Experimental setup - UV reactor combined with an electrolysis cell

The effluent was mixed with a magnetic stirrer. Gas flow rate was held constant at 0.1 ± 0.01 m^3_{STP}/h.

The electrolysis cell was equipped with a DSA Ti/IrO_2 grid with an area of 30 cm² and a stainless steel cathode with an area of 80 cm². Electrochemical experiments were carried out at constant current of 0.5 A.

Experimental investigation of electrochemical treatment was carried out in a divided cell with the conductance electrolyte sodium sulphate. To guarantee complete separation of the anolyte- and catholyte - circulation, the electrolyte loops were separated with a DuPont type Nafion 450 cation exchange membrane. The electrolysis cell was connected with the UV reactor system with silicon tubes. Electrolyte recirculation was provided by an inline flexible-tube pump. The electrolysis cell was equipped with a lab scale DC power supply.

2.2 Analysis

For analytical purposes samples of the EDTA solution were taken with a syringe at the 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 Tetrabutylammoniumhydrogensulfate and Tetrabutylammoniumhydroxide. Prior to analysis the EDTA samples were chelated with Fe(III)-ions and UV-absorption of the Fe(III)EDTA complex was measured at a wavelength of 260 nm. TOC analysis (Total Organic Carbon) was performed with a Shimadzu TOC-5000 analyzer.

3 Results and discussion

Concentration of the EDTA solution ($Na_2EDTA \cdot 2H_2O$, Fluka Chemika 03685, purum ≥ 97 %) was 1.34 mM and the volume of the reaction mixture was 800 ml. The experiments were carried out at constant temperature of 25 ± 2°C and constant pH 3.0 ± 0.3. To adjust the pH H_2SO_4 and NaOH was added to the synthetic effluent. Iron was added as $FeSO_4 \cdot 7H_2O$ (Merck KGaA 103965). In the presence of dissolved oxygen Fe(II)EDTA is immediately oxidized to Fe(III)EDTA .

Sodium sulphate (Merck KGaA 106649) was needed for providing sufficient conductivity in electrochemical experiments.

3.1 Photolysis of Fe(III)EDTA – 150W medium pressure lamp

Figure 3.1 shows a representative comparison of degradation and mineralization under UV-irradiation of air saturated synthetic effluent (UV/O_2 and UV/O_2/Fe-ions).

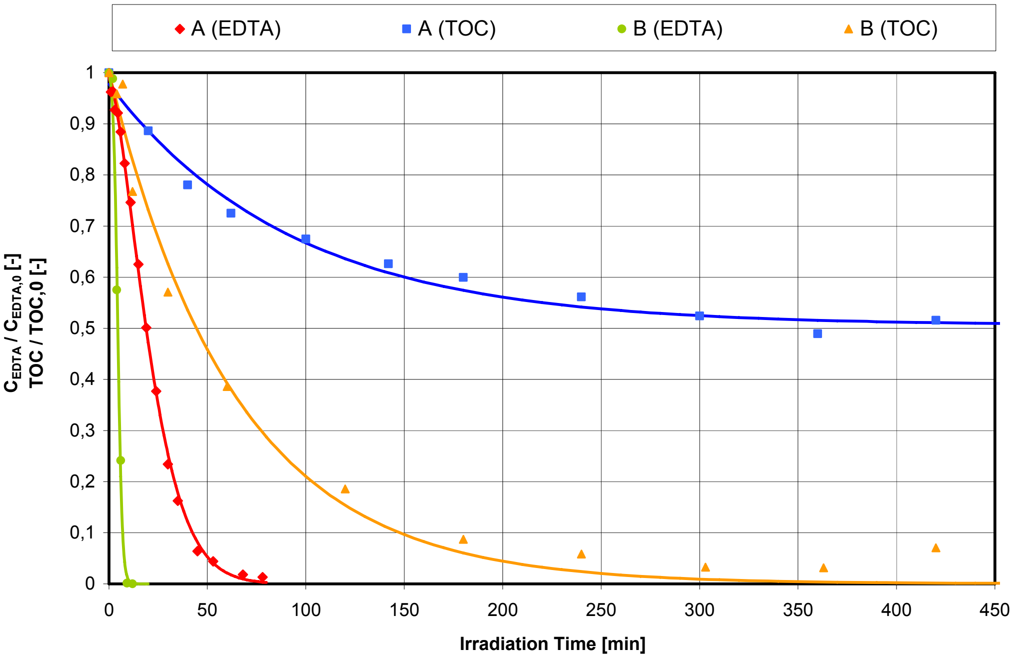

Figure 3.1: EDTA and TOC depletion for A (EDTA): EDTA depletion under UV irradiation, A (TOC): TOC depletion under UV irradiation, B (EDTA): EDTA depletion of Fe^{2+}-doped electrolyte under UV irradiation, B (TOC): TOC depletion of Fe^{2+}-doped electrolyte under UV irradiation (Fe^{2+} : EDTA = 1:1)

Under UV-irradiation degradation of EDTA undergoes fast 1st order reaction and mineralization will stop after several minutes (A-type experiments). Maximum TOC depletion by the UV/O_2-process is 50 %. Comparison indicates that mineralization is concurrent to degradation by cleavage. Heavy metal ion load – Fe^{+2} or Fe^{+3} – accelerates rate and extent of mineralization (B-type experiments). After 150 min irradiation time, 90 % mineralization is obtained with UV/O_2/Fe-ions. The reaction rate constant for 1st order EDTA degradation kinetic with and without Fe-ions give $k_{Fe(III)EDTA} = 0.08\ min^{-1}$ and $k_{EDTA} = 0.009\ min^{-1}$. The reaction rate for EDTA degradation nearly increased by an order of magnitude.

For detailed investigation of different EDTA to Fe-ions ratio the UV reactor was equipped with a Hg low pressure lamp (15 W).

3.2 Photolysis of Fe(III)EDTA – 15 W low pressure lamp

The effect of different molar ratio of Iron(II) to EDTA on rate and extent of reaction was determined at pH 3 ± 0.3. The dotted line in Figure 3.2 shows the EDTA degradation (UV/O_2) in comparison with UV/O_2/Fe-ions. Iron(III) to EDTA ratio was varied between 2:1 – 1:25.

Degradation of Fe(III)EDTA follows zero order reaction kinetic. Catalytic amounts of Fe-ions (Fe^{+2} : EDTA = 1:25 is equivalent to 0.05 mM Fe^{+2}) increase the reaction rate by a factor 30. Further acceleration was observed with higher amounts of Fe^{+2}. At a ratio 1:2 acceleration gives the best results ($k_{EDTA,\ C\ (1:2)} = 0.06\ min^{-1}$). Above a ratio of 1:2 Fe(III)EDTA degradation is affected negatively, presumably by an increasing amount of Fe^{+3} which becomes subject of hydroxide precipitation.

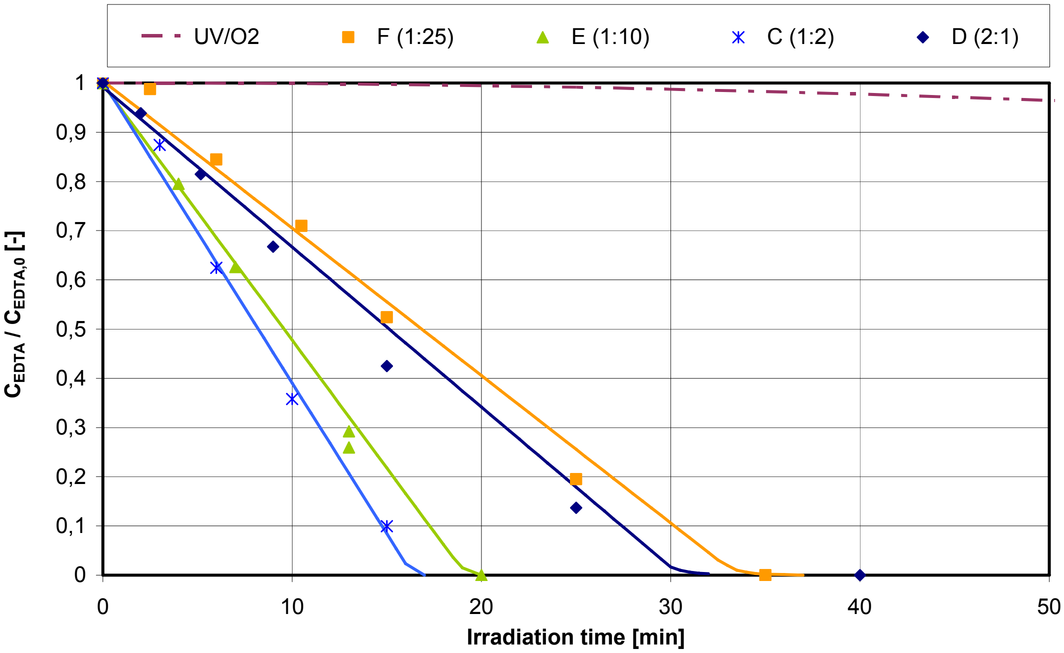

Figure 3.2: Variation of the Fe^{+2} : EDTA ratio; degradation of Fe(III)EDTA follows zero order reaction. A molar ratio of 1:25 accelerates the photolytic degradation tremendously. Reaction rate constant increases from $k_{EDTA,UV} = 0.003\ min^{-1}$ up to $k_{UV,Fe\_1:25} = 0.03\ min^{-1}$.

Beside EDTA degradation TOC depletion is a function of the molar ratio of Fe^{+2} : EDTA. Because of the large molar decadic extinction coefficient of Fe(III)EDTA ($\varepsilon_{254nm} = 8200 \pm 200$) UV irradiation is completely absorbed.

TOC depletion of Fe(III)EDTA is a dual phase process (Figure 3.3). The 1st phase – cleavage of acetic acid groups by forming CO_2 and formaldehyde – follows a 0-order reaction kinetics. Identical reaction rates were determined for ratio of Fe^{+2} : EDTA above 1:10 because of complete absorbance. At low ratios (F) 85 % of the incoming irradiation is absorbed, thus the decrease of TOC is retarded.

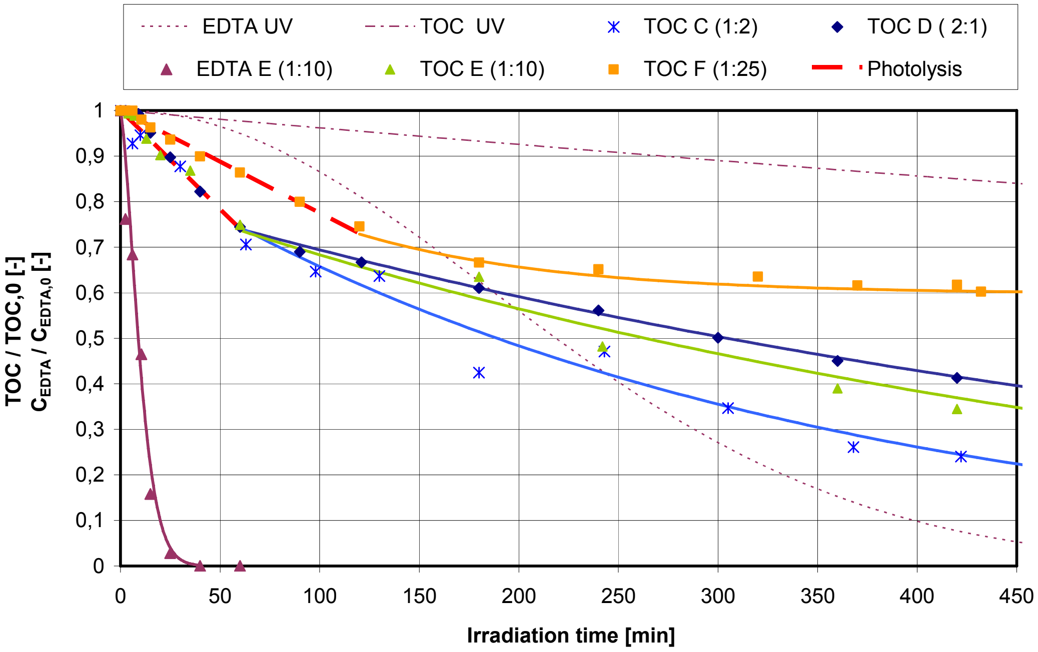

Figure 3.3: Variation of the molar ratio of Fe^{+2} : EDTA . "UV" indicates EDTA degradation and TOC depletion by UV/O_2-process. TOC depletion is a dual phase process. 1st phase follows 0-Order kinetics and represents the photolysis of Fe(III)EDTA. Mineralization in the 2nd phase is characterized by OH radical attack. OH radicals are generated from dissolved iron ions – $Fe(OH)^{+2}$ and the aqueous carrier.

As shown in Figure 3.3 TOC depletion in the 2nd phase of the process follows the same trend as EDTA degradation in the 1st phase (Figure 3.2). With increasing molar ratio of Fe^{+2} : EDTA mineralization is favoured and passes a maximum at a ratio of 1:2 (C, E, F). At higher molar ratio of Fe^{+2} : EDTA TOC depletion is retarded (D). This 2nd phase is characterized by OH radical attack. OH radicals are generated by irradiation and photolysis of $Fe(OH)^{+2}$ (favoured iron hydroxycomplex at pH 3). Too small amount of iron ions (F) results in a stagnation of TOC depletion. For comparison Figure 3.3 shows EDTA degradation and TOC depletion for the UV/O_2 process with the 15 W Hg low pressure lamp.

3.3 Electrochemical and photochemical treatment: Comparision

For comparison of the degradation efficiency of different AOP's and AEOP's, anodic oxidation (direct oxidation) and in combination with UV irradiation was investigated. For process cost evaluation of Advanced Oxidation Processes the specific energy consumption per unit persistent substance is needed.

In Figure 3.4 the results of EDTA degradation for the above AOP's respectively AEOP's are illustrated. Anodic Oxidation (1) and degradation by UV irradiation (2) at constant pH of 3 have similar reaction rate constants based on 1st order kinetics ($k_{EDTA,\,1} = 0.0038\ min^{-1}$, $k_{EDTA,\,2} = 0.0031$). Combination of both processes (3) accelerates degradation of EDTA ($k_{EDTA,\,3} = 0,0060\ min^{-1}$). The expected increase – superpose of both degradation curves – was not reached at all.

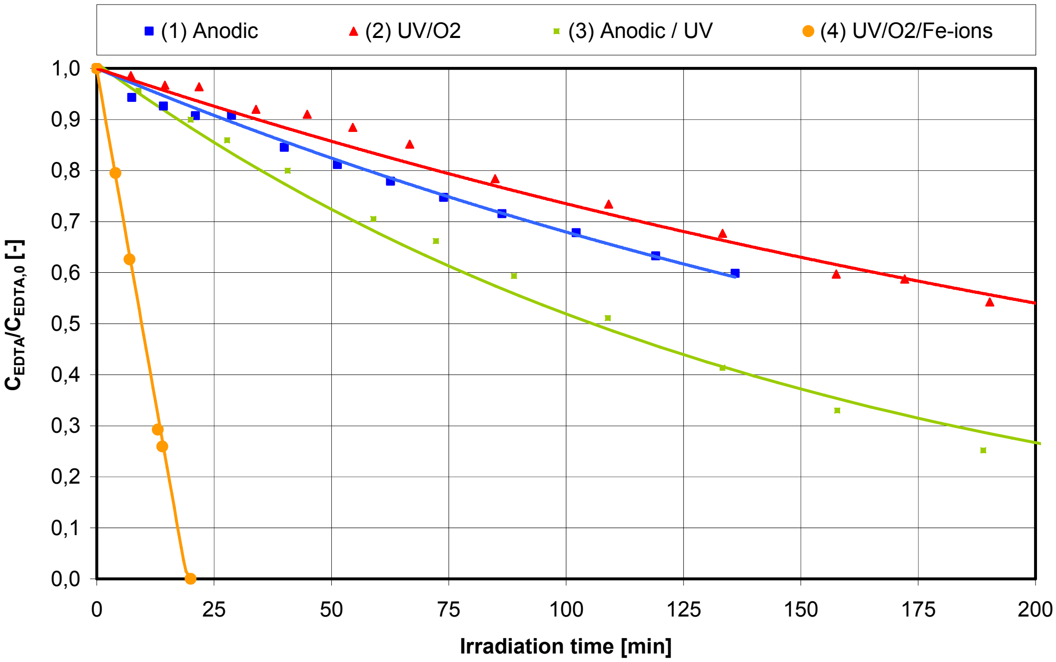

Figure 3.4: Comparison of different electrochemical advanced oxidation processes for EDTA degradation: Anodic Oxidation (1), UV-irradiation only (2), combination of anodic oxidation and UV irradiation (3), UV/O_2/Fe-ions (4)

For comparison purposes of TOC depletion the H_2O_2/UV process for mineralization of EDTA was investigated. The start concentration of hydrogen peroxide was 27 mM (EDTA : H_2O_2 = 1 : 20) according to the used ratio of Sörensen et al. (1998). 1 ml of a 30 % H_2O_2 solution was additionally added in 30 minute periods.

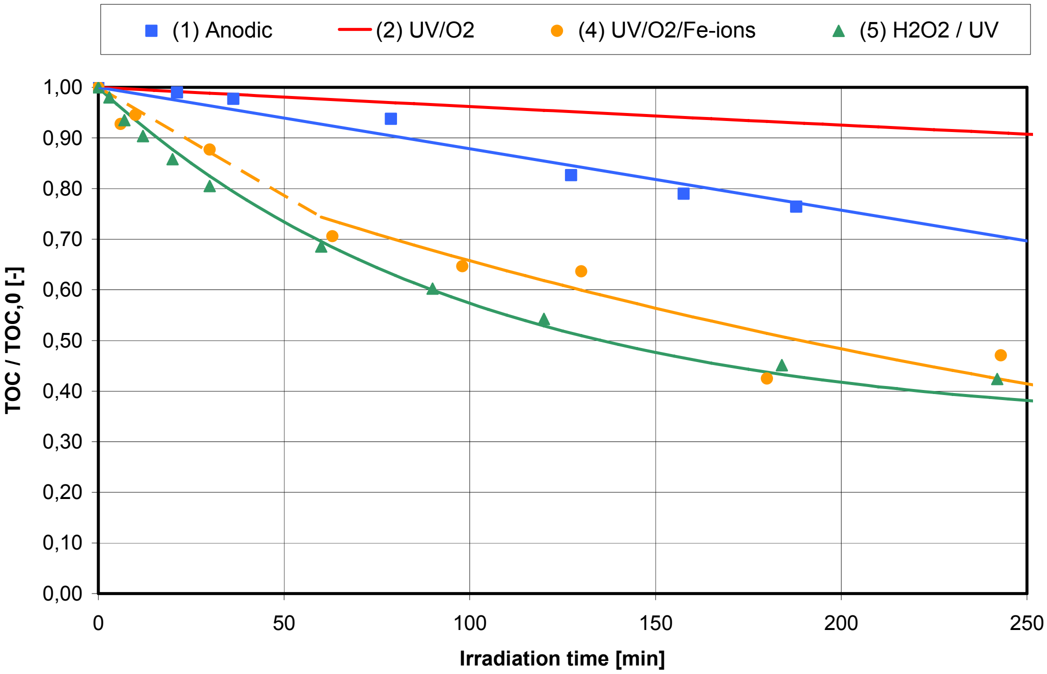

Figure 3.5: Comparison of different electrochemical advanced oxidation processes for EDTA mineralization (TOC depletion): Anodic Oxidation (1), UV-irradiation only (2), UV/O_2/Fe-ions (4), conventional H_2O_2/UV process

The UV/O_2/Fe-ions process (4) compared with the standard H_2O_2 process (5) needs much lower amounts of chemicals (0.19 g $FeSO4 \cdot 7H_2O$ respectively > 3.4 g H_2O_2 solution, 30%), but leads to the same mineralization results (60 % TOC reduction) after 250 minutes of operation.

3.4 Specific energy consumption

For the evaluation of the cost of operation of Advanced Oxidation Process the energy consumption per unit persistent substance (kWh/g or kWh/mol) is of importance. Figure 3.6 shows the specific gross power consumption in kWh/g EDTA for five different advanced oxidation processes. Full degradation of 1 g EDTA by the UV/O_2/Fe-ion process needs 0.02 kWh.

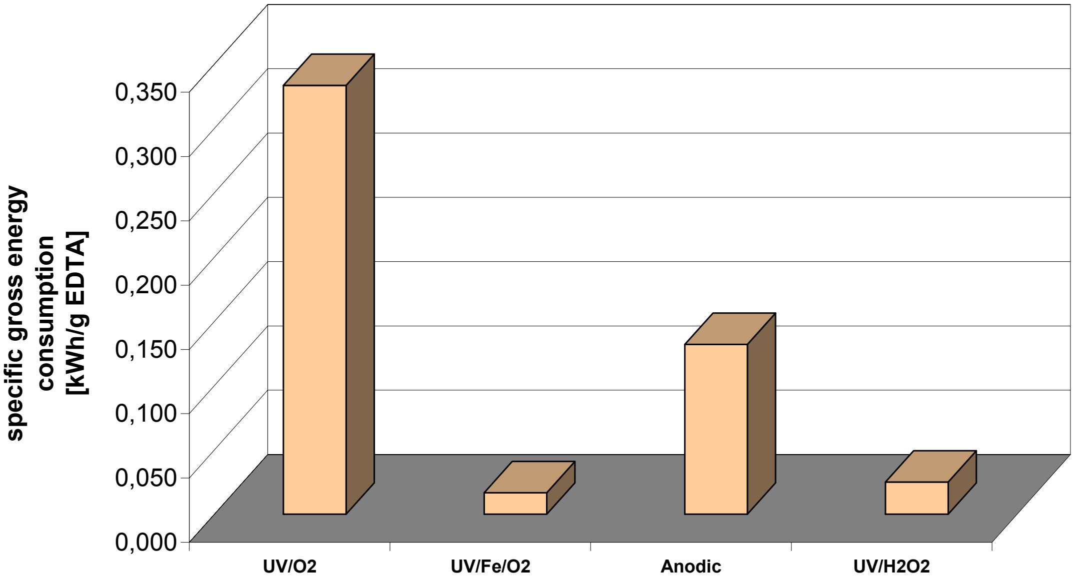

Figure 3.6: Specific gross energy consumption for four different AOP/AEOP. Best results for EDTA degradation were obtained with UV/O_2/Fe-ions process.

4 Summary

In this research project the influence of Fe-ions (Fe^{+2} respectively Fe^{+3}) on EDTA degradation and mineralization (TOC depletion) by UV irradiation and dissolved oxygen (UV/O_2/Fe-ions) was investigated. EDTA degradation follows a reaction kinetic 0-order. TOC depletion is a dual phase process. First phase is the photolysis of Fe(III)EDTA by cleavage off the acetic acid groups. After the destruction of the complexation properties of EDTA, Fe-ions are dissolved in the effluent. The TOC depletion in the second phase is limited by OH radical generation from $Fe(OH)^{+2}$ (favoured iron-hydroxycomplex at pH 3) and reaction with the organic matter. Catalytic amounts of Fe-ions leads to a tremendously accelerated EDTA degradation and TOC depletion compared with UV irradiation only (UV/O_2).

Further the EDTA reaction rate constant and the TOC reduction for four different AOP/AEOP-processes were determined (anodic oxidation with DSA Ti/IrO_2 grid as anode and in combination with UV irradiation (Anodic/UV). The UV/O_2/Fe-ions process results in highest EDTA degradation rate. TOC depletion yield after 250 minutes 60 % TOC reduction which is equivalent to the TOC reduction with a common H_2O_2/UV process. EDTA degradation and TOC depletion with UV/O_2/Fe-ions represents the most economic process in view of the specific gross energy consumption.

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