Degradation of EDTA and novel complexing agents in pulp and paper mill process and waste waters by Fenton's reagent

Kari Pirkanniemi [*], Sirpa Metsärinne, Mika Sillanpää

*University of Kuopio, Department of Environmental Sciences, Laboratory of Applied Environmental Chemistry,
P.O. Box 181, FI-50101 Mikkeli, Finland*

Abstract

Fenton's process was used in oxidative degradation of ethylediaminetetraacetic acid (EDTA) and novel complexing agents, namely BCA5 and BCA6, in distilled water and spiked samples of integrated pulp and paper mill waste water and ECF-pulp bleaching effluent. In waste water, over 90% of EDTA was degraded within 3 min when temperature was 60 °C, pH 4, and molecular ratio of $H_2O_2:Fe^{2+}:EDTA$ was 70:2:1 (0.26 mM EDTA) or higher. In spiked ECF bleaching effluent up to 42% of EDTA was degraded in similar reaction conditions, still higher than published results indicate biological waste water treatment of pulp and paper mill waste water being capable of. In pH 3, EDTA proved readily degradable by Fenton's process in otherwise similar conditions. According to these results, Fenton's process could be used as a pre-treatment method for EDTA-containing bleaching effluents prior to the biological waste water treatment. In addition, BCA5 and BCA6 proved their superiority in terms of degradability also by Fenton's process in both pH 3 and 4.
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Keywords: EDTA; BCA5; BCA6; Fenton's reaction; Bleaching effluent

1. Introduction

1.1. General introduction

Complexing agents, most importantly EDTA and DTPA, are used in wide range of industrial processes, such as metal finishing, photographic industry, textile industry, and pulp and paper industry. It has been estimated that one-half of the total consumption of complexing agents is used in household and industrial detergents. Their role in detergents is to reduce the concentrations of free metal ions, and hence to improve the efficiency of the product. In Scandinavia, however, the major use of complexing agents is in pulp and paper industry due to the remarkable role of this industry in the area and also due to the modern process technology in Scandinavian countries—namely ECF pulping process. For example in Finland, complexing agents' usage has increased by over 40% from 1991 [1], mainly due to the new ECF processes. In the absence of complexing agents, metal ions catalyse degradation of hydrogen peroxide and ozone and reduce the efficiency of the bleaching process. By binding transition metal ions, complexing agents suppress their catalytic activity.

1.2. Complexing agents' degradability

The above-mentioned complexing agents form stable complexes with metal ions that are generally known highly resistant. Their poor adsorptivity to sludge and resistance in biological WWTP operating under normal conditions make them difficult to remove from waste waters [2,3]. According to the European Union risk assessment report of EDTA only up to 30% of EDTA was degraded or removed from waste water with sludge at WWTP in most studies. However, in industrial WWTPs remarkably higher degradation levels were also observed [1]. Some publications indicate that alkaline conditions, instead of neutral or slightly acidic conditions accelerate the biodegradation of EDTA of the typical activated sludge plant [4].

Bleaching effluents are rather toxic to microbes at biological WWTP. This is partly because of relatively high H_2O_2 and other bleaching chemical concentrations, but also because of resin based compounds released during cooking and bleaching. If these waste water streams would be chemically treated before delivering to biological treatment, the overall efficiency of WWTP would presumably increase. At least many failures in operation of WWTP might be avoidable by better control of shock loads if pre-treatment was adopted. Even though the present concentrations of complexing agents at WWTPs are not high enough to harm the biological treatment system, the trend in reducing water consumption and increasing use of H_2O_2 in pulping process may result in an increase in concentrations of complexing agents [5]. It would therefore be desirable to degrade the complexing agents before biological waste water treatment. It would also increase the availability of nutrient nitrogen at the WWTP, which would also be beneficial, since nutrient nitrogen level is typically deficient in pulp and paper mill waste waters [6].

1.3. Complexing agents in receiving waters

In receiving waters, the concentrations of complexing agents may be notable. In German surface waters there were found EDTA concentrations up to 500 µg/l in 1993–1995 [1]. In addition, there are also partial degradation products and other stable complexing agents, such as DTPA. On the other hand, studies with EDTA show that even if complexing agents are highly hydrophilic they may adsorb to the sediment [7]. This finding combined to the well known photolability of Fe(III)EDTA and spontaneous intermolecular cyclisation of ethylenediaminetriacetic acid – a primary degradation product of EDTA – to ketopiperazinediacetatic acid [1], may to some extent explain lower EDTA concentrations in receiving waters than what could be estimated. Not surprisingly, increasing use of complexing agents has evoked concern over the impact of such chemicals in receiving aquatic environments. Concern over the environmental impacts and the prospective legislative limitations have already prompted a number of studies on the fate of EDTA and other complexing agents [4,8–10]. Reference documents on the best available techniques (BREF) published by the European commission pay attention to reducing complexing agent load. For example in the BREF for the pulp and paper industry [6], removal of complexing agents is mentioned as an emerging technology. Because of above-mentioned reasons, alternative complexing agents, such as N-bis[2-(1,2-dicarboxyethoxy)ethyl]glysine (BCA5) and N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6), are being searched. The molecular structures of complexing agents studied are presented in Fig. 1 and selected stability constants in Table 1. In contrary to neutral conditions, in low pH of this study, these ligands exist predominately in their protonated forms (e.g. Fe(III)H$_2$BCA6$^-$) and Fe^{3+} complexes are thermodynamically highly favourable [11,12].

1.4. Chemical degradation methods

Several advanced oxidation processes, AOPs, have shown promise in the decomposition of EDTA [9,10,15,16]. As in all
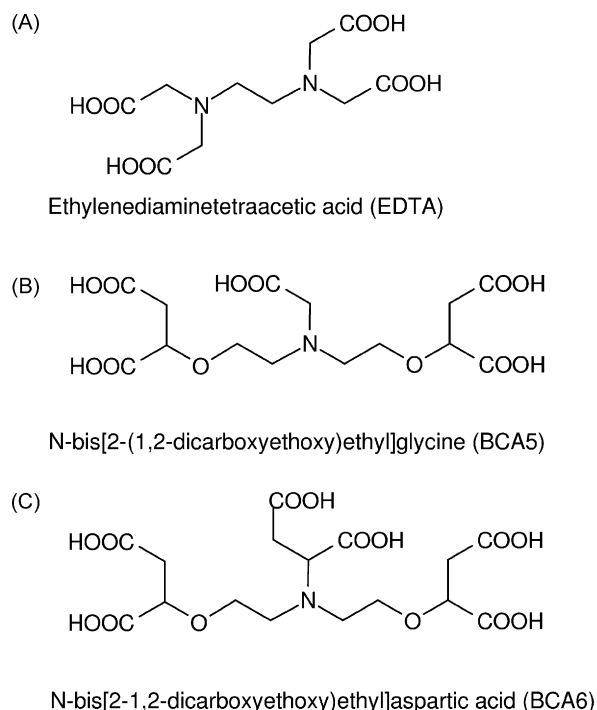

Fig. 1. Complexing agents studied. (A) Ethylediaminetetraacetic acid (EDTA), (B) N-bis[2-(1,2-dicarboxyethoxy)ethyl]glysine (BCA5), and (C) N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6).

chemical EDTA degradation methods, the speciation of EDTA plays an important role. In photochemical oxidation processes for example, the degradation rate of different metal-EDTA complexes varies markedly; CuEDTA, Fe(III)EDTA, ZnEDTA, and PbEDTA are degraded rapidly, while the removal of CoEDTA, NiEDTA, and especially MnEDTA is slow [10,15–17]. In addition, CrEDTA is totally unaffected by photocatalytic treatment [15]. Since the current state of complexing agent degradation is not acceptable [16], more advanced methods and more easily degradable complexing agents are needed.

In Fenton's reaction, which is already in use in industrial waste water purification processes, iron or copper ions catalyze dissociation of hydrogen peroxide to hydroxyl radical and hydroxide ion (Formula (1)) or to hydrogen ion and hydroperoxy radical (Formula (2)) [18].
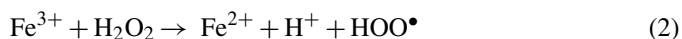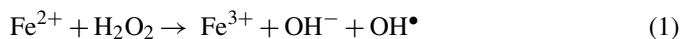
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^\bullet \tag{2}$$

Table 1
Stability constants of selected 1:1 metal-ligand species at 25 °C. Data obtained from [12–14]

Metal	EDTA	BCA5	BCA6
Ca^{2+}	10.6	7.4	7.7
Fe^{2+}	14.3	N/A	(9.8)[a]
Fe^{3+}	25.0	12.6	17.3
Mg^{2+}	8.8	5.9	6.0
Mn^{2+}	13.8	7.5	9.3
Zn^{2+}	16.4	8.1	11.3

[a] Unpublished preliminary result [13].

2. Materials and methods

2.1. Reagents

Hydrogen peroxide (H_2O_2) as 30% aqueous solution and HCl were obtained from Riedel-de Haën. The residual H_2O_2 was degraded by catalase enzyme (catalase from bovine liver), which was purchased from Sigma. Tetrabutyl ammoniumhydroxide was also obtained from Sigma. Na_2EDTA Titriplex®III, $FeCl_3$, and tetrabutylammoniumbromide were obtained from Merck, Germany. BCA5 and BCA6 were obtained from Kemira Oyj, Finland and they were of technical grade. Purities of BCA5 and BCA6 were 82.1 and 89.5%, respectively. Impurities are further explained by Metsärinne et al. [19]. $FeSO_4·7H_2O$ was purchased from VWR International Ltd., England. Methanol (HPLC grade) was delivered by Lab-Scan, Ireland. H_2SO_4 was obtained from Fischer Scientific UK Limited. Complexing agent-free ECF bleach effluent and integrated pulp and paper mill waste water were spiked with complexing agent and used in this research. Screening of suitable Fe concentration for oxidation studies was conducted in distilled water.

2.2. Oxidation procedure

An aquarium equipped with two reservoir heaters (Haake D1, Germany) was used as a water bath. It was placed on magnetic stirrers to enable mixing during the oxidation experiments. Conditions for oxidation experiments in distilled water, temperature 60 °C and pH 3, were selected on the basis of preliminary studies and literature [20,21]. In experiments with spiked waste water and bleaching effluent temperatures 20, 40, and 60 °C and pH 3 and 4 were, however, used after some preliminary experiments. The oxidation studies were conducted in brown 500 ml glass bottles, volume of test solution was 500 ml.

The pH of waste water and bleach was first adjusted to 3 with H_2SO_4. The 0.01 M $FeSO_4·7H_2O$ solution was prepared and diluted with EDTA spiked bleach or waste water so that suitable Fe concentrations were reached. EDTA concentration in bleach and waste water was 0.26 mM. The test solutions were heated up to the reaction temperature during 30 min, after which first samples were taken. Stop watch was started when H_2O_2 was added. pH was measured before sampling during the experiment. For HPLC analysis, a 15 ml sample was taken to a 20 ml vial. The samples were cooled rapidly in cold water and catalase enzyme was added to degrade the residual H_2O_2. The oxidation solutions and samples were protected from solar irradiation in order to avoid photochemical degradation of Fe(III)EDTA.

2.3. EDTA analysis by HPLC

EDTA was analysed as its trivalent iron complex by high-performance liquid chromatography (HPLC). The samples were first filtrated through 0.45 μm cellulose membrane filters (Millipore). The solution of 0.001 M $FeCl_3$ in 0.01 M HCl was used to convert the different EDTA species into Fe(III) complexes. This was done by diluting the samples with 0.001 M $FeCl_3$ in proportion 1:4. Fe(III) complexes were allowed to form for

at least 30 min in the dark. Analyses were made using HPLC with a Hewlett–Packard Series 1050 pump and Hewlett–Packard 4010 Series II UV-detection system. The analytical column was Spherisorb ODS2 (25 cm × 0.46 cm i.d.), UV detection was at 240 nm, column temperature 30 °C and injection volume 15 μl. A 15% methanol and 85% tetrabutylammoniumbromide (0.02 M) eluent was used with flow rate of 2 ml/min. The data was analysed with HP ChemStation software.

2.4. BCA5 and BCA6 analysis by HPLC

BCA5 and BCA6 were analyzed as described by Metsärinne et al. [19]. A 0.01 M tetrabutyl ammoniumhydroxide solution was prepared in distilled water and the pH of the solution was adjusted to 7.2 by using 85% o-phosphoric acid. Tetrabutyl ammoniumhydroxide and methanol were mixed together in proportion 1:1. The analysing conditions were as follows: flow rate was maintained at 1 ml/min, injection volume 25 μl, and detection wavelength 260 ± 5 nm. The column temperature was 36 °C. The data was analysed with HP ChemStation software.

3. Results and discussion

3.1. Screening of suitable catalyst concentration

Adequate amount of catalyst was screened by studying degradation of EDTA in distilled water with ferrous ion concentrations 0–0.9 mM and pH 3. Hydrogen peroxide (30%, w/v) was added so that the total concentration was 7.4 mM. Temperature was kept in 60 ± 1 °C As seen in Fig. 2, over 90% of EDTA was degraded after 3 min oxidation when Fe^{2+} concentration was above 0.5 mM. After 1 h oxidation over 96% EDTA reduction was reached with iron concentrations 0.2–0.9 mM, while 0.1 mM Fe^{2+} oxidized 45% of EDTA. Based on these results, 0.5 mM of Fe^{2+} was selected as catalyst concentration used in bleach and waste water oxidations studies, since increase in degradation above this concentration was only marginal. Usually the degradation rate increases with an increase in the concentration of Fe^{2+} [22–24] though the extent of increase is
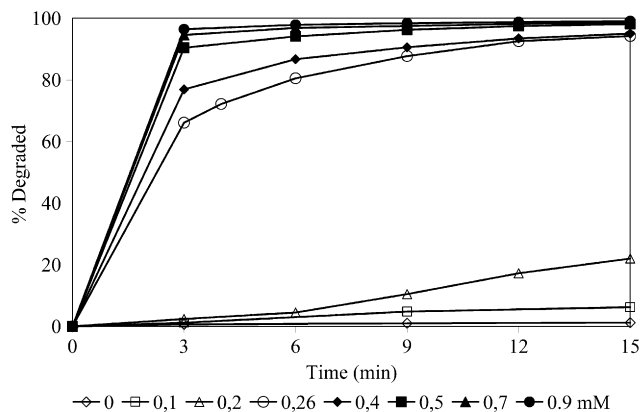

Fig. 2. Degradation of EDTA in distilled water by Fenton's reagent with Fe concentrations 0–0.9 mM and a maximum reaction time of 15 min. Fe concentration 0.26 mM equals EDTA:Fe molar ratio 1:1. *Reaction conditions*: Temperature 60 °C and pH 3.

sometimes observed to be marginal above a certain concentration as reported by and Kang and Hwang [20] and Rivas et al. [25]. Also, an enormous increase in the Fe^{2+} will lead to an increase in the unutilized quantity of iron salts, which will contribute to an increase in the total dissolved solids content of the effluent stream.

It was expected that all of the EDTA is complexed with Fe^{2+} in the beginning of the test when Fe^{2+} concentration was 0.26 mM (molar ratio 1:1) or more, since pH was feasible, no other metal ions were present, and contact time was undoubtedly sufficient for Fe(II)EDTA complexes to form. Speciation can be expected to change towards Fe(III) complex if free Fe^{3+} is present. The kinetics of Fenton's reaction is, however, of different rapidity. In pH 3 a higher thermodynamic stability of Fe(III)EDTA [26] plays naturally more important role while the reaction time increases. As seen in Fig. 2, EDTA degradation starts very slowly when Fe^{2+} concentration is less than 0.26 mM. Therefore, it can also be assumed that all or nearly all Fe^{2+} is complexed with EDTA when ferrous ion concentration is 0.26 mM or less. When complexed to EDTA, Fe^{2+} is incapable of participating Fenton's reaction and therefore only Fe^{2+} concentrations of 0.5 mM or above returned nearly identical degradation curves, which proves that a molar ratio of over 1:1 (in this experiment 2:1) was needed for all EDTA to form complexes with Fe^{2+} and – even more importantly – for a sufficient amount of free Fe^{2+} to be present for Fenton's reaction to take place. Nevertheless, according to the results it can be assumed that even with a molar ratio of 1:1 (0.26 mM) not all Fe^{2+} was complexed with EDTA, since EDTA degradation rate was still remarkably higher compared to the case were Fe^{2+} concentration was only one third of EDTA concentration. This means there seemed to be enough uncomplexed Fe^{2+} present to set the catalytic reaction on even when molar ratio was 1:1 and therefore not all EDTA was complexed with iron.

3.2. Experiments with spiked pulp and paper mill waste water and ECF bleaching effluent samples

Concentration of hydrogen peroxide plays a crucial role in the overall efficacy of the oxidation process. Usually it has been observed that the percentage of degradation of the pollutant increases with an increase in the dosage of hydrogen peroxide [15,23–25]. However, care should be taken while selecting the operating oxidant dosage; H_2O_2 is a rather expensive oxidant and residues are not welcome to the biological WWTP.

Samples were known free of EDTA or DTPA. Before spiking both samples were, however, tested free of known industrial-used complexing agents. Oxidation studies were carried out with six different H_2O_2 concentrations in pulp and paper mill integrated waste water and with three concentrations in the ECF-bleach plant effluent. Oxidation of EDTA was quite obviously more efficient in the waste water than in the bleach. After 3 min oxidation with H_2O_2 concentration 22.2 mM, over 98% of EDTA was degraded in the waste water, while in the bleach reduction with same H_2O_2 concentration was only around 30%. Increased reaction time or H_2O_2 concentration improved the EDTA degradation remarkably. Results are presented in Table 2.

Table 2
Degradation of EDTA in spiked samples of ECF pulp bleaching effluent and integrated pulp and paper mill waste water by Fenton's reagent. H_2O_2 concentrations 7.4–74 mM, pH 4, and Fe^{2+}:EDTA molar ratio 2:1 were used

H_2O_2 (mM)	Waste water			Bleaching effluent		
	3 min	15 min	60 min	3 min	15 min	60 min
7.4	53.5	58.4	60.4	26.9	43.1	59.8
11.1	74.1	82.2	82.7			
14.8	88.0	93.5	93.9			
18.5	91.8	97.8	98.2			
22.2	98.4	99.4	98.6	31.8	67.0	93.3
74.0	98.9	99.1	99.2	41.6	72.2	100.0

Bleach effluents contain a complex mixture of chemical components and higher concentration of organic matter in general, which explains lower degradation of EDTA in bleaching effluent. Metal speciation, which was not studied, plays most probably also a remarkable role in the degradation level differences. It is however important to realize that since the reaction condition is acidic the complexing agents may interfere the Fenton's reaction by complexing with Fe^{3+}, even if the kinetics of this complexation is remarkably slower comparable to the catalytic oxidation. It could be assumed, therefore, that only when the catalytic oxidation reaction is slow and pH relatively low this kind of speciation change of complexing agent may to some extent inhibit the degradation itself. However, since metal ions, including Fe^{3+}, are present in waste waters and the pH is low Fe(III) species may be expected to be the dominant [11,12,27].

Temperature and pH dependence of degradation of EDTA and BCA5 in spiked bleaching effluent was also tested (Fig. 3). It is generally known that pH slightly below 3 is favourable for Fenton's reaction to take place. Also limited solubility of ferric ion hydroxides at pH 4 or above limits the use of Fenton's reaction to low pH values [21]. Also in this experiment, there seemed to be a remarkable difference between pH 3 and 4 especially in lower temperatures. In pH 3, temperature increase from 20 to 60 °C caused only a marginal degradation improvement, if any, but in pH 4 the temperature increase was remarkable; no
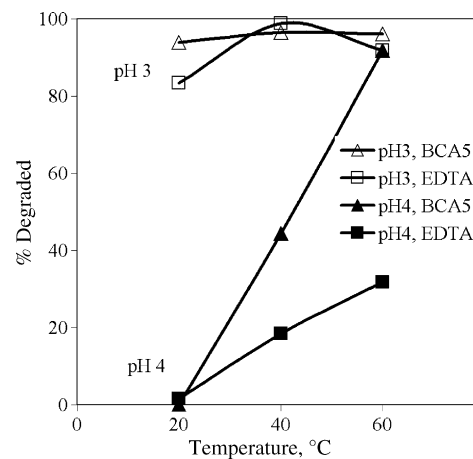

Fig. 3. Degradation of EDTA and BCA5 in spiked ECF bleaching effluent in pH 3 and 4 and temperatures 20, 40, and 60 °C after 3 min reaction time. Fe concentration 0.5 mM was used.
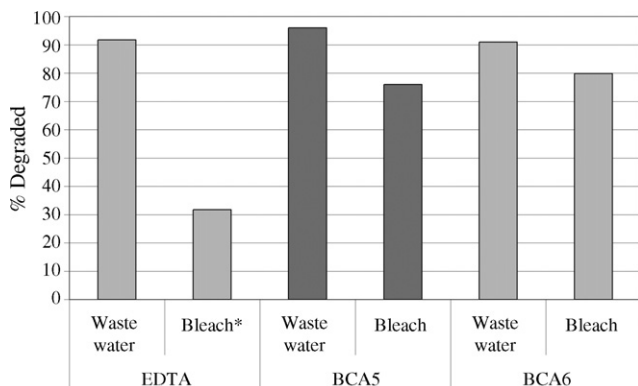
Fig. 4. Degradation of EDTA, BCA5, and BCA6 by Fenton's reagent. *Reaction conditions*: Reaction time, 3 min; temperature, 60 °C; pH 3; Fe^{2+} 0.5 mM, and H_2O_2 18.5 mM (except in EDTA bleaching effluent experiment, where H_2O_2 was 22.1 mM).

degradation of EDTA or BCA5 was found in pH 4 at 20 °C. In 60 °C both pH 3 and 4 yielded the same level of degradation with BCA5 in this degradation experiment of 3 min. It could, therefore, be assumed that change in speciation towards Fe(III)EDTA (or Fe(III)BCA5) from other metal complexes was not complete and quite obviously both lower pH and higher temperature increased the speciation change. Since the final degradation state was lower in bleaching effluent compared to waste water, there presumably were more free metal ions present and EDTA did not change its speciation rapidly enough. On the other hand, higher organic matter in bleaching effluent competes with EDTA decreasing the reaction speed of EDTA degradation.

Degradation experiments with EDTA, BCA5, and BCA6, as seen in Fig. 4, did not yield to as remarkable difference in degradation of complexing agent between waste water and bleaching effluent as with EDTA. On bases of this, it can be supposed that higher concentration of organic matter is not the only explanation for lower degradation level of EDTA in bleaching effluent. It is also known that BCA6 forms complexes with ferric ions only in millimolar solution [19], which yields in experiments with BCA6 to higher catalyst concentration. Initial molar ratio of H_2O_2 and EDTA (70:1) is undoubtedly high enough enabling oxidation of other compounds as well. It could also be assumed that in the presence in complexing agents, precipitation of ferric ion oxides or hydroxides at pH 4 did not play any significant role since BCA5 and BCA6 were still degraded efficiently. There was not found any difference in final degradation level of BCA5 or BCA6 compared to EDTA in integrated waste water. This is, however, because the Fenton's reaction was able to degrade also EDTA effectively in chosen reaction conditions. In experiments with spiked bleaching water, BCA5 and BCA6 were found more readily degradable as seen in Fig. 4.

4. Conclusions

Fenton's process proved highly effective in degradation of EDTA in spiked integrated waste water. With an initial molar ratio of 70:1 (H_2O_2 and EDTA) or higher, degradation of EDTA was nearly complete within 3 min of reaction time. In bleaching effluent the reaction was slower, yet higher compared to typical results from the traditional biological treatment such waste waters. Lower EDTA degradation level at pH 4 and low temperature in bleaching effluent is a major drawback in this study. It is, however, possible that there was more iron in integrated waste water to improve the catalytic activity. There apparently is a higher concentration of organic matter and presumably other chemical compounds competing with EDTA for Fenton's catalyst in bleaching effluent. Fortunately, pH decrease and temperature increase yielded to high removal of EDTA also in pH 4. According to the results, it is clear that Fenton's process is efficient in degradation of EDTA; with low molar ratios of Fe^{2+}:EDTA there is no uncomplexed ferrous iron present and therefore no degradation occurs, which is a proof for Fe^{2+} being the active catalyst. Effective removal of EDTA even in bleaching effluent within several minutes with a cost efficient catalytic degradation method is worth further examination as a pre-treatment method for bleaching effluents prior to biological waste water treatment. However, the novel complexing agents proved once again superior in terms of degradability. They were readily degraded also in pH 4, when temperature was high enough.

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