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KARI PIRKANNIEMI

Complexing Agents

A Study of Short-term Toxicity, Catalytic Oxidative Degradation and Concentrations in Industrial Waste Waters

Doctoral dissertation

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ABSTRACT

Background Complexing agents are widely used in various industrial processes and household products throughout the world. Amongst the well-known complexing agents, not only EDTA but also DTPA and NTA are widely used. Possible legislative restrictions of the use of biologically recalcitrant complexing agents brings about studies of novel and alternative products and at the same time more sophisticated degradation methods are being searched.

Materials and Methods This work studies the short-term toxicity of commonly used complexing agents. The assays used were *Daphnia magna*, *Photobacterium phosphoreum* (Microtox[®]), and *Raphidocelis subcapitata*. Also catalytic oxidative degradation of commonly used and novel complexing agents was studied. Both biomimetic metallophthalocyanines and Fenton's catalyst were used. Also the concentrations of complexing agents in Finnish electrolytic and chemical surface treatment plant waste waters were studied. The analytical methods used are: UV-vis spectrophotometry, HPLC, GC-FID, and GC-MS for complexing agents; TOC for organic load; ICP-AES for metal concentrations.

Results Free complexing agents proved to be rather non-toxic. They also proved to be effective in reducing heavy metal toxicity. In degradation experiments both adapted methods are effective with varying degradation rate for different complexing agents. In electrolytic and chemical surface treatment plant waste waters, complexing agents, namely EDTA, DTPA, and NTA were found to be present mostly in trace amounts, but some of the selected waste water samples also had relatively high concentrations. Concentrations were lower than PNEC_{aqua} value for EDTA, which is 2.2 mg/l. However, highest concentrations were not significantly lower in comparison to PNEC_{aqua}.

Conclusions Complexing agents are rather non-toxic compounds in terms of short-term toxicity. Their environmental fate is yet still under discussion. Traditional complexing agents can be effectively degraded: up to ninety percent of EDTA was degraded with Fenton's catalyst in spiked pulp and paper mill waste water. In Finnish electrolytic and chemical surface treatment industry, NTA seems to be a common compound in degreasing baths, while DTPA is in treatment baths. On the other hand, new chemically even more stable compounds are under constant research to improve the bath stability. The concern over the environmental impacts of complexing agents seems therefore to be too tightly focused on EDTA only.

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National Library of Medicine Classification: QV 290, WA 785, WA 788

CAB Thesaurus: chelating agents; EDTA; nitrilotriacetic acid; toxicity; degradation; concentration; catalytic activity; industrial wastes; waste water; heavy metals



To
Tux & GNU



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Finally, I wish to express my sincere appreciation to women in general,

Helsinki, Finland, March 2007





ABBREVIATIONS AND TRADEMARKS

1,3-PDTA	1,3-propylenediaminetetraacetic acid
ADI	Acceptable daily intake
AOP	Advanced oxidation process
APC	Aminopolycarboxylate
BCA3	N-bis[2-(carboxymethoxy)ethyl]glycine
BCA5	N-bis[2-(1,2-dicarboxyethoxy)ethyl]glycine
BCA6	N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid
BET	Brunauer, Emmett, and Teller method
Biotox[®]	Trademark of BioOrbit Oy, a toxicity assay equivalent to Microtox [®]
BOD	Biochemical oxygen demand, in Scandinavia BOD ₇ , elsewhere BOD ₅
BREF	Reference document on the best available techniques by the EU
<i>β</i>-ADA	<i>β</i> -alaninediacetic acid
CDTA	1,2-cyclohexanediaminetetraacetic acid
COD_{Cr}	Chemical oxygen demand with dichromate method
Cryptand-222	4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane
DOC	Dissolved organic carbon
DTPA	Diethylenetriaminepentaacetic acid
DTPMP	Diethylenetriaminepentakismethylenephosphonic acid
EC	European Commission
ECB	European Chemical Bureau
ECF	Elementally chlorine free (pulping process)
ED3A	Ethylenediaminetriacetic acid
EDDA	Ethylenediaminediacetic acid
EDDS	Ethylenediaminedisuccinic acid
EDTA	Ethylenediaminetetraacetic acid
ELV	Emission limit value
ERA	Environmental risk assessment
EU	European Union
FDA	U.S. Food and drug administration
GA	Gluconic acid
GC-FID	Gas chromatograph equipped with flame ionization detector
GC-MS	Gas chromatograph equipped with mass-selective detector
GRAS	Generally recognized as safe
HEDP	1-hydroxyethelene-1,1-diphosphonic acid
HEDTA	N-(hydroxyethyl)ethylenediaminetriacetic acid
HELCOM	Helsinki Commission, the Baltic Marine Environment Protection Commission
HPLC	High-performance liquid chromatograph
HRT	Hydraulic retention time
ICP	Inductively Coupled Plasma
IDA	Iminodiacetic acid
IDS	Iminodisuccinic acid
IPPC	Integrated pollution prevention and control (directive)
ISA	Iminodisuccinic acid
ISO	International Organization for Standardization
KPDA	2-Ketopiperazine-1,4-diacetic acid
KPMA	2-Ketopiperazine-1(or 4)-acetic acid
LED	Light emitting diode
MBCA3	N-bis[2-(methylcarboxymethoxy)ethyl]glycine
MePcS	Metallotetrasulfophthalocyanine

MGDA	methylglycinediacetic acid
Microtox[®]	Toxicity assay utilizing light emitting <i>Photobacterium phosphoreum</i> strain
NGO	Non-governmental organization
NHE	Normal hydrogen electrode
NOEC	No-effect concentration
NTA	Nitrilotriacetic acid
OSPAR	OSPAR Commission for the Protection of the Marine Environment of the North-East Atlantic
PARCOM	Paris Commission, superseded by OSPAR
PCDD/F	polychlorinated dibenzo- <i>p</i> -dioxines or furans
PFOS	Perfluorooctane Sulfonate
PNEC	Predicted no-effect concentration
POP	Persistent Organic Pollutant
Quadrol[®]	Commonly used registered trademark of THPED by BASF AG
REACH	Registration, Evaluation and Authorisation of Chemicals, EU regulation
SFS	Finnish Standards Association
SRT	Sludge retention time
TCF	Totally chlorine free (pulping process)
THPED	Tetra(2-hydroxypropyl)ethylenediamine
TIC	Total inorganic carbon
TOC	Total organic carbon
Trilon[®]	Trademark for complexing agents, like NTA and EDTA in 1930's by I.G. Farbenindustrie (now BASF AG) in Germany.
TTHA	Triethylenetetraaminehexaacetic acid
UV-vis	Spectral range including ultraviolet and visible areas
Versene[®]	Trademark for complexing agents by Dow Chemical Corporation
WWTP	Waste water treatment plant

LIST OF SYMBOLS

ΔH°_{298}	Standard enthalpy change at 298K
e	Electron
h^+	Valence band hole
$H_2O_2^{\bullet}$	Hydrogen peroxide radical
HO^{\bullet}	Hydroxyl radical
HOO^{\bullet}	Hydroperoxy radical
λ	Wavelength
$O_2^{\bullet -}$	Superoxide radical
OH	Hydroxide ion

LIST OF ORIGINAL PUBLICATIONS

The thesis consists of a summarizing updated review and the following six original publications, which are referred to in the text by their respective Roman numerals.

- Paper I** Mika Sillanpää and Kari Pirkanniemi (2001). Recent Developments in Chelate Degradation. *Environmental Technology* 22(7), 791-801
- Paper II** Kari Pirkanniemi and Mika Sillanpää (2002). Heterogeneous water phase catalysis as an environmental application: A Review. *Chemosphere* 48, 1047-1060
- Paper III** Mika Sillanpää, Kari Pirkanniemi, and Pasang Dhondup (2003). The Acute Toxicity of Gluconic Acid, β -Alaninediacetic Acid, Diethylenetriaminepentakismethylenephosphonic Acid, and Nitritotriacetic Acid Determined by *Daphnia magna*, *Photobacterium phosphoreum*, and *Raphidocelis subcapitata*. *Archives of Environmental Contamination and Toxicology* 44, 332-335
- Paper IV** Kari Pirkanniemi, Mika Sillanpää, and Alexander Sorokin (2003). Degradative Hydrogen Peroxide Oxidation of Chelates Catalysed by Metallophthalocyanines. *The Science of the Total Environment* 307, 11-18
- Paper V** Kari Pirkanniemi, Sirpa Metsärinne, and Mika Sillanpää (2007). Degradation of EDTA and Novel Complexing Agents in Pulp and Paper Mill Process and Waste Waters by Fenton's Reagent. *Journal of Hazardous Materials*. In Press
- Paper VI** Kari Pirkanniemi, Anna-Maria Vuorio, Sari Vilhunen, Sirpa Metsärinne, and Mika Sillanpää (2007). Complexing Agents in Waste Waters of the Finnish Electrolytic and Chemical Surface Treatment Plants. *Environmental Science and Pollution Research International*. In Press

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1 INTRODUCTION

Chelation (Greek: χηλή [chelè], meaning claw) is a process of reversible binding or complexation of a ligand. Industrially used chelating agents are manufactured organic compounds that form stable, soluble complexes in the form of a heterocyclic ring with multivalent metal ions attached by at least two non-metal ions with coordinate bonds (IUPAC 2003^a). According to various sources, the term chelate was first used by Morgan and Drew (1920). Although the terms ‘chelating agent’ and ‘complexing agent’ have certain differences in their meaning, in this study complexing agent is used.

Nitrilotriacetic acid (NTA, Trilon[®] A) is the first industrially produced complexing agent at I.G. Farbenindustrie in Germany since 1936. Ethylenediaminetetraacetic acid (EDTA, Trilon[®] B) was patented in Germany in 1935 and production started only four years later. In the U.S., production of EDTA began in 1948 (Potos 1965). Today there are dozens of producers and brands around the world, but the four most important producers, namely BASF, Akzo Nobel, Dow, and Solutia produced about ninety per cent of all aminopolycarboxylic acids in 1999 (Knepper 2003).

The most commonly used complexing agents are aminopolycarboxylic acids (APC) and organophosphonates. They are widely used in many industrial processes as well as in agriculture, detergents, and groceries. The reason to complex free metal ions varies from one process to another. Generally speaking, the presence of free transition metals, such as copper, iron, manganese or zinc, reduces efficiency or quality of the product due to their catalytic activity, precipitation or increased microbial growth. Most commonly used strong complexing agents form typically 1:1 complexes with di- or trivalent metal ions by binding through e.g. four oxygen and two nitrogen atoms, like EDTA (**Figure 1**). High stability of these compounds makes them ideal for many industrial processes, but may also cause problems in waste water treatment and presumably to some extent also in the receiving waters.

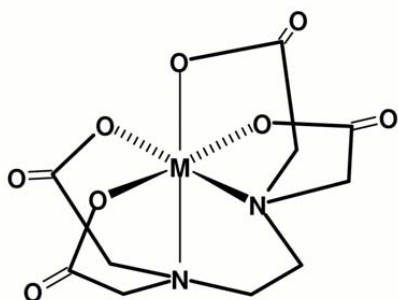


Figure 1. Cyclic divalent metal - EDTA complex

Pulp and paper industry utilizes complexing agents, mainly EDTA and diethylenetriaminepentaacetic acid (DTPA), to suppress the catalytic activity of transition metals. Uncomplexed metal ions catalyze the degradation of hydrogen peroxide and ozone, resulting in decrease in pulp strength and increased use of these bleaching agents.

Calcium, magnesium, and to a smaller extent iron, copper, and manganese increase water hardness. In detergents, complexing agents are used to reduce the concentrations of these free metal ions, and hence to improve the efficiency of the detergent. Anionic surfactants tend to form often insoluble salts with these metal ions. In addition, impurities like lipid residues may combine with metals and adhere strongly to surfaces, which is not acceptable especially in circuit board manufacturing or in decorative coatings in general (Dow 2006). EDTA concentration used as detergents in degreasing stages in surface treatment industry is typically around fifteen per cent (Quitmeyer 2006).

In electronic or chemical surface treatment processes, complexing agents are basically used to decrease metal precipitation from metal salts in treatment baths during treatment process and storage. Due to complexing agents, high metal ion concentrations in treatment bath are maintained and thus the quality of the final product is improved. Complexing agents are, depending on the treatment process, in relatively high concentrations in the treatment vats. In typical nickel plating processes, average EDTA concentration in process bath is around 15 g/l and in as high as 180 g/l in cadmium plating vats (EC 2005).

1.1 Consumption of complexing agents

The current trend of increase in the production of elementary chlorine free (ECF) pulp will also increase consumption of complexing agents in years to come. Estimated annual worldwide consumption of the most common aminopolycarboxylate complexing agents in 1996 was nearly 170,000 metric tons (Virtapohja 1998) and 200,000 metric tons in 2000 (Nowack and VanBriesen 2005, Jäger and Schul 2001, Schmidt *et al.* 2004). In 2002 total regional use of aminopolycarboxylate complexing agents, excluding NTA, in the U.S., Western Europe, and Japan was estimated to be approximately 150,000 metric tons (Davenport *et al.* 2003, Dow 2006). As seen from **Figure 2**, there is still a remarkable disagreement in the consumption of EDTA.

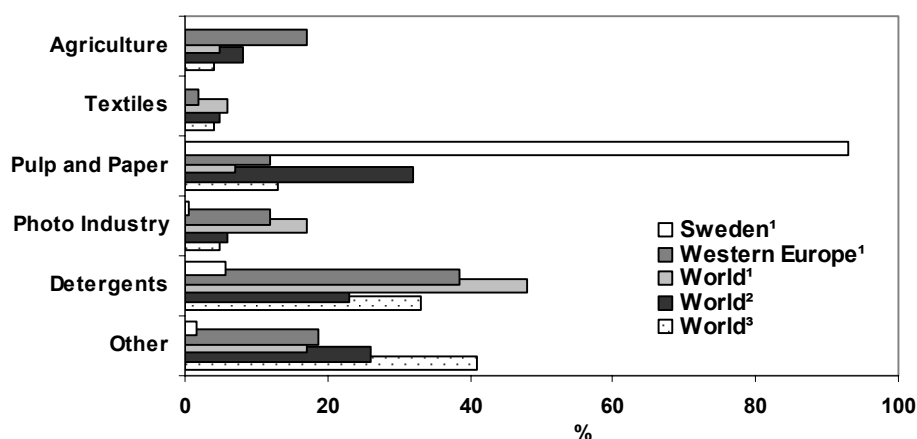


Figure 2. Statistical worldwide, Western European, and Swedish percentual EDTA usage. Data adapted and modified from: ¹) ECB (2004), ²) Davenport *et al.* (2003) and Dow (2006), and ³) Williams (1998). Due to the similar industrial profile, the percentual EDTA usage in Finland can be expected to be comparable to that in Sweden.

According to the European Union (EU) risk assessment report of tetrasodium ethylenediaminetetraacetate (Na₄EDTA) (ECB 2004), EDTA usage in Western Europe in 1999 was almost 35,000 metric tons calculated as H₄EDTA. A significant increase in usage has been observed, since according to Virtapohja (1998) only a total consumption of 13,600 metric tons was reported in 1981. The most important application in Europe was industrial and institutional detergents (**Figure 2**). In Sweden, and as speculated in Finland, the pulp and paper industry consumes over ninety per cent of total EDTA usage

(ECB 2004). It is also noteworthy; that DTPA is over three times more commonly used in today's pulp and paper industry than EDTA, at least in Finland (Ruonala-Lindgren, 2007). According to Knepper *et al.* (2002), two-thirds of DTPA sold in Europe is utilized in Finland, Sweden, and Germany, and the total usage in Europe was 14,400 metric tons in 2000 (ECB 2004). In early 1990's, the usage of DTPA was only one third of that (Jäger and Schul 2001). In Finnish pulp and paper industry alone, 9,300 metric tons was used in 2003 (Ruonala-Lindgren, 2007). Usage of other complexing agents, such as NTA, N-(hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), and tetra(2-hydroxypropyl)-ethylenediamine (THPED, aka Quadrol[®]), is less important yet not negligible; e.g. in Europe, NTA usage was estimated to be 20,000 – 27,000 metric tons in 1999, whereas that of HEDTA was 2,000 metric tons in 1981 (ECB 2004, ECB 2005, Knepper and Weil 2001, and Nowack and VanBriesen 2005). In the U.S., EDTA usage of 50,000 metric tons in 1987 and HEDTA usage of 18,000 metric tons in 1981 was reported (Nowack and VanBriesen 2005). The consumption of phosphonates (e.g. DTPMP) was 56,000 metric tons worldwide in 1998 and 17,000 metric tons in Western Europe in 2002 (Davenport *et al.* 2003) (**Figure 3**). Many of the readily biodegradable novel substitutes for EDTA are also already adopted in use, especially in Germany, even though their market share is still marginal; In 2000 usage of β -ADA, 1,3-propylenediaminetetraacetic acid (1,3-PDTA) and methylglycinediacetic acid (MGDA) in Germany was 0.15, 28, and 130 metric tons respectively (Knepper and Weil 2001, UBA 2001, and Schmidt *et al.* 2004). 10,000 cumulative metric tons of ethylenediaminedisuccinate (EDDS) was produced by 2002 after commercialisation in 1996 (RSC 2006).

In e.g. surface treatment industry, the share of the 'uncommon' complexing agents in the total consumption of complexing agents is most probably higher, since marketing of e.g. HEDTA and THPED is intensive. Also other less known – and biologically more recalcitrant – complexing agents, such as 1,2-cyclohexanediaminotetraacetic acid (CDTA) and diethylenetriaminepentamethylenephosphonic acid (DTPMP) are studied to improve the bath stability in electroplating industry (Saloniemi *et al.* 2002). Increased quality requirements also feed the need for research of many novel stable complexing agents, such as 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (cryptand-222) or then (Hancock 1997) and triethylenetetraaminehexaacetic acid (TTHA) (Jusys *et al.* 1999).

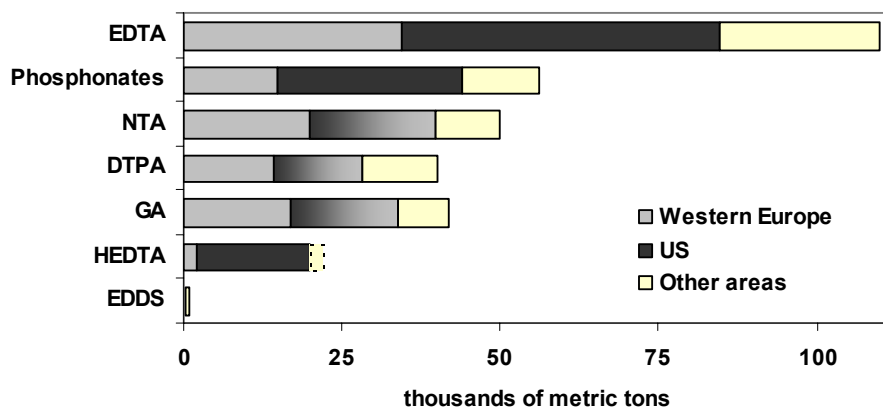


Figure 3. Annual world-wide consumption of some of the most commonly used complexing agents. The world-wide consumption is divided into the most important market areas; the U.S. and Western Europe. Gluconic acid, NTA, and DTPA consumption in the U.S. is expected to be comparable to Europe and HEDTA consumption in other areas is expected to be roughly comparable to European consumption. Phosphonates consists of DTPMP and 1-hydroxyethelene-1,1-diphosphonic acid (HEDP) as the most important compounds. Data presented is processed from the data acquired from Knepper and Weil (2001), Jäger and Schul (2001), Schmidt *et al.* (2004), Davenport *et al.* (2003) cited by Nowack (2003, 2004), Hera (2004), and Knepper *et al.* (2002). Note: Annual consumption of different complexing agents or different areas is not fully comparable, since original data is from the years 1997 – 2000 and 2002. The data covering the use of HEDTA was obtained from 1981.

Even though reducing chlorine consumption in pulp bleaching is highly beneficial to the receiving waters and to the environment in general, many questions concerning complexing agents need to be answered too. Indeed, there is still a disagreement in literature concerning the degradability of complexing agents during traditional biological waste water treatment as well as in their fate when released to the environment. One of the only commonly accepted facts concerning the degradability of EDTA and DTPA and many other complexing agents is their photolability when complexed with iron, copper or manganese (Jaworska *et al.* 2002). This extreme example of the importance of speciation on degradability also describes the complexity of this research topic.

According to literature the degradability of complexing agents varies remarkably from one waste water treatment plant (WWTP) to another. It is also most probable that there is a great time dependent variation in degradability of complexing agents at one particular WWTP. This might be caused by – among many other things – remarkable variation in

total load, which is a subject difficult to solve without a pre-treatment process of bleaching waters prior to the biological waste water treatment.

Complexing agents are rich in nitrogen; therefore, if not removed from the waste water before releasing to the environment, their degradation products are to some extent notable promoters of eutrophication – when they will finally degrade in the receiving waters. It would therefore be desirable to degrade the complexing agents before releasing to the environment – in biological WWTP or even before it.

1.2 Legislation, agreements, and recommendations

There is currently no legislation limiting the use of strong complexing agents in general in Finland or in European Union level. According to Williams (1998), industrial use of EDTA is banned in some states in the U.S., though a common ingredient in e.g. fast food dressings (McDonald's 2006). In European Union, EDTA is known as food additive no. E385, and is allowed to be used in e.g. minarines up to 100 mg/kg and canned food up to 250 mg/kg (EC 1995, 2006^b). In Germany, there is also some legislation limiting the use of strong complexing agents, e.g. annex 40 of the German waste water administrative regulation required the galvanic industry to avoid any EDTA release into waste water (Conrad 2004). There was also a joint statement on the reduction of water pollution by EDTA, which was issued by the Federation of the German Chemical Industry, BASF AG, several water supply federations and three ministries on 31 July 1991. This legally non-binding document expressed the willingness of the signatories to reduce EDTA loads in receiving waters by fifty per cent by the end of 1996 (UBA 2004, Knepper 2003). A 30-35 per cent reduction was achieved (Knepper *et al.* 2002), but from 1998 onwards sales of EDTA has also been increased (Schmidt *et al.* 2004).

A European Union regulation on detergents (648/2004, EC 2004) that entered into force in 2005 limited the use of persistent surfactants in detergents Union-wide targeted both for industrial and household applications. According to a recent Commission recommendation (2006/283/EC, EC 2006^c) the competent (permitting or supervisory) authorities should lay down emission limit values (ELV) or equivalent parameters or technical measures regarding Na₄EDTA in order to the installations concerned to operate by the end of October 2007. It is however interesting that the European Union does not

yet seem to be concerned with other widely used and biologically more recalcitrant complexing agents, such as DTPA.

The new European Union level chemical legislation may have certain effect on the use of complexing agents in the near future. The EC White Paper on a Strategy for a Future Chemicals Policy (EC 2001^b) proposed the establishment of a new legislative system called REACH (**R**egistration, **E**valuation and **A**uthorisation of **C**hemicals), which will regulate usage of both existing and new chemicals within a period of the following eleven years. The REACH is based on a top-down approach to chemical safety testing, in which the type of information required is dictated by the quantity of consumption (Combes *et al.* 2003). The European Parliament passed the new EU regulation (REACH) on December 13th 2006 (EC 2006^d). For substances manufactured or imported in quantities starting from ten metric tons, a chemical safety report will be required (EC 2006^{a,d}). It has been said that over 99 per cent of more than 30,000 chemicals on the market do not have sufficient safety data sheets that are publicly available (Thacker 2005). Extensive risk assessments that are produced by the European Union concerning complexing agents are related only to EDTA (ECB 2004) and NTA (ECB 2005). No other extensive chemical safety reports or risk assessments from other sources were found either. On the other hand, the REACH will pass the main responsibility of chemical safety to the producer or importer of the chemical and therefore there is no reason at this point to launch new assessments by the EU that would last years to complete.

The European Union has adopted the precautionary principle in the union-wide environmental and chemical legislation, including IPPC directive and REACH regulation. This means that precautionary approach should be widely applied; where there are threats of serious or irreversible damage to the environment, lack of scientific certainty should not be used as a reason for postponing cost-effective measures to prevent environmental degradation (EC 1996, EC 2006^d, EEA 2007).

Eco-labels were launched at the beginning of 1978 with German-based Blue Angel being the first on the market (Blue Angel 2006). One of the resellers of EDDS finds eco-labels such as Nordic Swan, Blue Angel, and EU Rose, an important factor in replacement of EDTA with more biodegradable ones (Octel 2003). Since EDTA and DTPA are virtually non-biodegradable, the regulations of e.g. Nordic Swan eco-label may ban their usage. Regulations vary, though, from one group of products to another (**Table 1**). To obtain a

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Chapter 1 Introduction

Nordic Swan eco-label for industrial detergents, the maximum NTA concentration is 0.1 per cent, even though it does fulfil the OECD (1993) criteria for biodegradability (Nordic Council of Ministers 2005). Earlier the use of EDTA was largely allowed too in small quantities, usually up to 0.1 per cent (Solyom and Lindfors 1998). Usage of EDTA or NTA is also specifically prohibited for cleaning products carrying EU Rose eco-label (EC 2001^a). In textile industry same limitation exists for EDTA and DTPA (EC 2002).

According to the Helcom recommendations and 17/8, 17/9, and 23/7 (Helcom 1996^{a,b}, 2002), and the Parcom recommendation 92/4 (Parcom 1992), EDTA and similar strong complexing agents should be substituted, when technically possible, by readily biodegradable substances.

Table 1. Listing of complexing agent banned by selected industry or product specific eco-label regulations. Many eco-label regulations include also maximum concentrations for complexing agents not totally banned. Data obtained and collected from Solyom and Lindfors (1998), EPA (2006), GEN (2000), NMN (2006), Nordic Council of Ministers (2005), and Blue Angel (2006).

	EDTA	DTPA	NTA	Phosphonates
Green Seal (USA)	-	-	-	Degreasers
Environmental Choice (Canada)	Boat and Bilge Cleaners Cleaners (general purpose) Hand Cleaner (Industrial)	-	Boat and Bilge Cleaners Cleaners (general purpose) Hand Cleaner (Industrial)	-
Nordic Swan (Scandinavia)	Cleaners and Degreasers (industrial) Detergents (dishwasher) Detergents (hand dishwashing) Floor Care Products Detergents (laundry, professional) Detergents (laundry, stain removers) Detergents (Shampoo, conditioner, liquid soap)	Cleaners and Degreasers (industrial) Cleaners and Degreasers (industrial)	Detergents (laundry, professional) Detergents (dishwasher) Detergents (laundry, stain removers) Detergents (shampoo, conditioner, soap etc.)	Floor Care Products
EU Rose (EU)	Cleaners (all purpose)	-	Cleaners (all purpose)	-
Eco Mark Program (Japan)	-	-	-	-
Blue Angel (Germany)	Towels (Fabric rolls) Wallpapers Paper towels	-	-	-

1.3 Chemical properties of commonly used complexing agents

1.3.1 Complex formation constants and speciation

Complexing agents are compounds that form highly stable water-soluble complexes with metal ions. Stability of the metal complex is highly dependent on pH and complex forming metal. Stability of the metal complex of these ligands – or complexing agents – is expressed as complex formation constant, which is also called stability constant. The complex formation constant of a metal complex is defined as follows:

$$K = [\text{MeL}] / [\text{Me}][\text{L}],$$

where K is the complex formation constant, which is usually expressed as a logarithm, $\log K$, $[\text{Me}]$ is the metal ion concentration, $[\text{L}]$ is the ligand concentration, e.g. EDTA, and $[\text{Me}][\text{L}]$ is the metal complex. Complex formation constant ‘is an equilibrium constant that expresses the propensity of a substance to form from its component parts’ (IUPAC 2003^b). The larger the complex formation constant, the more stable is the species. Complex formation constants of selected metal complexes are presented in **Table 2**. Complexing agents exist predominately in their complexed form, since in practise there is always a significant molar excess of at least alkaline earth metals present (Sillanpää *et al.* 2001).

Structures of complexing agents studied in **Papers I** and **III-VI** are shown in **Figure 4**. HEDTA and THPED (Quadrol[®]) have increasingly been marketed to be used in electrolytic and chemical surface treatment industry. THPED especially is being used to prevent deposition of copper in electroless copper plating process (Pauliukaitė *et al.* 2006, Knepper 2003, Norkus 2000). β -alaninediacetic acid (β -ADA), BCA5, and BCA6 have been proposed as more biodegradable substitutes for EDTA and DTPA. Sixty per cent of total consumption of phosphonates, mainly diethylenetriaminepentakismethylene-phosphonic acid (DTPMP) is used in industrial cleaning products. Phosphates were partly replaced by phosphonates, even though phosphate content is high in phosphonates and they also are poorly biodegradable (Davenport *et al.* 2003).

Table 2. Complex formation constants of 1:1 metal-ligand complexes at 25°C and ionic strength of 0.1 M. Values are expressed as log K. Complex formation constants are adopted from the following sources: **a)** Martell *et al.* (1997) cited by Nowack and Stone (2000), **b)** Azab and Hassan (1989), **c)** Rorabacher *et al.* (1969), **d)** Martell and Smith (1974), and **e)** Hyvönen *et al.* 2006, **f)** Dow Chemical Company, (20°C) (1990), **g)** Saloniemi *et al.* (2002), **h)** Anderregg *et al.* (20/25°C) (2005), **i)** Li and Byrne (1997), **j)** Räsänen *et al.* (2002), **k)** Smith and Martell (1976) cited by Byegård *et al.* (1999), **m)** Anderregg (1982, 20 °C) **n)** Holloway and Reilley (1960), **o)** BASF (2006^{a-c}), **p)** Knepper and Weil (2001), **q)** Pauliukaitė *et al.* (2006), **r)** Hyvönen (2007), **s)** Jäger and Schul (2001), and **t)** Jusys *et al.* (1999). Complex formation constants of DTPMP (and many other organophosphonates not included here) were rejected by recent IUPAC Technical Report (Popov *et al.* 2001) due to insufficient purity of the compound in the assays. The complex formation constants of DTPMP presented here are therefore to change in the future.

	NTA	β-ADA	EDTA	DTPA	DTPMP	BCA5	BCA6	HEDTA	THPED Quadrol®
Ca^{II}	6.4 ^{dop} -6.5 ^s	5.0 ^{ps}	10.6 ^{dps} -10.7 ^k	10.6 ^s , 10.7 ^h , 10.8 ^{ip} , 10.9 ^o	10.7 ^p	7.4 ^e	7.7 ^{ej}	8.1 ^s -8.2 ^o	
Cd^{II}	9.8 ^{mop}	8.2 ^p	16.4 ^p -16.5 ^{do}	19.0 ^{dp} -19.3 ^{ho}					
Cr^{III}	>10 ^m		23.4 ^k	22.1 ^h					
Cu^{II}	12.9 ^{dop} -13.1 ^s	9.3 ^b -12.6 ^{ps}	18.7 ^l -18.8 ^{qps}	21.0 ^l , 21.1 ^l , 21.4 ^{ps} , 21.5 ^{ho}	19.5 ^l -25.3 ^p	9.6 ^e	13.1 ^{ej}	17.4 ^l , 17.5 ^o , 17.6 ^l , 18.8 ^s	26.9 ^q
Fe^{II}	8.3 ^{qp} -8.8 ^m	8.9 ^p	14.3 ^{dop}	16.0 ^{ho} , 16.4 ^{dp} , 16.5 ^k			(9.8 ^l)	12.2 ^o	
Fe^{III}	15.9 ^{top} -16.3 ^{ms}	13.3 ^c -16.1 ^{ps}	25.0 ^p -25.1 ^{fos}	27.3 ^{hs} , 27.9 ^o , 28.0 ^p , 28.6 ^l	27.3 ^{g*}	12.6 ^e	15.5 ^l -17.3 ^e	19.8 ^{os}	
Hg^{II}	14.6 ^o		21.8 ^o	26.7 ^o					
Mg^{II}	5.4 ^m -5.5 ^{op}	5.3 ^p	8.7 ^o -8.8 ^{kp}	9.0 ^o -9.3 ^{kp}	10.8 ^p	5.9 ^e	5.9 ^l -6.0 ^e	7.0 ^{os}	
Mn^{II}	7.4 ^m -7.5 ^{dops}	7.3 ^{qps}	13.5 ^s , 13.8 ^{dop} , 13.9 ^k	15.1 ^l , 15.5 ^{ps} , 15.6 ^{hko}	13.6 st -17.3 ^p	7.5 ^e	9.2 ^l -9.3 ^e	10.8 ^{os}	
Ni^{II}	11.5 ^{mop}	11.4 ^p	18.5 ^p -18.6 ^{do}	20.2 ^{dhop}	19.0 ^{g*}			17.1 ^o	7.0 ^q -7.5 ^c
Pb^{II}	11.3 ^o		18.0 ^o	18.9 ^o					
Zn^{II}	10.7 ^{dhop}	10.0 ^p	16.4 ^{dp} -16.5 ^{ko}	18.3 ^{f,p} , 16.4 ^k , 18.6 ^{ho}	19.1 ^{g*} -20.1 ^p	8.1 ^e	11.3 ^e	14.5 ⁿ -14.6 ^o	

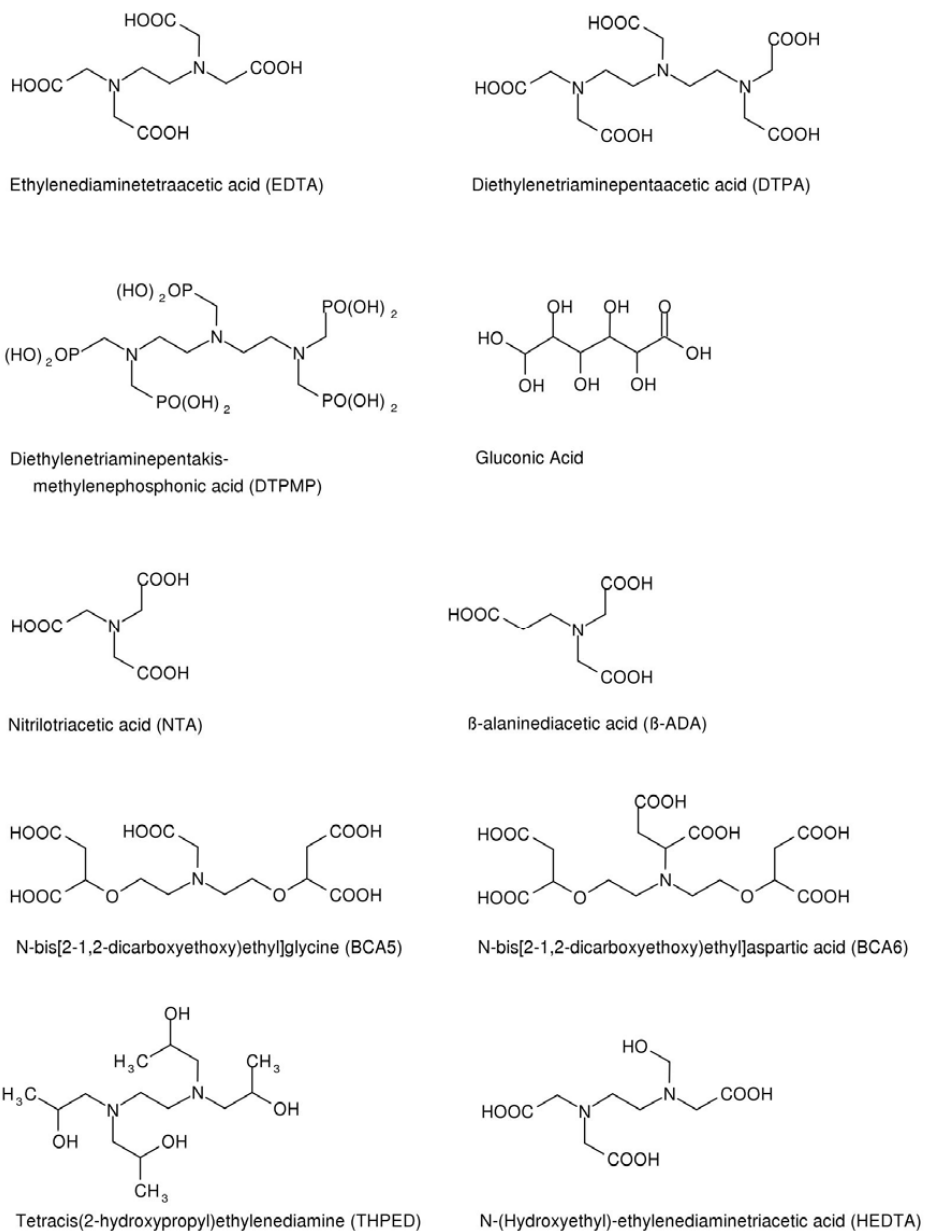


Figure 4. Structures of complexing agents. The short-term toxicity of gluconic acid, β -ADA, NTA, and DTPMP was studied in (III). Degradation of EDTA, DTPA, DTPMP, NTA, and β -ADA was examined in (IV). In (V), degradation of EDTA, BCA5, and BCA6 was studied and (VI) focuses on concentrations and load of NTA, EDTA, DTPA, HEDTA, and THPED.

In theory, speciation of complexing agents in certain pH can be calculated based on the known complex formation constants of the metal-ligand complexes and on the concentrations of metals and complexing agents. This approach assumes that thermodynamic equilibrium is reached but this is not always the case. The exchange kinetics may be rather slow, especially for NiEDTA and Fe^{III}EDTA (Nowack 2004). Xue *et al.* (1995) studied exchange kinetics of CaEDTA to Fe^{III}EDTA species and found half life of over 17 days from CaEDTA species in river water. Other compounds present in waste water or natural water, may interfere remarkably with the exchange kinetics, e.g. natural ligands like fulvic acids are known to be weak in interaction with phosphonates (Nowack 2004). According to Sillanpää *et al.* (2001), alkaline earth metal complexation plays a significant role in the speciation of EDTA and DTPA when there is a noticeable molar excess of complexing agents compared to transition metals.

1.3.2 Selectivity of complexing agents on metal ions

The selectivity of complexing agents on metal ions is largely dependent on the complex formation constant of the metal complex. In nuclear waste treatment selective complexing agents have been studied for years (Kappel *et al.* 1985, Means *et al.* 1978, Prapaipong and Shock 2001). It is possible to design tailor-made complexing agents with high selectivity to large metal ions. In these studies, it has been proven that the following characteristics favour larger metal ions: small ring size, presence of neutral oxygen donors, and replacement of ethylene bridges with cyclohexanediyl bridges (De Sousa *et al.* 1997). Stylishly tailored complexing agent has – due to the above mentioned characteristics – high affinity to the metal it is designed to complex. Hence metal complexes have high complex formation constants.

1.3.3 Environmental impacts of the complexing agents

Complexing agents contain roughly ten per cent of nitrogen. For normal growth algae need nutrients in a Redfield weight ratio 100:16:1 (C:N:P) (UNEP 2007). In inland waters limiting nutrient is usually phosphorus, but in sea areas also nitrogen. It is therefore assumed that they excite eutrophication where nitrogen is a limiting nutrient. Phosphonates, such as DTPMP – contain both phosphorus and nitrogen – are accelerators of eutrophication in both inland waters and sea areas. In some rare cases algal growth can also be limited by trace element, such as iron, copper, molybdenum or zinc deficiency, to

which complexing agents may also affect by increasing pass-through of metals at WWTP (Schmidt and Brauch 2004, Nowack 2003).

A major concern related to the increased worldwide use of complexing agents is metal pass-through and delayed metal sedimentation. Complexing agents are shown to increase transition metal levels in TCF pulp effluent (Saunamäki 1995), and thus metal pass-through in WWTPs. Complexing agents are also shown to affect metal balance in receiving waters and remobilization of metals absorbed onto a mineral surface by solubilization (Nowack 2003, 2004). On the other hand, studies with phosphonates show that they only have a weak influence on metal adsorption onto goethite in pH range from four to eight. Therefore, phosphonates are expected to have only a slight influence on metal remobilization in natural systems (Nowack 2003).

According to publications by European Aminocarboxylates Committee (EAC 2002) and the EU (ECB 2004), the predicted no effect concentration in the aquatic environment ($PNEC_{\text{aqua}}$) for EDTA is 2.2 mg/l based on no-effect concentration (NOEC) of EDTA for *Daphnia magna* (22 mg/l). EDTA concentration in the aquatic environment is according to the EAC (2002) practically always below this level. $PNEC_{\text{aqua}}$ for NTA is 0.93 mg/l (Kalf 2003, EAC 2003, ECB 2005). For DTPMP, $PNEC_{\text{aqua}}$ values of 0.06 mg/l (Jaworska *et al.* 2002) and 0.52 mg/l (Hera 2004) have been proposed. The low value could mainly be explained by high phosphorus content of the compound. In the metal plating industry, especially the circuit board manufacturing, there is a 'potential risk' on EDTA concentration exceeding $PNEC_{\text{aqua}}$ in the receiving waters (EAC 2003). Other applications where EDTA may be at risk are the pulp and paper industry, industrial and institutional cleaning, and photographic waste recycling (EAC 2006). Especially in Northern Europe, where known photolability of especially $Fe^{III}EDTA$ and $CuEDTA$ species do not play such an important role for the most time of the year, there is seasonally a risk for EDTA concentration – or concentrations of the complexing agents in general – to be above that in small water systems.

1.3.4 Short-term and chronic toxicity

There are several published studies, including (III), on short-term toxicity of complexing agents and their metal complexes. In general, according to many studies the short-term toxicity of all commonly used complexing agents either as a sodium salt or in a fully

protonated form is low (Nowack 2003). Actually, complexing agents suppress the short-term toxicity of toxic heavy metals (III, Nowack 2003, Schmidt and Brauch 2004), which characteristics is also utilized in medical applications in chelation therapy and in heavy metal poisoning (Schubert and Derr 1978, Wikipedia 2006). NTA, which is readily biodegradable, is also 'reasonably anticipated to be a human carcinogen' (ECB 2005, Schmidt and Brauch 2004, HHS 2005), but most presumably as Fe^{III} complex only, due to the intracellular Fenton's reactions (Ebina *et al.* 1986, Oberley 2002). The possible carcinogenicity of NTA is a great example of a case where environmental and health interests are somehow contradicting. Short-term toxicity of gluconic acid, NTA, β -ADA, and DTPMP is discussed more in detail later.

Complexing agents are expected to have harmful long-term effects in concentration at mg/l level only (Schmidt and Brauch 2004). Complexing agents are not expected to be bioaccumulative, since bioaccumulation usually increases with the increasing lipophilicity of a substance. For EDTA and NTA this is also experimentally confirmed (Bishop and Maki 1980 cited by ECB 2004; Bernhardt 1984 cited by Schmidt and Brauch 2004). EDTA is still found harmful to normal rat kidney cells: In a study with cell cultures, cell death and reduced colony-forming ability were observed at NaEDTA concentrations below 100 μ M that is at concentrations lower than required to chelate all the Ca²⁺ in the growth medium (Hugenschmidt *et al.* 1993). However, studies with uncomplexed complexing agents are of no relevance in real-life situations, since they do not exist in their uncomplexed form in nature (Sillanpää *et al.* 2001).

The guideline value for EDTA concentration in drinking water is 0.6 mg/l published by World Health Organization (WHO 2003, 2006). As mentioned earlier, EDTA is also approved to be used as a food additive in the U.S. and Europe. The EU risk assessment of EDTA (ECB 2004) summarizes that there is no cause for concern if consumers, workers or public are exposed to EDTA.

1.3.5 Concentrations in aquatic environment

In late 1980's it was found that EDTA is an anthropogenic organic compound that was detected in German surface waters at highest concentrations. Average concentrations in surface waters frequently amounted up to 50 μ g/l. Typical concentrations in industrialized countries are in the range 1 – 20 μ g/l. Highest EDTA concentrations in

natural waters found in literature are in Spain, (Rio Odiel) 600-2460 µg/l (Kowalik and Einax 2000) and in Jordan, (River Zerka) 900 µg/l (van Dijk-Looyard *et al.* 1990 cited by Schmidt *et al.* 2004). Increased use of DTPA is also seen from natural water concentrations (Kraus 2001, Schmidt *et al.* 2004). Except the highest concentrations on Rio Odiel, the concentrations even in these extreme cases were relatively low compared to the PNEC_{aqua} value for EDTA (2.2 mg/l). PNEC_{aqua} for DTPA is not yet available in literature.

Other complexing agents are either used in smaller quantities or they are readily biodegradable, such as NTA, and therefore not found in high concentrations. There are no published results on e.g. concentrations of the phosphonates in natural waters (Nowack 2004).

2 AIM OF THE STUDY

The aim of the reviews (**I and II**) of this study was originally to map the current understanding of complexing agent degradation and to learn the chemical and physical demands of heterogeneous catalysis in water phase applications to get a strong ground to further study. Literature search, as represented here, has been updated where needed in late 2006 and early 2007, since the original papers were already published several years ago.

In experimental section the aim was i) to study the suitability of two different catalytic oxidation methods – a novel biomimetic catalyst and Fenton's catalyst – for degradation of various complexing agents (**IV and V**), ii) to study the short-term toxicity of various complexing agents and their metal complexes (**III**), and iii) to study complexing agent concentration in Finnish electrolytic and chemical surface treatment plant waste waters, since their role in waste water treatment efficiency and heavy metal pass through is of interest from the point of view of environmental permitting and supervising of such facilities. Also the fact that EDTA seemed to be the only complexing agent, to which European Union-wide is concerned and the reference documents on the best available technologies (BREFs) are focused on EDTA neglecting other biologically recalcitrant and less studied complexing agents that are being marketed ever intensively. Therefore, there was a need for that kind of study (**VI**).

3 RECENT DEVELOPMENTS IN DEGRADATION OF COMPLEXING AGENTS

Degradation of complexing agents has been studied rather widely during the past fifteen years. Both chemical and biological methods have widely been studied. In earlier reports, EDTA and DTPA were categorized as compounds not likely to be degraded in the biological processes. However, it is nowadays known that even EDTA, which is known biologically recalcitrant, can be degraded at biological WWTP if conditions are favourable. However, in real-life situations the conditions are typically not very favourable. In earlier studies, the speciation was unfortunately often overlooked. It must be noted that the speciation plays a key role in the behaviour of complexing agents and determines their fate in the environment. It has been shown that the adsorption (Nowack and Sigg 1996), photochemical (Lockhart and Blakeley 1975) and biological (Miyazaki and Suzuki 1994) degradations strongly depend on the metal complexed by EDTA. Also taking into account the predominating molar excess of alkaline earth and transition metals, it can reasonably be expected that no complexing agent is present uncomplexed in waste waters (Sillanpää *et al.* 2001). As such, it is obvious that the studies on the break down – or other characteristics – of free complexing agents are of limited relevance in the field of environmental sciences. (I)

3.1 Advanced oxidation processes

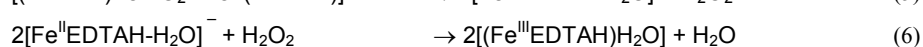
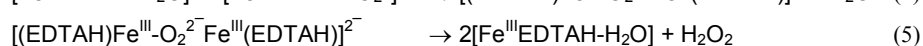
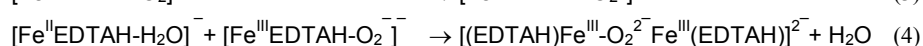
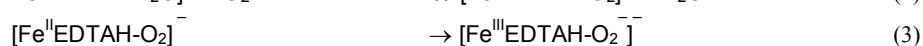
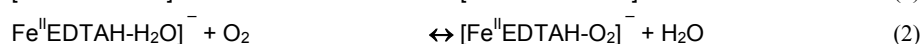
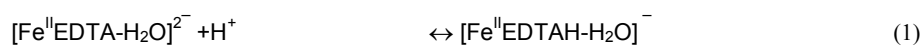
Advanced oxidation processes (AOP) have been shown to be promising in the degradation of recalcitrant organic pollutants. These processes apply combinations of radiation, oxidants – usually ozone or hydrogen peroxide – and catalysts for degrading the target compounds. Chemical oxidative degradation methods of complexing agents that have been published include: UV induced methods, various catalytic methods and their combinations. The oxidants used are ozone, hydrogen peroxide and molecular oxygen. (I)

3.2 Ozonation

A significant proportion of EDTA could be removed during drinking water treatment by ozonation (Brauch and Schullerer 1987, Schullerer and Brauch 1989). The presence of Ca and Cd had little impact on EDTA removal by ozonation, while the rate of EDTA degradation was reduced by ferric ions (Gilbert and Hoffmann-Glewe 1990). EDTA, spiked to obtained TCF bleaching effluent, was also effectively eliminated with ozone dose of 1400 mg/l (Korhonen *et al.* 2000). More recent studies concerning ozonation of complexing agents are largely focused on specific situations where requirements for low treatment costs are not strict, as in the treatment of certain radioactive waste streams (Gogolev *et al.* 2006) (I, updated)

3.3 Catalytic oxidative degradation

Oxidation of two different metal complexes of EDTA with molecular oxygen was studied under acidic conditions by Seibig and van Eldik (1997) and Zilbermann *et al.* (1998). According to the experiments with Fe^{II}EDTA complex, Fe^{II}EDTA is converted to Fe^{III}EDTA species before breakdown of the molecule (**Formulas 1 – 6**) (Seibig and van Eldik 1997). According to their suggested mechanism H₂O₂ is produced during the multi-step transformation reaction of Fe^{II}EDTA. Therefore, even in the case of molecular oxygen used, the actual oxidant may be hydroxyl radical. (I)



Most of the metal complexes of EDTA are known to form octahedral-bipyramidal complex, but e.g. [Fe^{II}EDTA-H₂O]²⁻ exists as a seven-coordinate form with a monocapped trigonal-prismatic geometry. In acidification, the metal-EDTA complex can be protonated to form a monoprotinated species, such as [Fe^{II}EDTAH-H₂O]⁻ adopting a pentagonal-bipyramidal geometry in solid state. With further acidification the diprotinated product [Fe^{II}EDTAH₂-O₂]⁻ predominates, and the complex adopts again a monocapped trigonal-prismatic geometry (Seibig and van Eldik 1997). Sillanpää *et al.* (2003) also studied the three dimensional geometry of metal complexes of e.g. EDTA, *Kuopio Univ. Publ. C. Nat. and Environ. Sci. 209: 1-83 (2007)*

DTPA, BCA6, and EDDS. According to their results, the iron complexes of all studied complexing agents, except DTPA and BCA6, were similar with only minor differences in bond lengths and angles. (I, updated)

3.4 UV induced oxidation processes

In UV induced oxidative degradation processes the metal speciation was reported to play an important role. The iron and copper complexes of e.g. NTA, EDTA, DTPA, and EDDS are generally known to be photolabile and therefore easily degraded if UV radiation is present. Manganese complexes, which are important in the pulp and paper mill waste waters (Rämö *et al.* 2000), are more recalcitrant to UV induced degradation than most of the other metal-EDTA or metal-DTPA complexes. In most publications the UV induced oxidation processes are used to remove minor concentrations of complexing agents from drinking water. In waste water treatment, limited UV penetration and high energy intensity practically prevent the adaptation of the method. On the other hand, new UV-LED based technology may raise new interest as a secondary treatment method for specific waste water streams, even if a prerequisite for low turbidity remains. (I, updated)

The published results concerning the pH dependence in the chemical degradation of EDTA are somewhat controversial. In photocatalytic degradation of CdEDTA and PbEDTA the pH does not seem to play an important role (Vohra and Davis 2000, Davis and Green 1999), but in photocatalytic degradation of NiEDTA acidic conditions are favourable (Madden *et al.* 1997). In UV/TiO₂ process acidic conditions are suggested to be favourable due to increased valence band hole potentials at lower pH values. On the other hand, at acidic conditions photolabile Fe^{III}EDTA species is thermodynamically favourable. The slow exchange kinetics naturally diminishes the importance of the above-mentioned matter (Madden *et al.* 1997). (I)

3.5 Biological degradation

Earlier studies considering decomposition of persistent complexing agents were focused on pure bacterial cultures capable of biodegrading EDTA. NTA has been known to be biodegradable for a long time (Means *et al.* 1980, Pfeil and Lee 1968,) and DTPA has been known resistant to biodegradation as EDTA (Means *et al.* 1980, Metsärinne *et al.* 2004). Aerobic gram negative bacterial strains DSM 9103 and DSM 6780 (BNC1) were

mentioned as the most promising ones in the degradation of EDTA (Klüner *et al.* 1998, Nörtemann 1999, Satroutdinov *et al.* 2000). No bacterial strain was found in literature to be able to degrade DTPA. (I)

3.5.1 Pure cultures

Uncomplexed EDTA was shown to inhibit growth of bacterial strain BNC1 presumably due to complexing and thus removing metals from the bacterial cell walls (Henneken *et al.* 1995). On the other hand, as said before, complexing agents are not present in waste waters in their uncomplexed forms. For biodegradation to take place by BNC1, EDTA must not be complexed with Fe^{III}, Co^{II}, Cd, Pb, Ni or Cu^{II}. Complexes with Ca and Mg are transportable through the cell membrane into the cell – and are possibly therefore biodegradable (Henneken *et al.* 1995, 1998; Klüner *et al.* 1998). Also for DSM 9103 which is located in the *Rhizobium-Agrobacterium* branch, Ca^{II}EDTA is the species that can undergo cellular uptake (Oviedo and Rodríguez 2003). Slow metal exchange kinetic has a remarkable role in the biodegradation of EDTA because of the strict speciation requirements. It is noteworthy that similar speciation dependency on biodegradation has also been found with other bacterial strains with other complexing agents, e.g. *Chelatobacter heinzii* and CaNTA (Willet and Rittmann 2003) or *Agrobacterium tumefaciens* and Ca^{II}/Fe^{II}IDA (Cokesa 2004; Cokesa *et al.* 2004). (I, updated)

The focus on the biodegradation of the complexing agents have been shifted to i) pilot scale reactors with actual sludge from WWTP possibly inoculated with the pure bacterial strain and ii) even more importantly to degradation studies with novel complexing agents. In the early 2000, studies focusing on pure bacterial strains seemed to be in the past or at least in minority: Some studies focusing on the influence of speciation on biodegradation were still published (Fang *et al.* 2003). (I, updated)

3.5.2 Biodegradation tests and laboratory studies

It is vital to mention that all seven different biodegradation tests reported in literature carried out for EDTA (Coupled units test, Zahn-Wellens test, MITI test, AFNOR test, Sturm test, OECD screening test and Closed bottle test) were in full agreement that EDTA is not biodegradable (Gerike and Fischer 1979). The European Union risk

assessment report (ECB 2005) confirms also that EDTA is not readily biodegradable. (I, updated)

At the same time, studies with more readily biodegradable complexing agents were performed. Especially biotechnologically produced ethylenediaminedisuccinic acid (EDDS) has been widely studied (Bucheli-Witschel and Egli 2001), as well as N-bis[2-(carboxymethoxy)ethyl]glycine (BCA3), N-bis[2-(1,2-dicarboxyethoxy)ethyl]glycine (BCA5), N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6), and N-bis[2-(methyl-carboxymethoxy)ethyl]glycine (MBCA3) (Metsärinne *et al.* 2007, Hyvönen *et al.* 2006). Also β -ADA (Sillanpää and Rämö 2001) and iminodisuccinic acid (IDA) (Hyvönen *et al.* 2003) have been suggested as possible substitutes for EDTA and DTPA in some processes. It is important to understand that when it comes to biodegradation, optical isomerization is an important factor; e.g. RR isomer of EDDS is resistant to biodegradation while RS and SS isomers are readily biodegradable (Takahashi *et al.* 1997). (I, updated)

3.5.3 Biodegradation of complexing agents in waste water treatment

Currently, it is a commonly accepted concept that both EDTA and DTPA can be degraded at biological WWTP if conditions are favourable. Some publications reveal that increased pH facilitates degradation. Perhaps a more practical approach is to increase sludge retention time (SRT) in order to increase the removal of complexing agents. There have also been reports that EDTA and DTPA may have a negative effect on the overall performance of a biological WWTP. However, based on literature, DTPA concentration up to 600 mg/l does not have any remarkable effect on the performance of WWTP (Larisch and Duff 1999). Such a high DTPA concentration is rather unrealistic. (I)

For EDTA removal, the optimum pH at the WWTP seems to be between 9 and 9.5, when a complete breakdown of the target molecule was obtained at a hydraulic retention time (HRT) of 1.5 hours (Gschwind 1992). It has been shown in several studies that EDTA can be removed at pH 8.5, in contrast to pH 6.5, suggesting that micro-organism use EDTA as a carbon and energy source only under alkaline conditions (Palumbo *et al.* 1994, van Ginkel *et al.* 1999^{a,b}, Virtapohja and Alén 1998). Biodegradability of metal-EDTA complexes present in waste waters is most expectably limited to complexes with Ca, Mg, and Mn (Henneken *et al.* 1995, 1998; Klüner *et al.* 1998; van Ginkel *et al.* 1999). (I)

1999^b). Thus, from thermodynamic point of view, it is reasonable that slightly alkaline conditions are favourable to biodegrade of EDTA. Exchange kinetics from Fe^{III}EDTA to CaEDTA is slow, half-life being approximately 20 days (Xue *et al.* 1995). Surprisingly enough, SRT of above 20 days was found to be necessary to remarkably remove EDTA in the first published studies (Gschwind 1992). More than ninety per cent removal of EDTA was later found with SRT of 12 or 10 days (Klünner *et al.* 1994, van Ginkel *et al.* 1999^a) (I)

3.6 Degradation products, intermediates, and pathways

The third approach to the research of the biological degradation of complexing agents is to study their degradation products and their degradation pathway. One interesting approach to the biodegradability is to study the presumable primary degradation products; if they are naturally occurring organic compounds the parent compound is more likely biodegradable. In the case of EDTA, the primary degradation products are biocidal (Takahashi *et al.* 1997 cited by Whitburn *et al.* 1999). Indeed, there are signs that EDTA and DTPA degrade only partially, which is sometimes difficult to identify. Though, being water-soluble, the degradation products remain in the water phase increasing the organic load and the amount of organic nitrogen in the treated waste water. Many of the primary and secondary degradation products of EDTA and DTPA are still able to form soluble complexes with metal ions, such as ethylenediaminetriacetic acid (ED3A), Ethylenediaminediacetic acid (EDDA), and iminodiacetic acid (IDA) (Figure 5). Some of the degradation products are expected to be even more recalcitrant to degradation than EDTA or DTPA themselves, such as 2-ketopiperazine-1,4-diacetic acid (KPDA), 2-ketopiperazine-1/4-acetic acids (KPMAs), and ketopiperazine (Nörtemann 1999, Nowack and VanBriesen 2005, ECB 2005). Baass *et al.* (2003) reported the primary biodegradation product of DTPA being ethylenediamineoxopiperazinetriacetic acid, which is strongly accumulated in the medium. The same observation for EDTA was also made in this study, but it was unfortunately published in the conference proceedings only (Pirkanniemi and Sillanpää 2001). (I, updated)

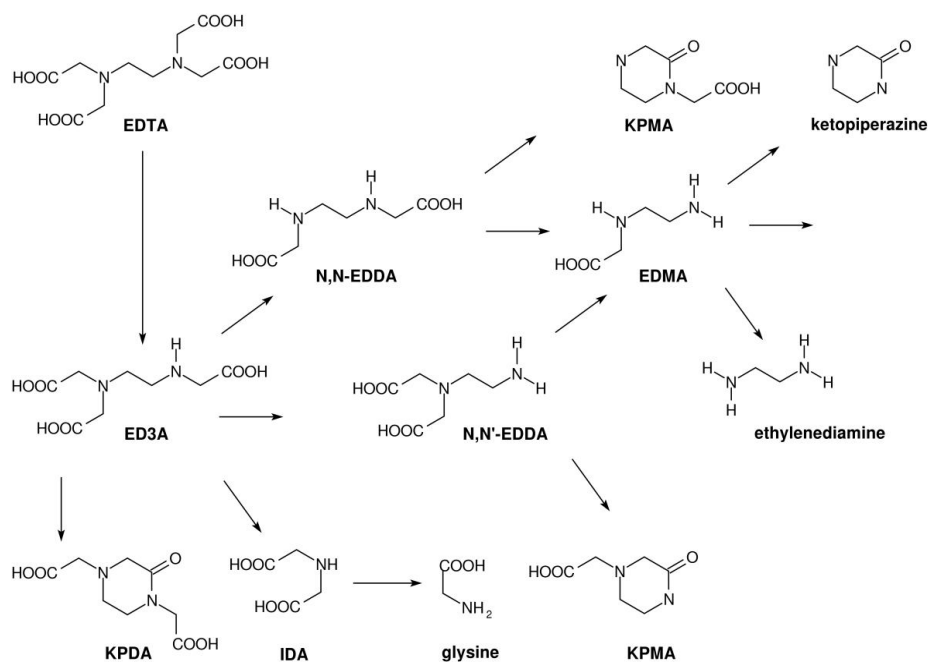


Figure 5. A collection of proposed and identified degradation products and pathways of EDTA. Pathways, intermediates, and degradation products are adapted from various sources, e.g. Gilbert and Beyerle (1992), Ternes *et al.* (1996, 1997), Höbel and Sonntag (1998), Sørensen *et al.* (1998), Krapfenbauer and Getoff (1999), Nörtemann (1999), Pirkanniemi and Sillanpää (2001), ECB (2004), Metsärinne *et al.* (2004), and Nowack and VanBriesen (2005). Further degradation intermediates are omitted. KPMA and KPDA have also been reported to form during sample preparation (esterification) by Alner *et al.* (1972). (I, updated)

4 HETEROGENEOUS CATALYSIS AS AN ENVIRONMENTAL APPLICATION

Heterogeneous water phase catalysis has been in focus for past years. In some cases, the term heterogeneous is in reality more or less misused, since the actual catalytic reaction is based on a leached catalyst, which was originally added as solid powder or as immobilized to a support. A reaction believed to be heterogeneous might after all be homogeneous. Rigorous proof of heterogeneity can be obtained only by filtering the catalyst at the reaction temperature before completion of the reaction and testing the filtrate for activity (Sheldon *et al.* 1998) (II).

In environmental applications the scale of used heterogeneous catalysts differs from those used in production processes. This can partly be explained by a need of a cheap catalyst, such as red mud or pillared clay, for waste water treatment. On the other hand, in production processes water is not typically used as a reaction medium, and because of that, many industrial catalysts are simply inapplicable. Among the catalysts studied in literature; zeolites, supported metal and metal oxide catalysts, and Fenton's catalysts are expected to have a relatively bright future in the oxidative treatment of certain waste water streams. In addition, in hydrogenation processes some novel approaches, such as so called fibre catalysts, are promising. (II)

Various noble metals (Ru, Pt, Rh, Ir, and Pd) and some metal oxides (Cu, Mn, Co, Cr, V, Ti, Bi, and Zn) have traditionally been used as heterogeneous catalysts. Very recently, immobilization of active homogeneous catalyst to support material has also increasingly gained interest as an environmental liquid phase application. This group of catalysts includes mainly some metal salts. (II)

One of the major drawbacks in the utilization of heterogeneous liquid phase catalysts is the relatively rapid deactivation of the catalyst in economically reasonable operating conditions. Heterogeneous catalyst may be deactivated mainly due to poisoning, sintering or leaching. Whatever the reason for deactivation, it is dependent on the catalyst, support, and treated water. Noble metals are highly sensitive to poisoning if halogen, sulphur or phosphorus containing compounds are present in the reaction media. With proper metal oxide support, poisoning of noble metal catalyst might be reduced. For example, alkali

metals and alkaline earth metals are suitable for this purpose. Hot and acidic medium promotes solubility of some metal oxides and therefore causes deactivation of heterogeneous catalysts by leaching of metal or metal oxide catalysts (Matatov-Meytal and Sheintuch 1998). (II)

4.1 Catalysts

Metal catalysts are almost with no exception noble metals. In most publications, metal catalysts were supported on metal oxide surface, e.g. TiO_2 , Al_2O_3 , ZrO_2 and CeO_2 or on activated carbon. Supporting noble metal catalyst on metal oxide surface has been reported to improve activity and stability of the catalyst (Matatov-Meytal and Sheintuch 1998). Also catalyst pretreatment such as calcination, sulphurization or reduction is an important factor, which affects remarkably final catalytic activity and/or stability of the catalyst (Karpel Vel Leitner *et al.* 2000). (II)

Metal oxides are classified according to physico-chemical properties. One of these properties is the stability of metal oxide. Metals with unstable high oxidation state oxides ($\Delta H_{298}^\circ < 9.5$ kJ/mol of O), such as Pt, Pd, Ru, Au, and Ag do not perform stable bulk oxides at moderate temperatures. Most of the commonly used metal oxide catalysts (Ti, V, Cr, Mn, Zn, and Al) have stable high oxidation state oxides ($\Delta H_{298}^\circ > 15.5$ kJ/mol of O). Fe, Co, Ni, and Pb belong to a group with intermediate stability of high oxidation state oxides ($\Delta H_{298}^\circ = 9.5 - 15.5$ kJ/mol of O). Another possible classification criterion is electrical conductivity: insulators have low electron mobility, and therefore their catalytic activity is generally poor. In addition, with some exceptions the n-type metal oxides are not catalytically active as oxidation catalysts. However, some of the non-conducting metal oxides are used as support in catalytic processes. According to Kochetkova *et al.* (1992), the catalytic activity of metal oxide catalysts during oxidation of phenol shows the following order: $\text{CuO} > \text{CoO} > \text{Cr}_2\text{O}_3 > \text{NiO} > \text{MnO}_2 > \text{Fe}_3\text{O}_3 > \text{YO}_2 > \text{Cd}_2\text{O}_3 > \text{ZnO} > \text{TiO}_2 > \text{Bi}_2\text{O}_3$. (II)

It is a well-known fact that metal oxides are usually less active catalysts than noble metals. Nevertheless, metal oxides are more suitable in many applications since they are more resistant to poisoning. In addition, combining two or more metal oxide catalysts may improve non-selectivity and catalytic activity, which may be an advantage in some environmental applications. (II)

4.2 Catalyst support materials

Usually supports are classified by their chemical nature in to organic and inorganic supports. Whatever the support material is, it plays an important role in immobilizing active catalyst. Principally, support has three main functions: i) to increase the surface area of catalytic material, ii) to decrease sintering and to improve hydrophobicity and thermal, hydrolytic, and chemical stability of the catalytic material, and iii) to govern the useful lifetime of the catalyst (Matatov-Meytal and Sheintuch 1998). Support may also improve the activity of the catalyst by acting as a co-catalyst. According to Cooper and Burch (1999), the presence of heterogeneous surface improves transfer of gaseous oxidant into the solution, which could also be understood as a function of the support.

(Paper II)

Reducing particle size increases surface area. Particle size cannot, however, be reduced unlimitedly, since pressure loss in industrial size reactors would increase remarkably. Other possibilities to increase the active surface area are to increase porosity or to apply appropriate support. By increasing the porosity the surface area of many common supports may be increased to 100 – 700 m²/g (BET). However, controlling reaction conditions inside the particles is difficult and porosity may decrease selectivity in some cases (Matatov-Meytal *et al.* 2001). With fibrous or woven support the active surface area of catalyst may be relatively high without any significant pressure loss (Andrews *et al.* 1996, Matatov-Meytal *et al.* 2000). Other support materials used in environmental applications include metal oxides, silica, zeolites, pillared clay, red mud, polymers and carbon black. **(II)**

4.3 Heterogeneous Fenton's reaction

Due to the differences in catalytic method, it is justified to approach Fenton's reaction separately from other metal or metal oxide catalyzed oxidation reactions. Iron or copper ions catalyze dissociation of hydrogen peroxide to hydroxyl radical and hydroxide ion (**Formula 7**) or to hydrogen ion and hydroperoxy radical (**Formula 8**) (Centi *et al.* 2000). **(II)**



Homogeneous Fenton's reaction is already in use in industrial waste water purification processes (Centi *et al.* 2000, Gogate and Pandit 2004^{a,b}). Several studies have been published concerning supporting Fenton's catalyst to various carriers, such as brick grain (Chou *et al.* 2001), MgO (Pak and Chang 1999), SiO₂ (Huling *et al.* 2000) and zeolite (Centi *et al.* 2000). Also copper or iron containing pillared clays were used as Fenton's catalysts (Abdellaoui *et al.* 1999, Barrault *et al.* 2000). In past years, waste water treatment with heterogeneous Fenton-like or photo-Fenton-like catalysts has become more common (Zheng *et al.* 2004, Yip *et al.* 2005). (II, updated)

4.4 Other catalytic heterogeneous oxidation processes

Traditional non-catalytic water phase oxidation processes need long reaction time, relatively high temperature (≥ 200 °C) and pressure (70 – 250 atm). When heterogeneous catalysts are utilized, reaction conditions in many cases can be turned milder. In environmental catalytic water phase processes an oxidant used is typically air or dioxygen. However, hydrogen peroxide and ozone are used as well. The low solubility of oxygen in water and the slow rate of air-to-liquid mass transfer limit the use of compressed air. Increase of pressure enhances solubility of oxygen, but it also increases running costs (Matatov-Meytal and Sheintuch 1998). It must be noted that when expensive reactants such as hydrogen peroxide or ozone are used, the running costs are high and therefore such processes should not replace more economic treatment methods such as biological degradation. However, some industrial waste streams may be too toxic or recalcitrant to be treated biologically, and this is where catalytic oxidation – or hydrogenation as well – is economically most favourable. (II)

4.4.1 Semiconductor photocatalysis

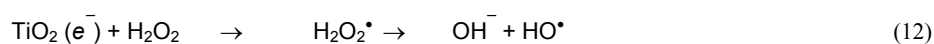
When aqueous solution of semiconductor photocatalyst, such as TiO₂ is excited with ultraviolet light ($\lambda < 380$ nm), electron-hole pairs develop (**Formula 9**). These electron-hole pairs have an oxidizing potential of 2.9V versus normal hydrogen electrode (NHE), which is enough to oxidize most pollutants present in aqueous waste streams (Hofstadler *et al.* 1993). (II)



The hole produced by irradiation reacts with water or surface-bound hydroxyl ion producing hydroxyl radical (**Formulas 10 and 11**) (Baird 1997). (II)



Electron released by irradiation of photocatalyst combines with dissolved molecular oxygen to produce superoxide radical, $\text{O}_2^{\bullet-}$ (Baird 1997). Hydrogen peroxide possibly added acts as an oxidant, but also as an electron scavenger instead of dissolved molecular oxygen (**Formula 12**). $\text{H}_2\text{O}_2^\bullet$ dissociates to hydroxyl radical and hydroxide ion even easier than H_2O_2 , because of presence of an extra electron (Hofstadler *et al.* 1993, Baird 1997). (**II**)



The major drawbacks in photocatalytic degradation of waste waters are i) the waste water is required to be transparent so as to enable absorption at the spectral region of semiconductor and ii) the slow complete mineralization in some cases (Herrmann *et al.* 1993). Some ideas have been published to enable use of photocatalysis even when the waste water is not transparent enough. In multiple tube reactor with TiO_2 coated hollow glass tubes UV light travels through the inside of hollow tubes while waste water flows over the outside of the tubes (Ray and Beenackers 1998). A similar idea is to embed TiO_2 into glass fibers to increase the penetration of UV light into the waste water solution (Hofstadler *et al.* 1993). (**II**)

4.5 Heterogeneous hydrogenating processes

Hydrogenation is a class of chemical reactions in which the net result is an addition of hydrogen. In environmental applications hydrogenation is studied in the treatment of hazardous waste, e.g. as hydrodechlorination. Contrary to oxidative treatment methods there is no risk of the formation of polychlorinated dibenzo-*p*-dioxines or furans (PCDD/F) (Frimmel and Zdražil 1995, 1997). (**II**)

Hydrogenation based denitrification of drinking water in the presence of noble- or transition metal catalyst is a promising method. However, at the current stage of development ammonium formation is still a severe problem. (Matatov-Meytal and Sheintuch 1998). (**II**)

5 MATERIALS AND METHODS

5.1 Sampling

Bleaching liquor samples from pulp mill and integrated pulp and paper mill waste water samples were obtained from mills known not to use complexing agents in their processes. Samples were kept refrigerated and in the dark. (V)

Waste water samples from surface treatment plants were collected in 2003 – 2006 largely during the pendency of environmental permit applications. Since the samples were collected within a four-year time scale, analytical methods and to some extent personnel performing the analyses had changed along the way. Results are thus not fully comparable from the analytical point of view. Samples were kept in the dark and frozen to prevent biodegradation, if not analyzed within five days. (VI)

5.2 Toxicity assays

The 24-hour toxicity assay with *Daphnia magna* was performed according to a standard SFS-EN ISO 6341:1996(E) (SFS 1996) and OECD Guidelines for Testing of Chemicals (OECD 2000) with slight modifications. Test organisms were less than 24 hours old females of the freshwater crustacean *D. magna*. Temperature was maintained at 21 ± 1 °C and a dark-light regime of 16 hours of light and 8 hours of darkness was used with a light intensity of less than 1000 lx. For each test concentration, three replicates with five daphnids in each were studied. The highest concentration of complexing agents and their metal complexes used for the toxicity assay with *D. magna* was 900 mg/l and 5 – 7 further diluted concentrations were used. Before the assays, test medium was aerated for two hours, but during the test, aeration was not used. The results obtained from toxicity assay are expressed as 24-hr.LC₅₀ values with 95% confidence interval. (III)

Toxicity assay with *Raphidocelis subcapitata* was performed according to a Finnish standard SFS 5072 (SFS 1986). Temperature was maintained at 22 ± 1 °C throughout the 72-hour test. Two simultaneous experiments were performed for each test concentration and the highest concentration of complexing agents was 1000 mg/l. The growth was estimated with in vivo fluorescence of chlorophyll (Labsystems, Fluoroskan Ascent) and

the results obtained from the toxicity assay are expressed as 72-hr.EC₅₀ values with 95% confidence interval. (III)

The Microtox[®] toxicity assay with *Photobacterium phosphoreum* was performed with BioOrbit 1257 luminometer and Biotox[®] test kit (BioOrbit Oy, Finland) according to the standard procedure described in the manual provided by the manufacturer. The light intensity was recorded before, and 15 minutes after an addition of the complexing agent solution to the test medium. Two simultaneous experiments were performed with each test concentration. The results obtained from the test are expressed as 15-min.EC₅₀ values with 95% confidence interval. (III)

5.3 Analytical methods

5.3.1 UV-vis spectrophotometry

The concentration of EDTA and other complexing agents were determined by UV-vis spectroscopy method according to Bhattacharyya and Kundu (1971) using Shimadzu UV-160 UV-vis spectrophotometer. The method to measure EDTA concentration is based on the absorbance maxima of Fe^{III}EDTA complex and trivalent iron at 258 nm and 305 nm, respectively. Under acidic conditions and with excess trivalent iron, the concentration of complexing agent can be determined by measuring the absorbance at these two wavelengths. The same method was adapted to measure the concentrations of the other complexing agents studied with slight shift in wavelengths of absorbance maxima of iron complex. The linear absorbance range of Fe^{III} complexes is roughly 10⁻⁵ – 7·10⁻⁵ M with all studied complexing agents. The method by Bhattacharyya and Kundu (1971) was selected because at the wavelength range used there was no significant influence caused by the absorbance of the blue-coloured catalysts. The analytical method and the data analysis with EDTA and other complexing agents are described more in detail earlier (Pirkanniemi 2000) (IV)

5.3.2 Gas chromatography

EDTA and DTPA were analyzed as their ethyl esters with Agilent Technologies 6890N gas chromatograph equipped with flame ionizing detector (GC-FID). The column was an HP-5 capillary column (30 x 0.25mm i.d.) with a 0.25 μm film thickness. Helium at a constant flow rate (3.5 ml/min) was used as a carrier gas. The injector and detector

temperatures were 300 °C and the column oven temperature program was as follows: initial temperature 100 °C (held for 3 min); increased at 15 °C/min to 290 °C; held for 10 minutes. Injection volume of 3 µl was used. Sample preparation was adopted from Sorvari *et al.* (1996). The temperature program was adopted from Virtapohja and Alén (1999). (V)

NTA, EDTA, DTPA, and HEDTA were analyzed as their ethyl esters with HP 6890 gas chromatograph equipped with mass selective detector (GC-MS). The column was an HP-5 capillary column (30 x 0.25mm i.d.) with a 0.25 µm film thickness. Helium at a constant flow rate (1 ml/min) was used as a carrier gas. The injector and detector temperatures were 250 °C and the column oven temperature program was as follows: initial temperature 100 °C (held for 1 min); increased at 60 °C/min to 200 °C; held for 5 minutes; increased at 50 °C/min to 250 °C and held for 9 minutes. Injection volume of 1 µl was used. Sample preparation and GC-MS specific matters were adapted from Sorvari *et al.* (1996). (V and VI)

5.3.3 Liquid chromatography

NTA, EDTA, DTPA, HEDTA, and THPED were analysed as their 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 FeCl₃ in 0.01 M HCl was used to convert the different complexing agent species into their Fe^{III} complexes. Unfortunately iron complexes of HEDTA and NTA were not possible to be distinguished and results were therefore verified by GC-MS. The samples were analyzed by two nearly identical methods and equipments. (V and VI)

Sample series A. Samples were diluted with 0.001 M FeCl₃ solution in proportion 1:4. Fe^{III} complexes were allowed to form for at least thirty minutes or overnight 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 x 0.46 cm i.d.), UV detection was at 240 nm, column temperature 30 °C and injection volume 15 µl. A 15 per cent methanol and 85 per cent tetrabutylammoniumbromide (0.02 M) eluent was used with flow rate of 2 ml/min. The data was analysed with HP ChemStation software. (VI)

Sample series B. 9 ml of sample was mixed with 1 ml of 0.001 M FeCl₃. Fe^{III} complexes were allowed to form overnight in the dark. Analyses were made using HPLC with a Perkin Elmer Series 200 pump and Perkin Elmer Series 200 UV/VIS-detector. The analytical column was Phenomenex LUNA 5 μ C18(2) (25 x 0,46 cm), UV detection was at 254 nm, column temperature 20 °C and injection volume 20 μ l. A 10 per cent methanol, 0.002 M tetrabutylammonium-bromide, and 0.03 M sodium acetate eluent was used with a flow rate of 1.2 ml/min (pH of the eluent was adjusted to 3.25). The data was analysed with TotalChrom Navigator-LC software. (VI)

BCA5 and BCA6 were analyzed as described by Metsärinne *et al.* (2005). A 0.01 M tetrabutyl ammoniumhydroxide solution was prepared in distilled water and the pH of the solution was adjusted to 7.2 using 85 per cent *o*-phosphoric acid. Tetrabutyl ammoniumhydroxide and methanol were mixed in proportion 1:1. 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 x 0.46 cm i.d.), Analytical conditions were as follows: flow rate was maintained at 1 ml/min, injection volume 25 μ l, and detection wavelength 260 \pm 5 nm. The column temperature was 36 °C. The data was analysed with HP ChemStation software.(V)

5.3.4 Metal analysis by ICP-AES

Metal analyses were performed with Thermo Elemental IRIS Intrepid II XDL Duo ICP-AES. pH was adjusted to approximately three with 0.1 M H₂SO₄ to dissolve precipitated metals. Then the samples were filtrated through 0.45 μ m cellulose membrane filters (Millipore). In some samples all precipitates were not dissolved completely and therefore in those cases the metal concentrations are not accurate. Before the final metal analysis with ICP-AES, samples were diluted to concentration up to 10 mg/l for each metal. (VI)

5.3.5 TOC analysis

TOC analyses were performed with Shimadzu TOC 5000A TOC analyzer equipped with ASI 5000A auto sampler. Before the analysis, pH was adjusted to approximately three to maximize the solubility of metal ions. When visible precipitates were still present, samples were filtrated (0.45 μ m Millipore filter). When the sample was filtered the result was expressed as dissolved organic carbon (DOC). (VI)

6 RESULTS AND DISCUSSION

6.1 Short-term toxicity of complexing agents

As expected, the complexing agents proved rather non-toxic themselves in all three toxicity assays. They also proved capable of reducing metal toxicity by binding them into a stable complex. Especially DTPMP, which forms the most stable complexes, was capable of reducing cadmium toxicity. From the environmental point of view this is however not beneficial; the more stable a metal-complexing agent complex is, the lesser the possibility for it to degrade at the WWTP. This increases the heavy metal pass through at the WWTP and this also increases nitrogen load to the receiving waters. In addition, if DTPMP was used, phosphor load to the receiving waters increases. **(III)**

It is important to understand that metal complexes are more toxic than uncomplexed complexing agents and at the same time less toxic than the metals themselves. It could be summarized that from the toxicological point of view, the most important characteristics of complexing agents are their ability to keep metals biologically available by delaying their sedimentation. **(III)**

The short-term toxicity of complexing agents with *Daphnia magna* is highly dependent on the metal, as seen in **Figure 6**. It is evident that the free complexing agents and their Mn complexes are relatively non-toxic compounds. Uncomplexed gluconic acid (GA) and β -ADA, as well as Mn- β -ADA and Mn-DTPMP did not yield any LC₅₀ value what so ever even at the highest concentration of 900 mg/l. In practice, it is unrealistic to study short-term toxicology at higher concentrations. **(III)**

There was no significant difference in the toxicity between the free complexing agents and their Mn complexes, except in the case of GA. Mn-GA proved more toxic than uncomplexed GA. On the contrary, Cd complexes were dramatically more toxic than free complexing agents or Mn complexes. This reveals that the the source of toxicity of Cd complexes is coming from Cd toxicity. This is also in agreement with previous results with DTPA (Sorvari and Sillanpää 1996). According to the results, the toxicity of equimolar Cd complexes, other than Cd-DTPMP, was quite similar to what have been reported as the toxicity of plain Cd (0.2 mg/l, 48-h.LC₅₀ *D. magna*) (Sankaramanachi and

Qasim 1999). The toxicities obtained by Sorvari and Sillanpää (1996) were basically in the same range as the results presented here yielding the EC_{50} values of 610 and 940 mg/l with EDTA and MnEDTA, respectively. The toxicities of other Cd complexes studied were more than tenfold the toxicity of Cd-DTPMP (**Figure 6**). This can be explained by the fact that DTPMP forms thermodynamically strongest complexes with metal ions among the complexing agents studied. Consequently, it is able to reduce the Cd toxicity more than the other complexing agents. This impact is however rather insignificant, since Cd-DTPMP is still more than 270 times more toxic than uncomplexed DTPMP. In earlier study by Sorvari and Sillanpää (1996), the 24-h. EC_{50} value with Cd-EDTA was 310 mg/l, which is several orders lower than the toxicity (LC_{50}) of all of the Cd complexes presented here. Even though the results are not fully comparable due to the renewed SFS standard, it can be seen that EDTA forms a highly more stable complex than the complexing agents in this study and is therefore able to reduce Cd toxicity. It is notable that from the environmental point of view, the ability to reduce heavy metal toxicity of complexing agents is in the end meaningless or can even have a negative impact, if their use increases heavy metal pass-through at the WWTP. (III)

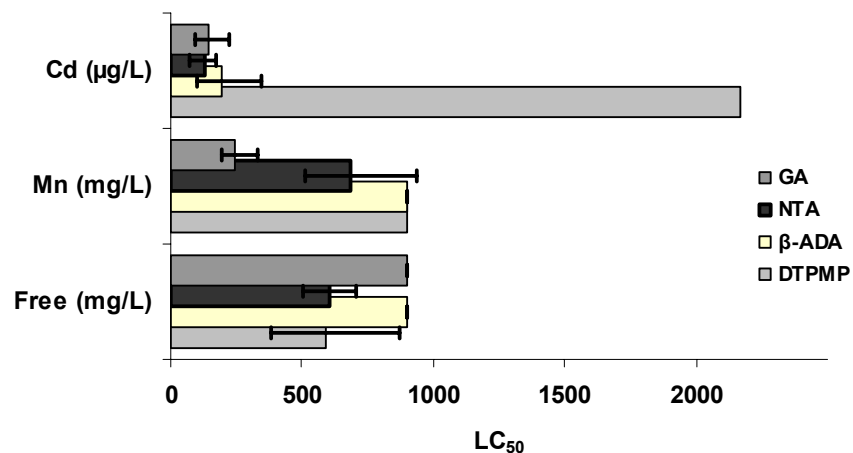


Figure 6. 24-h. LC_{50} values of free complexing agents and their Mn and Cd complexes obtained with *D. magna*. Note: LC_{50} of Cd complexes are expressed in $\mu\text{g/l}$ rather than mg/l.

The results obtained with the toxicity assay with *Raphidocelis subcapitata* are rather similar to those obtained with *D. magna*. The short-term toxicity of uncomplexed DTPMP is approximately 10 – 15 times higher (EC_{50} value 6 mg/l) than those of GA, β -ADA, and NTA (EC_{50} values 76, 69, and 96 mg/l, respectively). Mn-GA, Mn-NTA and Mn- β -ADA were significantly more toxic than their uncomplexed species, while Mn had no impact on the DTPMP toxicity (**Figure 7**). This observation is logical for DTPMP, since it forms much more stable Mn-complexes ($\log K_{\text{Mn-DTPMP}} = 13.6$) than other complexing agents studied ($\log K_{\text{Mn-}\beta\text{-ADA}} = 7.3$ and $\log K_{\text{Mn-NTA}} = 7.5$) (**Table 2**). Some enhancement in the algal growth in the presence of Mn complexes was observed when concentrations of 0.32 mg/l or lower were used. However, the most stimulating concentration was not measured. The growth stimulation may be explained by the presence of stimulating Mn or by the ability of algae to use nitrogen from NTA and β -ADA for its metabolism. However, in both cases, at least a partial breakdown of the Mn complex is required and, therefore, both stimulating factors were available to the alga. Both NTA and β -ADA are known – as earlier mentioned – to be readily biodegradable. (III)

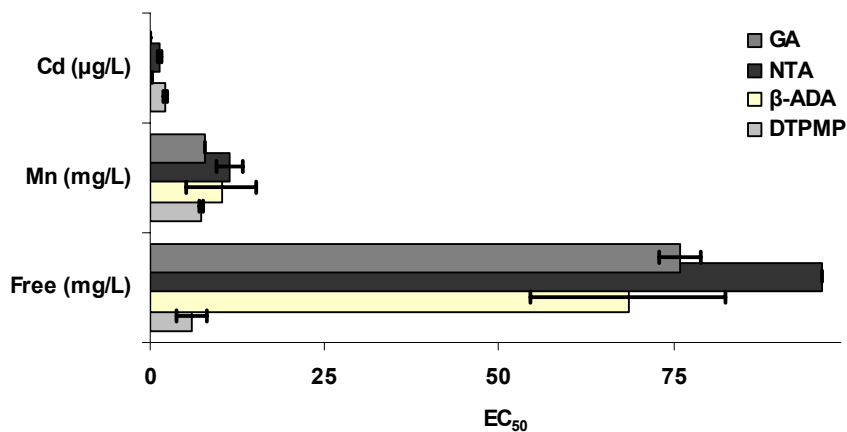


Figure 7. 72-h. EC_{50} values of free complexing agents and their Mn and Cd complexes obtained with *R. subcapitata*. Note: EC_{50} of Cd complexes are expressed in $\mu\text{g/l}$ rather than mg/l.

The clear stimulating effect for *Photobacterium phosphoreum* was observed with especially DTPMP and Mn-DTPMP, when lower concentrations were used. In addition, Mn- β -ADA and Mn-NTA increased the bioluminescence by approximately 10 per cent. In contrast to *R. subcapitata*, DTPMP was less toxic for *P. phosphoreum* than GA or β -ADA (**Figure 8**). All free complexing agents were relatively non-toxic, in particular if compared to the toxicities of DTPA or especially EDTA (EC_{50} values 125 and 3.17 mg/l, respectively) (Sillanpää and Oikari 1996). Mn-GA was the only Mn complex that revealed higher toxicity than the corresponding free complexing agent. This can be explained by the weaker thermodynamic stability of the Mn-GA compared to other Mn complexes. Thus, GA is unable to reduce the toxic action of Mn. In the case of uncomplexed NTA, the toxicity achieved in this study with Microtox[®] is over six times lower compared to what Sankaramanachi and Qasim have published (1999). This difference in results needs further examination. Unfortunately, other published results of toxicity of uncomplexed NTA with Microtox[®] toxicity assay were not found. Otherwise, the results are in great agreement. Similarly to the results obtained with the other two bioassays, the Cd complexes proved several orders more toxic than free complexing agents or their Mn complexes. Again, DTPMP was able to reduce the toxicity of Cd more than other complexing agents, yielding EC_{50} value comparable to earlier published results with Cd-EDTA and Cd-DTPA (1.87 and 0.69 mg/l, respectively) (Sillanpää and Oikari 1996). (III)

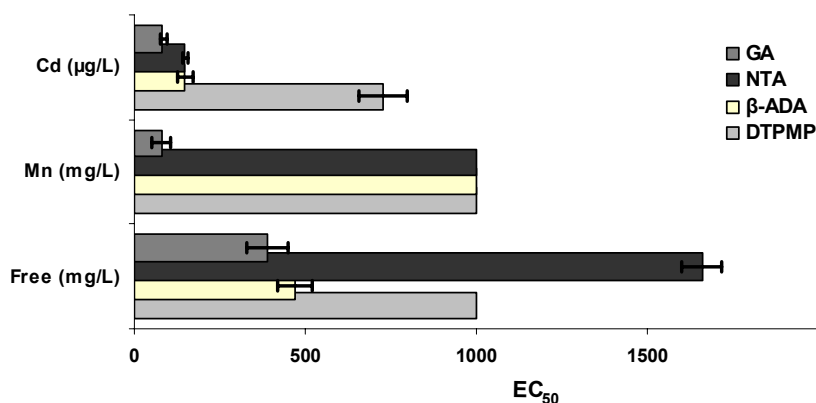


Figure 8. 15-min. EC_{50} values of free complexing agents and their Mn and Cd complexes obtained with *P. phosphoreum* toxicity assay (aka Microtox[®]). Note: EC_{50} of Cd complexes are expressed in $\mu\text{g/l}$ rather than mg/l.

R. subcapitata proved far more sensitive to studied complexing agents and their metal complexes than either of the other two organisms. *R. subcapitata* proved five to ten times more sensitive compared to *P. phosphoreum* with all other free complexing agents, except DTPMP, for which the difference was even more remarkable (**Figures 6 – 8**). With all complexing agents, the sensitivity of *R. subcapitata* comparable to *P. phosphoreum* also increased further, when Mn or Cd were bound with them. *D. magna* was not as sensitive as the other two toxicity assays were. Cd-DTPMP proved less toxic than the other two Cd complexes. Again, DTPMP, which is the most stable complex from the thermodynamic point of view, had the best ability to reduce the toxicity of Cd. It is, however, important to understand that even though DTPMP was capable to reduce the Cd toxicity to some extent, it does not make DTPMP any superior from the environmental point of view. As a matter of fact, higher stability of metal-DTPMP complexes would possibly increase the pass through of these toxic heavy metals from the WWTP. In addition, DTPMP is the only phosphor containing complexing agent in this study – which is its major drawback – since phosphor has a key role in eutrophication. . The sensitivity of the toxicity assays decreased in the following order: *R. subcapitata* > *P. phosphoreum* ≥ *D. magna*. However, the sensitivity of the toxicity assays to Mn complexes decreased in the following order: *R. subcapitata* > *D. magna* > *P. phosphoreum*. (**III**)

6.2 Catalytic oxidative degradation of complexing agents

6.2.1 Metallophthalocyanines as catalyst

In degradation experiments, five metallophthalocyanine (MePcS) catalysts, namely FePcS, MnPcS, CoPcS and NiPcS, were studied in the degradative oxidation of NTA, β -ADA, EDTA, DTPA and DTPMP with H₂O₂. The studied catalytic oxidation method proved effective in the oxidation of most studied complexing agents with used catalyst : substrate : H₂O₂ molar ratio of 1 : ~10 : ~100. Among five studied metallophthalocyanines (MePcS), FePcS proved most active, while manganese, nickel and chromium containing catalysts showed practically no catalytic activity (**Figure 9**). (**IV**)

Metal speciation proved an important factor in the degradability of Mn, Zn, Ca, Cu and Fe complexes of the studied complexing agents (**Figure 10**). Iron complexes were far more degradable than the others. It has to be underlined that the well-known photolability did not play any role in these experiments, since the sample vials were carefully protected against light. Also the poor degradability of copper complexes, which also are

photolabile, proves that photodegradation did not play any role. In contrary to EDTA, DTPA was practically nondegradable, except when complexed with iron. This is an unfortunate observation, since the importance of DTPA in the pulp and paper industry is the factor that practically limits the possibility of the adaptation of MePcS catalyzed oxidative degradation to the minimum. (IV)

The most active catalyst among studied MePcS's was FePcS while MnPcS, CoPcS, and NiPcS showed practically no catalytic activity (Figure 9). CoPcS exhibited some catalytic activity in degradation of β -ADA, NTA, DTPMP and DPTA, but was inactive in the oxidation of EDTA. In the presence of FePcS the degradation of uncomplexed complexing agents increases in order DTPA < β -ADA < DTPMP < NTA < EDTA. In latter case 54 per cent of pollutant was eliminated after one hour. In the case of DTPA, the primary degradation products could also form iron complexes, and therefore could affect the results in spectrophotometric analysis. Therefore, in some particular cases the spectrophotometric method could show increased concentrations of complexing agent even though cleavage of the side group might have happened. Attempts to resolve this problem using GC-MS were mostly unsuccessful. However, the results obtained were in the same range with those from GC-MS. Some degradation products of EDTA, such as ED3A, EDDA, and KPPS's were also identified (Pirkanniemi and Sillanpää 2001). (IV)

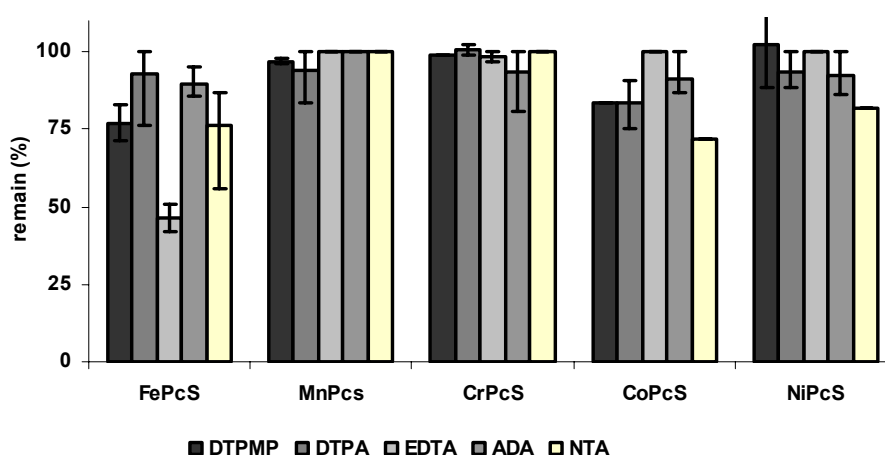


Figure 9. The degradability of complexing agents using several MePcS' as catalyst.

Surprisingly, the catalytic activity of FePcS towards β -ADA, which on the other hand is relatively biodegradable, was quite low: Only ten per cent could be eliminated within an hour. On the contrary, NTA, which is structurally quite similar to β -ADA and also readily biodegradable, was degraded more efficiently. Taking into account the superior catalytic activity of FePcS, which was also observed in earlier studies by Sorokin *et al.* (1995), it was selected to be used in further studies. (IV)

Speciation of the complexing agents is an important factor, which determines their biodegradability, photodegradability, toxicity, bioavailability, and adsorption characteristics. It is important to study not only the degradability of free complexing agents, but also the degradability of their most common and important metal complexes. This work studies degradability of five complexing agents both uncomplexed and complexed with five metals, namely Ca, Fe^{III}, Mg, Cu, and Zn as well as sodium complexes (marked as 'free' in the Figures). FePcS was used as catalyst in these experiments. Within a contact period of an hour, the degradation of iron complexes of all complexing agents studied was sixty to one hundred per cent (Figure 10). It is noteworthy that during all experiments the samples were strictly protected against solar irradiation. The well-known photolability cannot therefore be an explanation for the better degradability of Fe^{III} complexes. On the contrary, copper, calcium and zinc complexes were poorly degradable. However, NTA and β -ADA complexes of these metals were more readily degraded. This is quite expectable, since the complex formation constant of NTA complexes of Cu, Ca and Zn are generally low relatively to those of other complexing agents studied. (IV)

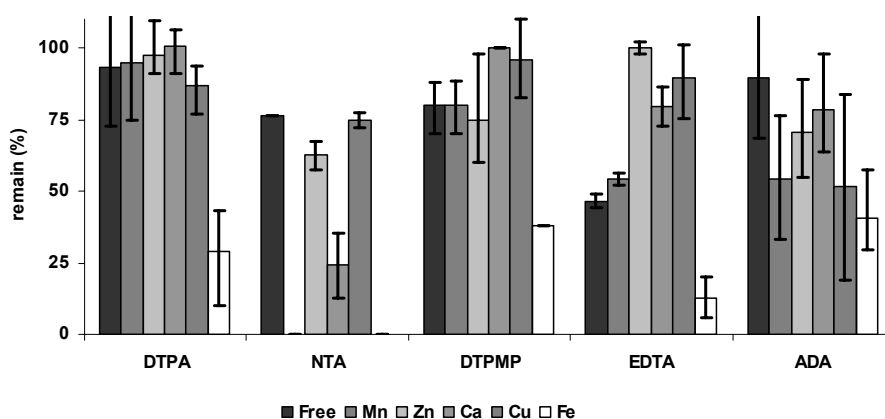


Figure 10. The degradability of the complexing agents with MePcS catalyzed H₂O₂ oxidation method.

The complex formation constants of Zn- β -ADA and Ca- β -ADA were not available when article was published. However, due to the structural similarity between β -ADA and NTA, it was reasonable to suggest that the complex formation constants are at the same level, which is the case (**Table 2**). On the other hand, correlation between complex formation constants of metal complexes and their degradability was found only in the case of NTA. In the case of β -ADA (especially Cu- β -ADA), the experimental errors in determination of final concentrations were high, owing to the difficulties in analytical procedure. However, the easier degradability of iron and manganese complexes can be clearly seen. The highest activity is in most cases achieved in the beginning of the experiment when all concentrations are higher. However, the most relevant iron, manganese, sodium, copper and calcium EDTA complexes can be successfully eliminated, the conversions being 93, 76, 68, 62, and 49 per cent, respectively, after three hours of reaction. The reason for the stability of ZnEDTA complex is not yet understood. (IV)

Study with MePcS's as catalyst was planned be a base for further studies with immobilized heterogeneous catalysts. Four types of heterogeneous metallophthalocyanine catalysts impregnated in silica were prepared, but none of them showed any catalytic activity whatsoever in water-phase degradation of complexing agents. Impregnated heterogeneous metallophthalocyanine catalysts were supported according to published methods (Sorokin and Tuel 1999, 2000) and obtained from the first author of the above-mentioned articles. The surface areas of amorphous and mesoporous silicas were 180 – 612 m²/g and phthalocyanine species supported were FePcS, FePc(CH₂Cl)₄, and FePc(NO₂)₄. (IV, updated)

6.2.2 Fenton's reagent as catalyst

Fenton's reaction was used for the degradation of complexing agents in two kinds of spiked pulp and paper mill waste waters, namely bleaching effluent and integrated waste water. EDTA, BCA5, and BCA6 were used as complexing agents. Temperature and pH dependence of degradation of EDTA and BCA5 in spiked bleaching effluent was also tested (**Figure 11**). It is generally known that pH slightly below three is favourable for Fenton's reaction to take place. At pH above three ferric ion is known to form oxides, hydroxides, and oxohydroxides that tend to precipitate (Ghiselli *et al.* 2004). In this study, there seemed to be a remarkable difference between pH values three and four, 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 degradation of EDTA or BCA5 was found in pH 4 at 20 °C. In 60 °C both pH 3 and pH 4 yielded the same level of degradation with BCA5 within three minutes. It could, therefore, be assumed that change in speciation to 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 time of EDTA degradation. (V)

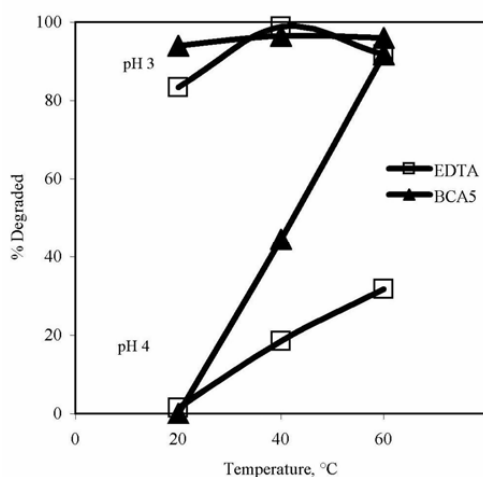


Figure 11. Degradability of EDTA and BCA5 with Fenton's reagent in temperatures 20, 40, and 60 °C and pH 3 and 4. (V)

Degradation experiments with BCA5 and BCA6, as seen in **Figure 12**, did not show any remarkable difference in degradation of complexing agent in waste water and bleaching effluent as in the case of EDTA. 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 mM solution (Metsärinne *et al.* 2005), which results, in experiments with BCA6, to higher catalyst concentration. Initial molar ratio of H₂O₂ and EDTA (70:1) is undoubtedly high enough enabling oxidation of other compounds as well. It could also be assumed that in the presence of 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. No difference in final degradation level of BCA5 or BCA6 compared to EDTA in integrated waste water was found. This is, however, because the Fenton's reaction was able to degrade also EDTA effectively in the chosen reaction conditions. In experiments with spiked bleaching water, BCA5 and BCA6 were found more readily degradable as seen in **Figure 12. (V)**

Fenton's process proved highly effective in degradation of EDTA in spiked integrated pulp and paper mill waste water. With an initial molar ratio of 70:1 (H₂O₂ : EDTA) or higher, degradation of EDTA was nearly complete within 3 minutes of reaction time. In bleaching effluent the reaction was remarkably slower, yet higher compared to typical results from the traditional biological treatment of pulp and paper mill waste waters.

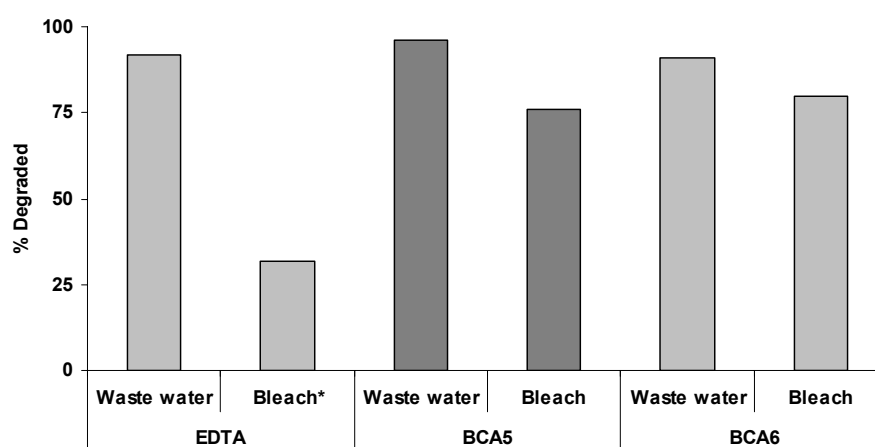


Figure 12. Degradability of EDTA, BCA5, and BCA6 in spiked waste water and bleach. (V)

Lower EDTA degradation level at pH 4 and mild temperature in bleaching effluent is a major drawback. It is, however, possible that there was more ferrous iron in integrated waste water to improve the catalytic activity. There apparently is higher concentration of organic matter and presumably other chemical compounds competing with EDTA for Fenton's catalyst in bleaching effluent. Fortunately, pH 4 and higher temperature yielded high removal of EDTA. According to the results, it is clear that Fenton's process is efficient in degradation of EDTA; with low molar ratios of Fe^{II} : EDTA, there is no uncomplexed ferrous iron present and therefore no degradation occurs, which proves that Fe^{II} is 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. 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. If the complexing agent is readily biodegradable, the use of Fenton's process for degradation as a pre-treatment method is, however, unreasonable. (V)

6.3 Complexing agents in industrial waste waters

In analyses of Finnish electrolytic and chemical surface treatment factories the complexing agent concentrations were investigated. Industry was known to have a trend in replacing EDTA in some process baths – mainly in degreasing phases – with more readily biodegradable ones, such as NTA. On the other hand, there are published studies on chemically more stable complexing agents in surface treatment industry, especially in such use where the costs of bath liquid in remarkable and increased stability is therefore a major economical issue. Strong complexing agents, such as 1,2-cyclohexanediamino-tetraacetic acid (CDTA) and diethylenetriaminepentamethylenephosphonic acid (DTPMP) are studied therefore to improve bath stability (Saloniemi *et al.* 2002). Increased quality requirements also feed the need for research of many novel stable complexing agents, such as cryptand-222 or then (Hancock 1997) and triethylenetetra-aminehexaacetic acid (TTHA) (Jusys *et al.* 1999). Also DTPA was expected and proved to be more widely used than e.g. the BREF indicates. (VI)

Half of the waste water samples from Finnish electrolytic and chemical surface treatment plants were found to have noticeable concentrations of complexing agents. EDTA and DTPA concentrations were up to 1.2 and 1.4 mg/l, respectively. DTPA seems to be the

most commonly used complexing agent in facilities with coppering processes, but also in some facilities with degreasing and pickling processes only. HEDTA and THPED were not positively identified with HPLC and other peaks representing possible complexing agents for further study with GC-MS were not found either. In some samples analyzed with HPLC, high iron concentration prevented detecting complexing agents in general. Therefore, when results obtained with HPLC were not clear, they were confirmed with GC-MS. With HPLC, NTA and HEDTA were not possible to be distinguished and therefore only the presence of either one was detected. According to chemicals used in the facilities, this unrecognized compound was expected to be HEDTA in one case, but in other cases NTA. Interestingly, there were traces of NTA in many waste waters, which could have otherwise been explained as a common impurity of EDTA, but EDTA was not found in these samples. In degreasing baths EDTA seems to be replaced by NTA rather commonly nowadays. Also traces of HEDTA were found in some cases, but it was most probably a degradation product of EDTA in process baths and therefore not included in the results in **Table 3. (VI)**

When metal concentration, calculated as a sum of Cr, Cu, Fe, Mg, Mn, Ni, and Zn was low, no complexing agents were present either. This is rather obvious because if concentrations of metals are low due to the high rinsing water consumption, the concentrations of complexing agents are low too. According to the results, if complexing agents are present, metals are present also, which, on the other hand, can also be understood as low metal concentrations means low complexing agent concentration. This observation supports the bases of the traditional compliance monitoring by underlining the importance of limiting metal concentrations in waste waters of the metal industry. It is also noteworthy that not all facilities use complexing agents studied and therefore no correlation can be made between different concentrations. **(VI)**

According to these results, it can be roughly estimated that the total complexing agent load to receiving waters from Finnish surface treatment plants is up to one ton. This estimation is very inaccurate, since it is based on concentrations of single samples and in many cases the complexing agent concentration was below analytical determination limit ($S/N=3$). Samples were, however, taken from fifty per cent of such facilities in Finland. Also, TOC and metal concentrations were comparable to those obtained from Finnish environmental protection database maintained by the Ministry of Environment and

regional environmental authorities, which proves that in most cases waste water was of average quality for each specific facility. (VI)

In the very beginning of the study, the pulp and paper industry was known to be estimated to cover over ninety per cent of total complexing agent consumption in Finland. It was also foreseen that the intensive chemical waste water treatment may be able to reduce complexing agent concentration, especially if equipped with ion exchangers or sand filters and when carefully operated. There is hardly any complexing agents present in the waste waters of surface treatment industry. On the other hand, even though the concentrations are not high according to this study, there has been waste water treatment failures related to the treatment of degreasing bath concentrates. Therefore, complexing agents are not without any importance in this industry. More likely the waste water treatment operators have valuable hands-on experience on mixing of various waste water streams; too high portion of even pre-treated degreasing concentrate yields to higher metal concentrations in the effluent. Also, increased chemical costs and impaired economy has finally forced them to use multi-stage rinsing with adequate shaking prior to rinsing stages, both of which reduce chemical leakage to the waste waters and therefore makes operation of waste water treatment equipment easier. This kind of improvement is welcome, especially since typically waste water treatment equipment seems to run near or over the rated capacity. (VI)

It would have been interesting to present reduction percentages of complexing agents in chemical waste water treatment. Unfortunately this is rather difficult, since there are several influent flows with varying flow rates in typical electrolytic or chemical surface treatment plant. This issue was also out of the scope of this study. (VI)

Compared to the waste waters from the pulp and paper industry, the concentrations in electrolytic and chemical surface treatment plants are rather low. It is a well known fact that pulp and paper mill waste waters contain typically up to 10 mg/l of either EDTA or DTPA. (VI)

Table 3. Detected complexing agent concentrations in the Finnish electrolytic and chemical surface treatment plant waste waters. Samples with no complexing agents found omitted from the table. (VI)

Facility	TOC (mg/l)	Complexing agents (mg/l)										Metals (mg/l)			
		EDTA	DTPA	Other	Cr	Cu	Fe	Mg	Ni	Zn	sum	P	Q		
														sum	(mg/l)
A	7.6	+		0.02	0.1	N/A	N/A	0.09	0.02	0.2	N/A	18			
B	N/A			HEDTA ^(*)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	61			
E	40.9	0.4	0.1		1880	42	270	13.2	32	10.5	2260	57.6	0,06		
F	71.8	1.2		<0.04	0.2	<0.1	11.3	<0.07	1.9	13.8	<0.04	5			
I	28.7		0.4	<0.04	0.2	<0.1	12.5	<0.07	<0.04	12.7	17.2	60			
M	182.4	0.3	0.2		0.5	<0.05	0.1	6.7	<0.07	1.6	8.8	<0.04	12		
N	95.0	+++		<0.04	<0.05	<0.1	2.9	0.05	0.1	3.2	0.4	3			
O	28.5	0.6	++	<0.04	0.4	0.2	24.8	<0.07	<0.04	25.6	0.9	160			
P	15 ⁽⁵⁾			NTA++	0.4	0.07	<0.1	0.5	<0.07	0.1	1.1	3.0	2		
Q	10.7	0.3	1.4		0.08	<0.05	<0.1	14.5	0.12	<0.04	14.7	<0.04	1		
V	N/A	1.0		NTA+	<0.04	0.2	<0.1	3.0	<0.07	1.1	4.3	0.2	35		

7 EXECUTIVE SUMMARY

The European Union has produced two risk assessment reports on complexing agents, specifically NTA and EDTA (ECB 2004, 2005). On other complexing agents there are not as much of published information. However, DTPA, which is very commonly used in the pulp and paper industry or in the surface treatment industry, is rather obviously not more readily biodegradable than EDTA. It is also known that more stable complexing agents are studied in certain specific industrial uses, such as certain electroplating process baths. According to the production quantities found in the literature, other, typically more recalcitrant, complexing agents are being produced in increasingly higher quantities.

The day this paragraph is written (12/13/2006), the European Parliament passed the new long-awaited chemical regulation (REACH, EC 2006^{d,e}). Even though the direct costs of the regulation is estimated to be only about 0.06 per cent of annual chemical sales (Thacker 2005), the new regulation may complicate the introduction of new, probably more readily biodegradable complexing agents compared to e.g. EDTA or other complexing agents being on the market before 1981. In the phase one the target is in new chemicals and testing of products not making any profits is expensive. However, the white paper on a strategy for a future chemicals policy in the EU (EC 2001^b) is based on the precautionary principle, whereby chemicals are considered to be unacceptably hazardous unless proven otherwise, and the substitution of hazardous substances by less hazardous ones is encouraged, wherever possible (Combes *et al.* 2003). Therefore, ultimately more biodegradable complexing agents may be assumed to reach a higher market share, even if usage of biologically recalcitrant complexing agents will never be fully banned.

Since complexing agents are used in very large quantities (>1000 metric tons), more environmental data is expected to arise within few years due to the new EU regulation. The commonly used complexing agents may be expected to have mainly similar and summative health or environmental impacts, it is, therefore, important to estimate the impact of the use of e.g. both EDTA and DTPA to $PNEC_{\text{aqua}}$ to the receiving waters or to the dietary acceptable daily intake (ADI). At the moment complexing agents – other than EDTA and NTA – seem to be almost completely forgotten in the means of legislation and NGO interest. The overflowing concern of the use of EDTA in eco-label regulations –

even at the expense of concern on other complexing agents – seems to promote e.g. usage of DTPA. It is difficult to understand the limitations for the usage of NTA in the eco-label regulations, since most of the possible substitutes are recalcitrant to biodegradation, even if not of concern of NGOs. In other words: NTA, which is readily biodegradable, has gained too much attention from the environmental point of view. As presented in **Figure 3**, the usage of many of the ‘rare’ ligands was already fairly comparable to the usage of EDTA at the turn of the millennium and there is no reason to believe that e.g. the usage of DTPA or its market share had decreased during past ten years – quite opposite would be a more sophisticated estimate.

The number of published studies dealing with environmental behaviour of complexing agents have increased dramatically from roughly twenty annual articles in the mid 1990’s to nearly fifty in last years (Nowack and VanBriesen 2005). The basic assumptions of the harmfulness of these compounds have not yet changed much lately. The concern of i) increased pass-through of heavy metals at the WWTP, ii) the delayed heavy metal sedimentation, iii) the low biodegradability of the molecule in general, and iv) the participation to eutrophication being the most typically applied reasons for suggested limitation of use of these ligands or the environmental study of these compounds in general. It could be said that not much of new findings have risen – or the original assumptions have not been proven wrong. It is also noteworthy that according to the precautionary principle adopted in the European Union environmental and chemical legislation, lack of scientific certainty should not be considered as a justification for the use of chemicals. The ever-increasing chemicalization seemed to get us to raise our arms – at least until the REACH.

It is a generally acceptable principle that drinking water should not contain xenobiotic compounds. Therefore, recalcitrant xenobiotic compounds should not be released to the receiving waters either. On the other hand, if the compound is allowed to be used as a food additive in concentrations as high as 100 mg/kg (EC 1995) and is generally recognized as safe (GRAS) by the U.S. Food and Drug Administration (FDA) with a dietary acceptable daily intake (ADI) of 2.5 mg/kg (FDA 2004; WHO 2003, 2006), it is from a scientific point of view rather two-faced to be worried about the trace amounts of it in drinking water. Release of recalcitrant xenobiotic compounds to the environment – especially in high quantities – is still not acceptable.

There are plenty of harmful persistent organic pollutants (POP) in large scale everyday use that are also released to the environment, such as perfluorooctane sulfonate (PFOS) – an antifoaming agent used at the hard chrome plating plants to suppress evaporation or dropletting of hexavalent chrome, nonylphenol and nonylphenoethoxylate – non-ionic surfactants or bromated fire retardants like hexabromocyclododecan – to name a few. It can be expected that reduction of their use is the priority in the following years and that less harmful compounds, such as complexing agents, are not to get as much attention.

7.1 Toxicity and environmental impacts of complexing agents

Free complexing agents are rather non-toxic in terms of short-term toxicity. It is actually rather absurd that if the results obtained are misunderstood, the most recommended complexing agents would be those with highest chemical stability. Of course, the results need to be understood in a quite opposite way; the high stability of the complex, which suppresses the short-term toxicity of the heavy metal ion, is an unwanted characteristic in the field of environmental sciences. The differences in short-term toxicities of studied complexing agents and also of those studied elsewhere do not play any remarkable role, since the short-term toxicities of the heavy metal ions are remarkably higher. It is, however, important to recognize that these compounds are rather non-toxic themselves. These results would, however, be even of higher interest, if the short-term toxicity of the partial degradation products were also presented. These were not available in the literature either, although Takahashi *et al.* (1997) mentioned some degradation products of EDTA being biocidal.

It could be summarized that short-term toxicity of studied or other widely used complexing agents is not a dominating character when complexing agents are set in the order of superiority from the environmental point of view. Especially in detergents, however, the anticipated human carcinogenic characteristic of NTA (ECB 2005, Schmidt and Brauch 2004, HHS 2005) is a major limitation for the use of the compound which could otherwise be considered reasonably environmental friendly.

Jaworska *et al.* (1999) introduced a term ‘transparent biodegradation profile’, which describes well the difference between the degradation profiles of some of the novel complexing agents, e.g. EDDS and EDTA. All achievable primary degradation products – or metabolites – of these novel complexing agents are also known to be readily

biodegradable, naturally existing compounds. In the case of EDTA and DTPA, recalcitrant degradation products, such as KPPS's have recently been reported, but practically no comprehensive studies of the complete degradation of those compounds in real-world situations have been published. Unfortunately the degradation products identified in this project were published in the conference proceedings only (Pirkanniemi and Sillanpää 2001).

7.2 Catalytic degradation

Metallophthalocyanine catalysts were not studied earlier in the degradation of complexing agents. In this study, depending on the catalyst and metal speciation, complexing agents proved degradable to some extent, e.g. up to ninety per cent of EDTA was degraded. In this method speciation plays at least as an important role as in biodegradation.

Since metallophthalocyanines have been studied mainly in the presence of organic solvent their catalytic behaviour is not completely known in water solutions. It is, however, a well-known fact that a change in monomer – dimer structure is an important issue in their catalytic activity. The solvent used as well as the catalyst concentration plays also a major role in the catalyst activity. Since metallophthalocyanines proved ineffective as impregnated heterogeneous water phase catalysts, further studies were not performed. Catalytically active metallophthalocyanines are also rather expensive to produce for waste water treatment purposes while cheaper active catalysts, such as Fenton's catalyst, are available. If further development of catalytically active impregnated catalysts in water phase is successful, the situation may change. This kind of catalyst development and molecule design was out of the scope of this project.

Fenton's catalyst proved active in the degradation of complexing agents. Since in real-life situations EDTA and DTPA are not efficiently degraded at biological WWTP, chemical pre-treatment of complexing agent containing waste waters could be one of the options to look for – if readily biodegradable complexing agents are ruled out. Largely due to the new REACH regulation, it can be expected that recalcitrant complexing agents will ultimately be replaced by more readily biodegradable ones where supreme long-term chemical stability is not needed.

The reaction pH requirement of Fenton's reaction is a drawback, which was known in the beginning. When it comes to the degradation of complexing agents it is also a matter of speciation. In low pH, Fe^{III} complexes are generally speaking favourable. On the other hand, also protonated metal complexes are – depending on the metals and pH – typically dominant. In that case the stability of the metal complex is usually remarkably lower compared to the tabular values of the complex formation complexes of the metal complexes, which are given in neutral pH. In practical situations conditional stability constants should be used and better understood. In the case of Fenton's reaction the significance of speciation needs more follow-up research especially when it comes to the role of divalent iron and its protonated complexes.

7.3 Concentrations in waste waters

The complexing agent concentrations in waste waters of Finnish electrolytic or chemical surface treatment industry were not above PNEC_{aqua} of EDTA. The PNEC_{aqua} for DTPA is fairly expected to be in the same range as for EDTA. Compared to the known complexing agent concentrations in waste waters of e.g. brewing industry or juice producers (5 – 9 mg/l) (EASG 2003) or the pulp and paper industry, the concentrations are remarkably low. In the surface treatment industry, however, many harmful heavy metals are used and the complexing agents increase their pass-through – especially if pre-treated waste waters are not sewerred to the municipal WWTP. It would therefore be desirable to use readily biodegradable complexing agents.

Phosphonates, such as DTPMP, were not studied in the waste waters at all. Afterwards it could be said that this is a drawback. In decorative surface treatment industry highly efficient detergents are a major quality factor, and since phosphonates usage is extensive, they are most expected to be used in some installations. This same scientific ignorance concerning the role of phosphonates in the world of complexing agents is, however, seen elsewhere as well: according to Nowack (2003, 2004), not much is known about their behaviour.

In surface treatment industry adoption of readily biodegradable complexing agents would in some cases cause problems in bath stability and product quality, since the life times of typical treatment baths are rather long; calculated in months or even in years. In addition to that, the extreme reaction conditions require high chemical stability of the compound.

Complexing agents concentration found in Finnish surface treatment plant waste waters may be considered acceptable. More information on possible use of novel recalcitrant complexing agents would be needed though.

7.4 Conclusions

In this study it was shown that: i) complexing agents are rather non-toxic compounds in terms of short-term toxicity, if not complexed with toxic metals. They can also suppress the short-term toxicity of heavy metals. ii) Even biologically recalcitrant complexing agents can be chemically degraded. iii) Complexing agent concentrations in Finnish electrolytic and chemical surface treatment waste waters are relatively low.

There is insufficient scientific information about especially primary degradation products of complexing agents, especially EDTA and DTPA. Low pH in Fenton's process for example is favourable in intermolecular cyclization – the formation of KPPS's – of the primary degradation products. More data are needed concerning the degradability and toxicity of complexing agents and the primary degradation products. Readily biodegradable complexing agents need to be studied so that they can be introduced in wider scale of industrial and household use. Also in the BREFs published by the European Union it should be taken into account that there is a wide range of complexing agents – other than EDTA – in everyday use.

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