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BIODEGRADABILITY OF ETHYLENEDIAMINE-BASED COMPLEXING AGENTS

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Abstract—Biological degradability of ethylenediamine derivatives depends on the type and number of substituents. The susceptibility to biodegradation decreases in the sequence of substituents $-COCH_3$, $-CH_3$, $-C_2H_5$, $-CH_2CH_2OH$, $-CH_2COOH$ and with polysubstitution. The biodegradability depends also on the kind and number of nitrogen atoms. Complexing agents with a single-nitrogen atom in the molecule (e.g. NTA) succumb relatively readily to biodegradation whereas, compounds with two or more tertiary amino groups are biologically highly stable and do not undergo biodegradation even in experiments with activated sludge adapted at an age of up to 30 days (EDTA, DTPA, PDTA, HEDTA). A lowering of the degree of substitution brings about an increased susceptibility to biodegradation. This holds, e.g., for replacement of tertiary amino groups with secondary ones; thus the symmetrically disubstituted ethylenediamine-N,N′-diacetic acid (EDDA) possesses still sufficient complexing ability while belonging already to the group of potentially degradable substances. © 2001 Elsevier Science Ltd. All rights reserved

Key words—complexing agents, chelating agents, biodegradability, ethylenediamine derivatives, aminopolycarboxylic acids

1. INTRODUCTION

Chelating agents based on ethylenedi(tri)amine (polyaminopolycarboxylic acids), e.g. EDTA, DTPA, HEDTA or PDTA, are used in washing powders, cleaning products, electroplating, metal finishing, photographic and textile industry, pulp and paper production and others. Approximately, 50% of the total production is used in household and industrial detergents to control levels of free metal ions in wash and cleaning solutions and to support the performance of surfactants (e.g. EDTA reduces the decomposition of peroxoborate and significantly increases the bleaching efficiency of the detergent formulation).

EDTA and DTPA have been found in measurable concentrations in river water (up to $100\,\mu g\,l^{-1}$) (Dietz, 1987; Frimmel *et al.*, 1989; Pitter *et al.*, 1999), in drinking water (up to $40\,\mu g\,l^{-1}$) (Dietz, 1987) and in sewage-treatment plant effluents (up to $300\,\mu g\,l^{-1}$) (Kari and Giger, 1996).

The biological degradation of EDTA was usually not observed in the biological step of a sewage-treatment plant even under nitrifying conditions (Alder *et al.*, 1990; Madsen and Alexander, 1985; Kari and Giger, 1996). In some special cases, slow aerobic degradation of EDTA has been reported (Tiedje, 1975; Belly *et al.*, 1975; Means *et al.*, 1980). The biological transformation of EDTA, DTPA, and HEDTA was surveyed by Egli *et al.* (1990). A successful isolation of EDTA-degrading bacteria was reported in the last decade (Lauff *et al.*, 1990; Nörtemann, 1992; Witschel *et al.*, 1997; Witschel, 1999). Some of them were able to grow with EDTA as the sole source of carbon, nitrogen and energy.

The cause of the relative biological stability of EDTA and related ethylenediamine-based compounds has not yet successfully explained. Only compounds containing one nitrogen atom in the molecule (e.g. NTA) have shown biological degradability. A relationship exists between the chemical structure and biodegradability of organic substances (Pitter and Chudoba, 1990). The relationship between the structure of complexing agents and their biodegradability remains to be answered.

Complexing agents bidegradation in the environment depends on complexation with metals. The complexes with high stability constants may adversely influence their transport to the cell (Witschel, 1999). However, some authors even approved biodegradability of very stable Fe^{III} complexes (Belly *et al.*, 1975). The first experiments were performed with

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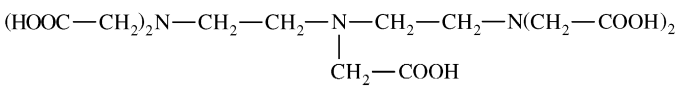


NTA, but dependence of biodegradability on stability constants were not confirmed (Gudernatsch, 1975).

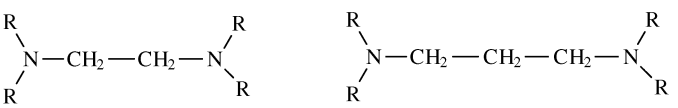
Experiments with the degradability of ethylenediamine derivatives with different kinds and number of substituents (mono-, di-, tri- and tetrasubstituted derivatives) were therefore carried out. The following substituents were selected: $-CH_3$ (methyl). $-CH_2CH_3$ (ethyl), $-CH_2CH_2OH$ (hydroxyethyl), $-CH_2COOH$ (carboxymethyl), and $-COCH_3$ (acetyl).

EXPERIMENTAL

Initial concentrations of complexing agents about $100\,mg\,l^{-1}$, what correspond to EDTA $0.34\,mmol\,l^{-1}$ were used in these experiments. The main cations in biological testing medium are calcium, magnesium and iron at concentrations 0.25, 0.1 and $0.001\,mmol\,l^{-1}$, respectively. It is supposed, that EDTA and similar complexing agents react with metals in molar ratio 1 : 1. Together with iron concentration it means, that complexes with Fe^{III} can be neglected. The negative influence of metal complexes is not considered, because negative influence of calcium and magnesium on biodegradability was not observed (Gudernatsch, 1970,1975; Huber, 1974; Swisher *et al*., 1967).

Chemicals

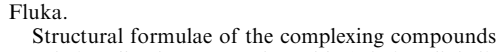
The basic structure of the ethylenediamine or propylenediamine derivatives can be depicted as follows:



Compounds with the following substituents R were used: methyl ($-CH_3$), ethyl ($-CH_2CH_3$), hydroxyethyl ($-CH_2CH_2OH$), acetyl ($-COCH_3$) and carboxymethyl ($-CH_2COOH$) groups. These compounds and the complexing agents listed below were subjected to the biodegradability test procedures. All chemicals were of analytical grade and were purchased from Merck and Fluka.

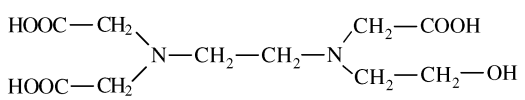
Structural formulae of the complexing compounds used:

Ethylenediaminetetraacetic acid (ethylenedinitrilotetraacetic acid) **EDTA**:

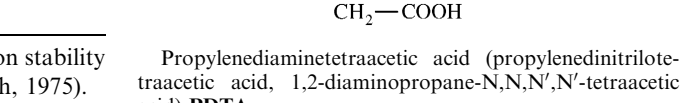


Ethylenediamine-N,N′-diacetic acid (N,N′-ethylenediglycine) **EDDA**:

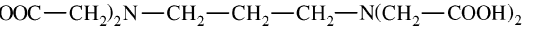
N-(2-hydroxyethyl)ethylenediaminetriacetic acid [N-carboxymethyl-N′-(2-hydroxyethyl)-N,N′–ethylenediglycine] **HEDTA**:



Diethylenetriaminepentaacetic acid (diethylenetrinitrilopentaacetic acid) **DTPA**:



Propylenediaminetetraacetic acid (propylenedinitrilotetraacetic acid, 1,2-diaminopropane-N,N,N′,N′-tetraacetic acid) **PDTA**:



Degradation methods

Two methods were combined for evaluating the complete biodegradability: the method of assaying dissolved organic carbon (EN ISO 7827) suitable for assessing ready biodegradability ($X_0 = 30\,mg\,l^{-1}$, S_0= DOC $50\,mg\,l^{-1}$) and the Zahn-Wellens Test (EN ISO 9888) for assessing potential biodegradability ($X_0 = 30\,mg\,l^{-1}$, S_0= DOC $50\,mg\,l^{-1}$). Ready biodegradability means degradation of compounds by nonadapted activated sludge or adapted sludge at sludge age mean biomass retention time (MBRT) 5 days (lag-phase approximately till 10 days). Sludge age 5 days usually corresponds to conditions at most treatment plants. Potential biodegradability means, that tested compounds are degradable under certain conditions (e.g. sludge age longer than 5 days). The substances under study were the only sources of organic carbon for the microbes of the inoculum. The inoculum was either non-adapted activated sludge collected at the municipal water treatment plant in Prague or an activated sludge adapted at different sludge age in the range of 5–30 days, which corresponds to the relations in medium- to low-load biological water treatment plants (Čech and Chudoba, 1988; Pitter and Chudoba, 1990; Pitter and Sykora, 1996).

Adaptation means inoculum acclimation to given conditions (experiments with different sludge age). Due to longer sludge age slow-growing microorganisms were privileged, which was more important than inductive enzymes formation.

Tests for checking inhibition and for assessing the abiotic degradation according to the rules given in appropriate standards were performed in parallel with biodegradation experiments.

The results of the biodegradation experiments were assessed based on the following parameters:

D_t–biodegradation degree in % DOC at time t,
D_{max}–maximum degradation degree in % DOC,
t_1–lag phase,
t_2–degradation period after the terminated lag phase until 90% decomposition is achieved,
r_x–decomposition rate after the end of the lag phase (DOC drop in mg referred to 1 g initial activated sludge dry solids per 1 h),
S_0–initial concentration (DOC) of the substance under study,
X_0–initial activated sludge dry solids concentration,
A–sludge age.

Analytical methods

Dissolved organic carbon (DOC) was determined on SHIMADZU TOC 5050 analyser after sample filtration through a 0.45 μm pore-size filter.