

Biodegradation of selected substances used in liquid fertilizers as an element of Life Cycle Assessment

Magdalena Borowiec, Marta Huculak, Krystyna Hoffmann, Józef Hoffmann¹

Wrocław University of Technology, Institute of Inorganic Technology and Mineral Fertilizers

¹ Corresponding author: Józef Hoffmann, Politechnika Wrocławska, Institute of Inorganic Technology and Mineral Fertilizers, ul. Smoluchowskiego 25, 50-372 Wrocław, Poland, e-mail: józef.hoffmann@pwr.wroc.pl

The results of laboratory investigations into the aerobic biodegradation of chelating compounds in water medium under static test conditions are presented. It was found that nitrilotriacetic acid (NTA) and glutamic acid diacetic acid (GLDA) are more readily biodegradable than ethylenediaminetetraacetic acid (EDTA) commonly used in the production of liquid fertilizers. Biodegradation was evaluated on the basis of compound decay and changes in COD.

Keywords: Life Cycle Assessment, chelating compounds, biodegradation.

INTRODUCTION

Because of the increased environmental pollution, the substances entering the natural environment are subject to close scrutiny. Consequently, methods aimed at gaining a deeper insight into the effects of such substances on the environment and at reducing them are being developed. One of these methods is Life Cycle Assessment (LCA). One of the basic assumptions of LCA is research of environmental aspects and potential influences in the whole cycle of product life, from taking materials out, the period of their production and finally their removal. This is done through both the identification and quantity assessment of the materials and energy used and the wastes discharged into the environment and the assessment of the environmental impact of the materials and the wastes^{1, 2}.

Micronutrients are very important as the primary and secondary nutrients in plant nutrition. However, the amounts of micronutrients required for optimum nutrition are much lower. Micronutrient deficiencies have been verified in many soils. Furthermore, they occur in soil in the forms which are unavailable for uptake by the plant. This deficiency should be supplemented by micronutrient fertilizers. These sources are classified as inorganic, synthetic chelates, natural organic complexes, and fritted glasses. Chelated micronutrients are widely used in agriculture and are strongly promoted by the fertilizer industry³⁻⁵. Chelates are complex compounds characterized by good solubility in water but they dissociate only to a slight degree and micronutrient chelates protect metal cations against reduction in the soil and facilitate their uptake by leaves⁵.

The bond between the organic chemical and the inorganic nutrient must be strong enough to protect the nutrient. Also, the chelating agent must not be harmful to plants. Several organic substances (like chelating agents) are used to produce chelates. EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid) are the synthetic chelates most commonly used for the production of micronutrient fertilizers. They are also used in cleaning and washing agents and in many other industries. Their biodegradation is practically not observable in the biological stage of sewage treatment and they persist in the environment, consequently there are increasing concerns about their use^{6, 7}. They are also said to be

insufficiently biodegradable and accumulate in the environment for as long as 15 years⁷⁻⁹. Biodegradability should be the factor determining the suitability of chelating compounds for the production of liquid fertilizers.

Nitrilotriacetic acid (NTA) is a biodegradable chelating agent that is weaker than EDTA but widely used in cleaning processes and detergent applications¹⁰. Small amounts of NTA can be easily removed from drinking water by bank filtration and ozone treatment. However, the IARC (International Agency for Research on Cancer) Working Group has recently classified NTA as a possible carcinogen to humans on the basis of animal experiments¹¹.

Glutamic acid, N,N-diacetic acid (GLDA) is a readily biodegradable chelating agent that can be used as an alternative for NTA and EDTA. It has an exceptionally high solubility at high and low pH. On trials, GLDA has proved to have an optimal balance between biodegradability, metal chelation and the easiness of use^{12, 13}. A large number of toxicity tests reveal that GLDA is not a dangerous chemical and has excellent properties with regard to environmental and human toxicity. GLDA can be regarded as non hazardous when put into water^{13, 14}.

EXPERIMENTAL

The aim of biodegradation tests is to determine the microbiological decomposability of individual organic compounds and their mixtures. When organic substances are used by microorganisms as nutritional substrates, the substrate content decreases while the biomass increases. If the chemical compounds are not decomposed by microorganisms, they either occur in concentrations toxic to the microflora or are resistant to biodegradation¹⁵.

The main biodegradability tests recommended by OECD are: biodegradability determination by the method of activated sludge under kinetic conditions and the investigation of the aerobic biodegradation of organic compounds in water medium under static test conditions.

Both methods exploit the properties of activated sludge, which is a mixture of various microorganisms that are able to decompose organic substances.

The course of biodegradation is evaluated from the decay of the investigated compound in a sample and from the changes of the concentration of the activated sludge biomass and in the chemical oxygen demand (COD).

Table 1. Biodegradation of complexing substances under static conditions over 20 days

	EDTA		GLDA		NTA	
	without glucose	with glucose	without glucose	with glucose	without glucose	with glucose
Degree of biodegradation [%]	65.26	63.68	93.11	94.94	100 (16 days)	100 (13 days)
Degree of COD _{Mn} reduction [%]	48.09	49.89	42.22	52.21	89.31	89.79
Degree of COD _{Cr} reduction [%]	55.64	59.22	43.86	58.24	98.52	99.08

Sometimes, if necessary, the time it takes the microorganisms in the activated sludge to adapt, i.e. the period in which no or insignificant elimination of the investigated compound takes place, is determined. During the adaptation of microorganisms inductive enzymes are produced. The latter decay as the particular substrate in the substratum is exhausted. The presence of various micronutrients, acting as enzyme activators, in the mineral substratum, is conducive to the appearance of inductive enzymes^{15, 16}.

Biodegradability was determined by carrying out the aerobic biodegradation of the investigated compounds in water medium under static test conditions in accordance with Polish Standard PN-88/C-05561¹⁶.

Biodegradation under static test conditions is evaluated by determining the rate of decay of the investigated compound (dissolved in a synthetic mineral substratum inoculated with standard activated sludge) under aerobic conditions, without access to light, at room temperature, over 20 days. Mineral substratum seeded with 1.5 dm³ of standard activated sludge (taken from a sewage treatment plant's aeration tanks) was put into three flasks placed in magnetic stirrers and connected by air pipes. A sample of the tested compound dissolved in a synthetic mineral substratum was added to each of the first two flasks while the third flask was treated as reference. About 2.5 g of EDTA (which corresponds to a concentration of about 1.67 g/dm³) or about 10 g of a 38% solution of GLDA (which corresponds to a concentration of about 2.5 g/dm³) and about 2.5 g of NTA (which corresponds to a concentration of about 1.67 g/dm³) were placed in the first and second flasks. 100 cm³ of 0.1% glucose (as a source of easily decomposed carbon and energy for microorganisms) was added to the second flask.

Biodegradation under static conditions was estimated as a degree of compound reduction and degree of COD reduction. COD_{Mn} determination by the permanganate (oxygen consumption) method was carried out in accordance with Polish Standard PN-EN ISO 8467:2001¹⁷. In all the cases, prediluted samples were used. In the case of the samples taken from flasks 1 and 2, it was 1 cm³ of the sample per 99 cm³ of water and for the reference test – 10 cm³ of the sample per 90 cm³ of water. The chemical oxygen demand in the dichromate method is an index of consumption of the oxygen coming from the reduction of potassium dichromate by organic substances and some easily oxidizable inorganic substances. COD_{Cr} determination by this method consists in determining the number of milligrams of potassium dichromate in terms of the O₂ consumed for the oxidation of organic compounds in the analysed sample. Oxidation is conducted in sulphuric acid medium in the presence of silver sulphate as the catalyst. The same amount of the solution, i.e. 5 cm³, was taken from flask 1 and 2 and 20 cm³ from flask 3. The determination was carried out in accordance with Polish Standard PN-ISO 6060:2006¹⁸.

The concentrations of the investigated substances were determined by the compleximetric titration analysis method in alkaline medium, using MgCl₂ against eriochrome black T.

DISCUSSION OF TEST RESULTS

The aim of the investigations was to determine the degree of biodegradation of the complexing compounds of ethylenediaminetetraacetic acid (EDTA), the most commonly used in the liquid fertilizers production, nitrilotriacetic acid (NTA), which was used in fertilizers production and which is readily biodegradable but has cancerogenic properties, and glutamic acid N,N-diacetic acid (GLDA) as a substitute for EDTA and NTA. Biodegradation was evaluated from the decay of the compound in the sample and from the changes in COD. The results of the investigations into the biodegradation process are shown in table 1.

The degree of compound reduction (X_t) over time (t) was calculated from this formula:

$$X_t = \frac{(C_{t=0} - C_t)}{C_{t=0}} \cdot 100 \quad [\%]$$

where:

C_{t=0} – the concentration of the compound at time t = 0, g/dm³;

C_t – the concentration of the compound after time t, g/dm³.

The degree of COD reduction (Y_t) over time (t) was calculated from this formula:

$$Y_t = \frac{a - (b - c)}{a} \cdot 100 \quad [\%]$$

where:

a – COD at time t=0, mg/dm³, O₂;

b – COD after time t, mg/dm³, O₂;

c – COD in reference test after time t, mg/dm³, O₂.

The results of the reduction of chelate content in the samples taken in the course of the biodegradation process show that the biodegradation of nitrilotriacetic acid (NTA) and glutamic acid N,N-diacetic acid (GLDA) proceeds much faster and to a larger degree than that of EDTA (fig. 1). NTA is totally biodegraded after 16 days without glucose and after 13 days with glucose as the source of easily decomposed carbon and energy for microorganisms. For EDTA the degree of biodegradation (the diminution of the compound in the sample) was found to be about 64% at a concentration of circa 1.7 g/dm³ after 20 days of biodegradation. Glucose did not have an influence on the degree of EDTA reduction. The small amounts of GLDA were observed after 20 days of biodegradation process, but in accordance with organic compounds decomposing classification it can be rated as a readily biodegradable¹⁵.

The decomposition of organic compounds might be characterized by the degree of chemical oxygen demand (COD) reduction. In accordance with this classification EDTA and GLDA can be classified as biodegradable

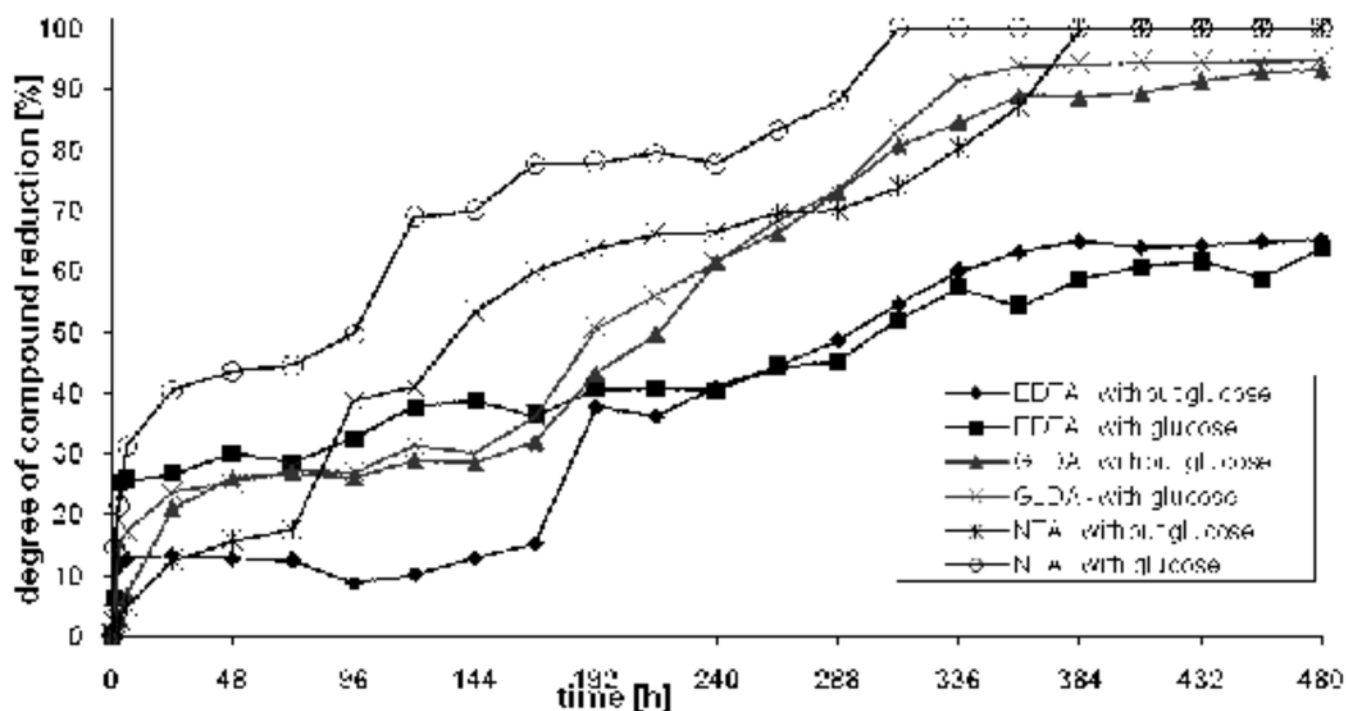


Figure 1. The degree of EDTA, GLDA and NTA reduction during the biodegradation process under static conditions

(especially by dichromate method) and NTA as an easily biodegradable (tab. 1)¹⁵. The degree of COD reduction by dichromate method is higher than by permanganate method. It is connected with oxidizing properties of using oxidant – potassium dichromate is stronger oxidant than potassium permanganate. The addition of glucose had an influence on the increase of the degree of COD reduction (tab. 1). GLDA can be treated as readily biodegradable but its decomposition probably runs through indirect phases (the degree of COD reduction can provide this).

CONCLUSION

NTA and GLDA are characterized by high biodegradability (the degree of biodegradation being in a range of 93 – 100%), but NTA demonstrates faster and greater biodegradation than GLDA. GLDA can be treated as readily biodegradable but its decomposition probably runs through indirect phases (the degree of COD reduction can provide this). EDTA biodegradation tests proved non-biodegradability of this compound. The addition of glucose (as a source of easily decomposed carbon and energy for microorganisms) speeded the decomposition of biodegradable compounds up and increased the degree of COD reduction. GLDA can be applied as new effective and environmental friendly chelating agents.

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