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Biodegradability of the compounds introduced with microelement fertilizers into the environment

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The results of laboratory studies into the oxygen biodegradation of chelating substances in aqueous medium under kinetic and static test conditions with added glucose as an additional source of carbon, are presented. It has been found that S,S-ethylenediaminedisuccinic acid (S,S-EDDS) and methylglycinediacetic acid (MGDA) are more readily degradable than ethylenediaminetetraacetic acid (EDTA), most commonly used in the production of microelement fertilizers. It has also been found that the presence of additional carbon sources accelerates biodegradation.

Keywords: biodegradation, microelement fertilizers, EDTA, S,S-EDDS, MGDA.

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INTRODUCTION

The microelements contained in liquid fertilizers, e.g. iron, manganese, zinc, copper, boron, chlorine and nickel, are necessary for plant metabolism. They are components of the active centres of many indispensable enzymes, take part in photosynthesis and water photolysis. But in the presence of other components they may form sparingly soluble salts whereby their effectiveness decreases[1]. For this reason organic compounds which complex microelements (making them more available to plants) are used in the production of liquid fertilizers. Such chelates are very well soluble in water but their dissociation is slow whereby microelements are only gradually released from the fertilizers to assume an ionic form. The fact that the chelates strongly complex the above elements means that heavy metal emission into the environment increases[2, 4].

Because of the environmental constraints the main criterion for the use of a given fertilizer component is its biodegradability. The biodegradation of such a compound should be correlated with the rate of the uptake of the complexed microelement by plants.

Biodegradability is an organic compound's ability to undergo microbiological decomposition. This is a multistage process proceeding with the simultaneous participation of several microorganisms, owing to synergy. The effectiveness of the degradation is determined by several factors such as: the composition and activity of the microflora, the type of contamination, the presence of other compounds and nutrients, the temperature, the environment's pH, the oxygen access and so on. Regardless of changing environmental conditions, micro-organisms are able to adapt and use the compounds that are not substrates or products of their own metabolism as building and energy-providing substances.

If microorganisms use a given compound as a nutritional substrate, its fraction decreases while biomass increases. If the concentration of the compound does not decrease, the latter is not biodegradable or its content is toxic. Compounds which undergo degradation in over 80% are considered to be readily biodegradable, in 60% as biodegradable and in less than 20% as sparingly biodegradable[3].

Both natural and synthetic compounds are used for complexing fertilizer microelements. The most commonly used synthetic complexing agent is ethylenediaminetetraacetic acid (EDTA) in the form of sodium salt. Owing to its strong complexing properties the substance is used in industrial applications on a massive scale. In recent years it has turned out that although its microbiological degradation is possible under laboratory conditions, its degradation in the natural environment is very slow. Moreover, it can last in the environment for as long as 15 years, which may pose a potential risk to living organisms and result in heavy metals availability and eutrophication of waters[2, 4 – 6]. Because of these concerns, substitutes for EDTA, which would be characterized by quicker and more effective degradation and by a comparable or better effectiveness of complexing fertilizer microelements, are sought.

The subject of the present investigations are S,S-ethylenediaminedisuccinic acid (S,S-EDDS) and methylglycinediacetic acid (MGDA)[4].

EDDS is a structural isomer of EDTA. It forms three stereoisomers [S,S], [R,S] and [R,R], but only the first of them is a promising candidate for use in the production of liquid microelement fertilizers owing to its biochemical degradability[6]. S,S-ethylenediaminedisuccinic acid (S,S-EDDS) is a naturally occurring compound produced by *Amycolatopsis orientalis*. This suggests its easy availability and lower production costs[6, 8]. Under proper conditions (pH, concentration) its metal ion bonding effectiveness is equal to or even higher than that of EDTA. It is also completely atoxic to plants and animals. But above all it has been found to be completely degradable by microorganisms[6, 9, 10].

Methylglycinediacetic acid (MGDA) is a compound which only recently has been industrially produced, but it is found to be equally valuable as EDTA for the production of fertilizers. It is produced synthetically from amino acids through the substitution of two acetyl groups for the amino group[6]. Its ability to form complexes with metals

is very strong, even higher than that of EDTA, and its biodegradability is over 90%[6, 11].

EXPERIMENTAL

The biodegradation of the chelating compounds was investigated by two methods: the oxygen biodegradation of organic compounds in aqueous medium under static test conditions, according to Polish Standard PN-88/C-05561 and the determination of the effectiveness of biochemical oxidation by activated sludge under kinetic conditions according to Polish Standard PN-72/C-04550[12, 13].

Both methods exploit the properties of activated sludge as a biocoenosis which, owing to the diversity of micoorganisms contained in it, is able to decompose organic compounds.

The method of the oxygen biodegradation of organic compounds in aqueous medium under static test conditions consists in determining the rate of decay of an organic compound in a mineral substrate inoculated with activated sludge, under oxygen conditions in the dark at room temperature for twenty days[12]. The tested compound in the amount of about 4 g/dm^3 dissolved in a synthetic mineral substrate inoculated with standard activated sludge was placed in three 3 dm^3 flasks arranged in a row on magnetic stirrers and connected by an oxygen feeding tube. Besides the tested compound, 100 ml of 0.1% glucose (an agent aiding the biodegradation of some organic compounds, being a source of easily decomposed carbon and energy for microorganisms), was added. The third flask was a reference flask.

Biodegradation under static conditions was evaluated from the decay of the tested compound in the sample and from the changes in the chemical oxygen demand (COD). COD was determined by the permanganate method and by the dichromate method in accordance with standards PN-85/C-04578/02 and PN-74/C-04578/03[14, 15]. The former method consists in determining the amount of potassium permanganate in terms of oxygen consumed for the oxi-dation of the organic compounds and some easily oxidizing inorganic compounds present in the tested sample[14]. The latter method consists in determining the milligrams of potassium dichromate in terms of oxygen consumed for the oxidation of the organic compounds and some inorganic compounds present in the analyzed sample. The oxidation is conducted in a sulphuric acid medium with silver sulphate added as the catalyst[15].

The biodegradation of organic substances by the activated sludge method under kinetic conditions consists in measuring the contents of the substances in the inflow prior to the contact with activated sludge and in the outflow after the contact with the activated sludge under kinetic conditions in a special model stand. Twenty four litres of synthetic sewage were fed into a supply tank once every 24 hours. The liquid contained basic mineral and organic component and its composition corresponded to the typical domestic sewage and a solution of the tested substance in different concentrations. Activated sludge was placed in an aeration tank. Then the flow in the amount of 1 dm^3/h was dispensed from the supply tank into the aeration tank. Initially the tested compound content amounted to about 1 g/24dm^3 and then every week the content was increased appropriately up to 10 g/24dm^3. The time of the inflow/sludge contact in the aeration chamber was 3 hours[13].

100 mass % disodium salt of ethylenediaminetetraacetic acid (EDTA), a 30 mass % solution of trisodium salt of S,S-ethylenediaminedisuccinic acid (S,S-EDDS) and a 40 mass % solution of trisodium salt of methylglycinediacetic acid (MGDA) were tested. The salt of methylglycinediacetic acid, under the trade name Trilon® M liquid, was obtained by courtesy of BASF The Chemical Company.

DISCUSSION OF RESULTS

The aim of the investigations was to determine the biodegradability of the complexing agents: sodium salt of ethylenediaminetetraacetic acid (EDTA), used in the production of fertilizers, and sodium salt of S,S-ethylenediaminedisuccinic acid (S,S-EDDS) and sodium salt of methylglycinediacetic acid (MGDA) as potential replacements for EDTA. Biodegradation under static conditions was evaluated on the basis of the decay of the compound in the sample and changes in COD (tab. 1).

The reduction of COD (Y_t) over time (t) was calculated from the formula[12]:

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

where:

a – COD at time t=0, mg/dm^3, O_2,

b – COD after time t, mg/dm^3, O_2,

c – COD in the reference sample after time t, mg/dm^3, O_2.

The degree of compound reduction (X_t) over time (t) was calculated from the formula[12]:

$$X_t = \frac{(C_{t0}-C_t)}{C_{t0}}\cdot 100 \quad [\%]$$

where:

C_{t0} – the compound concentration at time t = 0, g/dm^3,

C_t – the compound concentration after time t, g/dm^3.

According to the results of the chelating compound content reduction in the samples taken in the course of biodegradation, S,S-ethylenediaminedisuccinic acid (S,S-EDDS) and methylglycinediacetic acid (MGDA) biodegrade much faster and to a greater degree than ethylenedi-

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

	EDTA		S,S-EDDS		MGDA	
	without glucose	with glucose	without glucose	with glucose	without glucose	with glucose
compound reduction [%]	54.9	54.9	100 (after 9 days)	100 (after 7 days)	100 (after 12 days)	100 (after 8 days)
COD_{Mn} reduction [%]	40.0	37.9	50.7	75.2	63.7	83.5
COD_{Cr} reduction [%]	55.8	63.6	79.2	86.8	69.7	86.6

aminetetraacetic acid (EDTA) (Fig. 1.). S,S-EDDS biodegrades completely after 7 days when glucose is used as an additional source of carbon and after 9 days without glucose. For EDTA the degree of biodegradation (the compound content reduction in the sample) was found to be about 55% at a concentration of 3.3 g/dm^3 after 20 days of biodegradation. The presence of glucose had no effect on the degree of EDTA reduction. Also methylglycinediacetic acid (MGDA) turned out to be more readily biodegradable than EDTA. Its reduction amounted to 100% after 8 days of biodegradation with glucose and after 12 days of biodegradation without glucose.

The degree of COD reduction in the tested samples increases with the degree of reduction of the tested compound. The highest degrees of COD reduction, both for

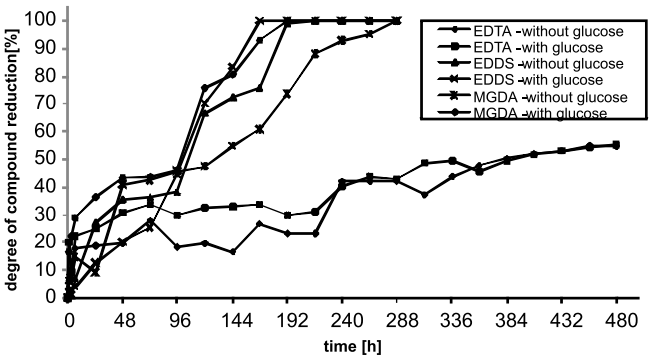

Figure 1. The degree of the reduction of complexing compounds: EDTA, S,S-EDDS and MGDA in course of biodegradation in the static test

the permanganate method and the dichromate method, were observed for S,S-ethylenediaminedisuccinic acid (S,S-EDDS) – 75.2% for the permanganate method and 86.8 % for the dichromate method with glucose and for methylglycinediacetic acid (MGDA) – 83.5% for the permanganate method and 86.6% for the dichromate method with glucose. Thanks to the use of glucose as an additional source of carbon higher degrees of COD reduction relative to the tests without glucose were achieved. The determined COD reduction degrees show that both S,S-EDDS and MGDA are readily degradable according to the classification of degradability of organic compounds. No intermediate decomposition products were found to be present in the tested sample[3, 12]. In the case of EDTA, COD decreased proportionally to the decay of the compound in the sample – by 40% for the permanganate method both with and without glucose and by more than 50% for the dichromate method.

Biodegradation under kinetic conditions was evaluated on the basis of the decay of the compound in the sample. The percentage of compound reduction in the sample was calculated by comparing the concentration of the tested compound in the inflow prior to the contact with activated sludge and in the outflow after the contact with the activated sludge. The percentage of reduction of the chelating agents depending on the concentration of the compound is shown in Tab. 2.

An analysis of the compound reduction results shows that at lower concentrations the substances degrade faster. For an activated sludge the contact time of 3 hours methylglycinediacetic acid (MGDA) proved to be the most readily biodegradable and the obtained results suggest that it will be more readily biodegradable than ethylenediaminetetraacetic acid (EDTA) which has been used so far.

CONCLUSION

All the tested complexing compounds were characterized by biodegradability above 50%. The degree of biodegradation was in a range of 55 – 100%. The highest degree and fastest rate of biodegradation were observed for S,S-EDDS. This process was the slowest in the case of EDTA. Glucose as an additional source of carbon and energy for micro-organisms accelerates biodegradation and increases the degree of COD reduction. The fact that S,S-ethylenediaminedisuccinic acid and methylglycinediacetic acid (MGDA) undergo complete biodegradation indicates that the compounds can be used as replacements for EDTA which is commonly used in the production of microelement fertilizers.

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Table 2. Biodegradation of complexing substances under kinetic conditions

	EDTA		S,S-EDDS		MGDA	
weight of compound –inflow [g]	concentration - inflow [g/dm^3]	degree of reduction [%]	concentration - inflow [g/dm^3]	degree of reduction [%]	concentration - inflow [g/dm^3]	degree of reduction [%]
1	0.0421	100	0.0134	100	–	–
2	0.0844	70.3	0.0274	73.9	0.0418	100
5	0.2103	44.5	0.0631	70.8	0.0872	87.7
7.5	0.3147	21.7	0.0949	63.3	0.1269	72.3
10	0.4227	14.0	0.1285	50.5	0.1693	67.2

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