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Oxidative Neutralization of the Commodity Form of the Pesticide Zineb

T. N. VOLGINA, V. T. NOVIKOV and A. I. TATARKINA

*Tomsk Polytechnic University,
Prospekt Lenina 30, Tomsk 634050 (Russia)**E-mail: Volgina_t@mail.ru*

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Abstract

The way of oxidative mineralization of the commodity form of the pesticide zineb under mild conditions was investigated. The destruction of organic components of the drug of the second class danger up to low-toxic compounds occurs in the bulk of the electrolyte under the action of oxidants formed electrochemically *in situ* in sulphuric-acid solutions of zineb. Simultaneously with this, on the cathode, more than on 90 % zinc ions formed as a result of hydrolysis of the acting substance zineb that is zinc salt of *N,N'*-ethylenebis(dithiocarbamic) acid, were reduced.

Key words: neutralization, zineb, indirect electrooxidation, electrolysis of sulphuric acid, hydrolysis, mineralization, deep oxidation

INTRODUCTION

With the development of agriculture and industry, the number of developments is annually increased and volumes of the production of special preparations, such as pesticides designed for the destruction of various species of pests, grow. The list of these substances is constantly updated due to the emergence of new, more efficient analogues. As a consequence, the cull, charge-off and accumulation of the banned or unusable preparations, are carried out. Warehouses for the storage of such off-grade pesticides are environmentally dangerous, since the flush of toxic substances into reservoirs, their scattering during the storage and transportation are possible. Besides, during the bulk storage, poisonous chemicals acquire another chemical structure and unpredictable toxicity due to the interaction with each other, water and air oxygen.

To reduce the number of such storages in Russia and decrease the anthropogenic load on objects of the environment is only possible

through the neutralization of accumulated off-grade toxins. However, existing technologies, such as combustion and plasma-chemical destruction do not meet requirements of the environmental compatibility and efficiency, require large investments and not always can be applied for the neutralization of mixtures of pesticides of the unidentified composition and structure.

Lately, researchers' attention has increasingly been attracted by electrochemical methods. Among them, indirect electrooxidation takes the leading place – the process, in which when electrolyzing electrolyte, various strong oxidants providing the mineralization of organic compounds of a various structure are generated. Selecting the electrolyte type, electrodes material and parameters of the oxidation process, one can neutralize any pesticides and similar eco-toxicants.

The goal of the present work is the study of the process of neutralizing the pesticide zineb by a complex of oxidants ($\text{H}_2\text{S}_2\text{O}_8$, H_2SO_5 , H_2O_2 , O_2 and O_3) formed on lead electrodes at the passage of electric current through sulphuric acid solutions.

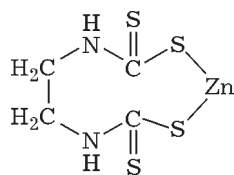
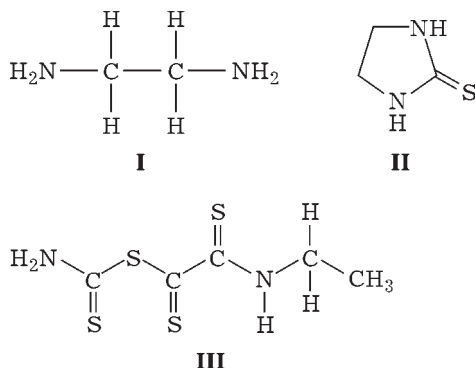
Fig. 1. Zinc salt of *N,N'*-ethylene-bis(dithiocarbamic) acid.

Fig. 2. Organic metabolites of zineb.

EXPERIMENTAL

The mineralization of zineb up to non-toxic components was conducted out in a diaphragmless electrolyzer (volume up to 30 dm³) equipped with lead electrodes with the working area of 10 cm² and magnet stirrer, in 30–70 % solutions of sulphuric acid at the current density of 0.1–1 A/cm², temperature of 20 °C and atmospheric pressure. The concentration of zineb was 100 mg/L and 100 mg in 30 mL of sulphuric acid solution (approx. 3.3 g/L).

The efficiency of oxidation of the commodity form of the pesticide under laboratory conditions was evaluated by simple and available physicochemical methods of analysis: 1) by spectrophotometric measurements of the solutions studied in the visible and ultraviolet re-

TABLE 1

Maximum permissible concentrations in water bodies of fishery value and the class of hazard components zineb of pesticides and their metabolites [8]

Substances	MPC, mg/L	Hazard class
Zinc <i>N,N'</i> -ethylene-bis(dithiocarbamate)	0.0004	2
OP-7	0.3	3
Zinc	0.01	3
Carbon sulphate	1	2
Ethylenediamine	0.001	3
Ethylenethiourea	0.001	3
Ethylene thiuram monosulphide	0.0002	1

gions of the spectrum; 2) by determining the total content of organic substances on the microprocessor analyzer Ecotest-120; 3) by measuring the concentration of zinc ions in the solution bulk by the dithizone method [7] and by method of inversion voltammetry [4].

RESULTS AND DISCUSSION

Zineb is a fungicide of the group of carbamates [1] that is used as 0.3–0.5 % water suspensions for the prevention of various diseases of plants. According to TU 6-01-501-75, the active substance of the preparation is zinc salt *N,N'*-ethylene-bis(dithiocarbamate) acid (ZEBDC) (Fig. 1) with the concentration of 80 mass %. Accessory components are the surfactant of the brand OP-7 (as a wetter) and sulphite alcohol spent liquor (as the suspension stabilizer).

The presence of zineb in the habitat is strictly regulated (Table 1) and not hazardous in acceptable limits. In soils at agrochemical consumption norms, it is decomposed during 2–12

TABLE 2

Change of the chemical consumption of oxygen at zineb hydrolysis in sulphuric acid solution, mg O/L

Time of hydrolysis, h	Concentration of sulphuric acid, mass %			Concentration of Zn ²⁺ , mg/L
	30	50	70	
0	950	950	950	5.4
25	750	827	873	12.2
50	683	798	854	543.6
75	672	780	843	543.6
90	668	770	836	543.6

weeks, in water, at the temperature of 18–20 °C and pH 6 it is completely destructed during 4 days and at the pH of 3.5 during 2 h [2]. However, at adverse storage conditions of the substandard forms of pesticide, zineb becomes unstable and decomposes more than on 50 % during one year with the formation of carcinogenic metabolites (see Table 1, Fig. 2), *viz.*, ethylenediamine **I**, ethylenethiourea **II**, ethylene-thiuram-monosulphide **III** and carbon disulphide.

It is known [4] that the active substance of the technical form of zineb in aqueous solutions of H_2SO_4 is hydrolysed according to the reaction $\text{ZEBDC} \rightarrow \text{NH}_2\text{-CH=CH-NH}_2 + \text{CS}_2 + \text{Zn}^{2+}$

The experiments conducted showed (Table 2) that the maximal rate of hydrolysis of ZEBDC was achieved in 30 % solutions of H_2SO_4 where the maximally possible amount of zinc ions in the solution and of carbon sulphide in the gas phase was observed simultaneously with the decrease of the content of organic carbon.

Table 2 data indicate that hydrolysis of ZEBDC in solutions with a high content of cineb occurs slowly and for the reduction of the value of the chemical oxygen demand (COD) to 30 mg O/L (according to the requirements to the composition and properties of water of recreational water use) a long time period is necessary. This is due to the fact that the forming intermediates are more stable in the acidic medium, than the initial condition. In addition to this, the accumulation in the bulk of zinc ions (see Table 2) occurs, for the precipitation of which additional chemical reagents should be introduced.

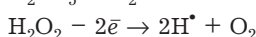
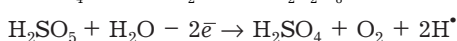
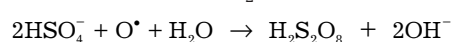
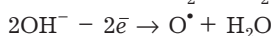
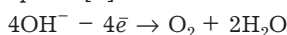
It is known that the further transformation of organic components up to the simplest compounds is possible when adding such individual oxidants, as oxygen, ozone, permanganates, dichromate's, nitric acid, metal oxides, the Fenton's reagent *etc.* [3]. However, the process that allows obtaining oxidants in situ is most efficient, for example, when passing the constant electric current through aqueous solutions of sulphuric acid [6]. This approach allows combining electrochemical and chemical transformations in one system. Supposedly, at the non-direct oxidation of the hydrolysed mixture of the commodity form of zineb, the following processes occur in parallel:

TABLE 3

Change of the content of CCO and Zn^{2+} in the course of indirect electrooxidation of zineb, mass %

Indicators	Time, min				
	0	60	120	180	240
CCO	100	75	62	57	48
Zn^{2+}	100	38	23	12.5	2.5

1. The synthesis of oxidants in the anode space [9]:



2. The synthesis of oxidants in the electrolyte [9]:

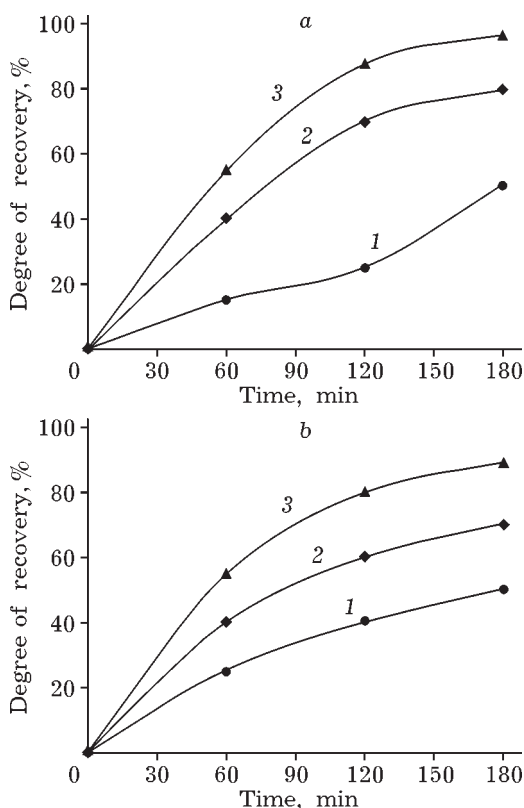
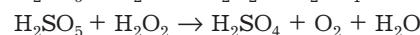
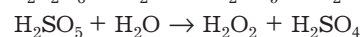
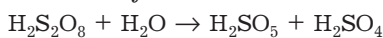


Fig. 3. Effect of the concentration of the electrolyte H_2SO_4 (C_e) at the current density $D_i = 0.50 \text{ A/cm}^2$ (a) and current density at $C_e = 50 \text{ mass \%}$ (b) on the degree of reduction of zinc ions in the process of indirect zineb electrooxidation ($C_z = 3.3 \text{ g/L}$, $T = 293 \text{ K}$): a - C_e (%): 30 (1), 50 (2), 70 (3); b - D_i (A/cm^2): 0.1 (1), 0.25 (2), 0.5 (3).

3. Oxidation of organic components of zineb in the bulk of the electrolyte and on the anode by the scheme: an organic compound \rightarrow alcohols \rightarrow aldehydes \rightarrow carboxylic acids \rightarrow carbon dioxide, sulphur dioxide and water.

4. Electrochemical reduction of some organic products of the destruction of zineb and zinc ions: $\text{Zn}^{2+} + 2\bar{e} = \text{Zn}^0$.

At the concentration of H_2SO_4 of 40 mass % and current density of 0.75 A/cm^2 , the potential of the lead cathode is equal to $-1.2 \dots -1.3 \text{ V}$ and the potential of the anode representing lead dioxide is 2 V (relatively to SCE) At such a distribution of potentials, the most favourable conditions for the separation of zinc from the solution are provided (Table 3).

The conducted research showed that the efficiency of Zn^{2+} reduction is affected by the current strength and hydrolysis rate of ZEBDC that depends on the concentration of sulphuric acid (Fig. 3).

The results obtained indicate that the hydrolysis rate of zineb is increased with the increase of the concentration of sulphuric acid. As a result, the maximal amount of Zn^{2+} ions are liberated that are further reduced to Zn^0 on the cathode (see Fig. 3, a).

The use of the acid with the concentration of more than 50 mass % leads to the decrease of the electrical conductivity of the solution, which significantly increases the energy consumption on the electrochemical process of reduction of the metal. Consequently, the isolation efficiency of the metal from the solution is

TABLE 4

Change of the content of Zn^{2+} at electrolysis, mass %

Compounds	Time, min				
	0	30	60	90	120
Zineb	100	13.5	2.4	1.2	0
SSS of zinc	100	8.3	0.4	0	—

largely determined by the current density (D_i). The optimal value of D_i lies in the range of $0.5\text{--}0.75 \text{ A/cm}^2$ (see Fig. 3, b), since at $D_i < 0.25 \text{ A/cm}^2$ the separation rate of metal ions on the cathode is sharply reduced and at the current densities of more than 0.75 A/cm^2 organic components of zineb are mineralized with the formation of a large amount of gases. This may lead to the entrainment of a portion unreacted components in the aerosol form.

At high values of the current density a strong corrosion of electrodes (Pb is cathode, PbO_2 is anode) and contamination of the electrolyte by toxic lead in the form of Pb^{2+} and PbSO_4 are observed.

In order to establish the negative influence of organic and inorganic impurities, present in the commodity form of zineb, on reduction of zinc ions, electrolysis of the state standard sample (SSS) Zn^{2+} in sulphuric acid medium was carried out (Table 4).

The presence in the commodity form of the pesticide of components, poorly soluble in water, has a minor effect on the reduction rate of Zn^{2+} . Consequently, zinc will be efficiently isolated not only from the solution but also from

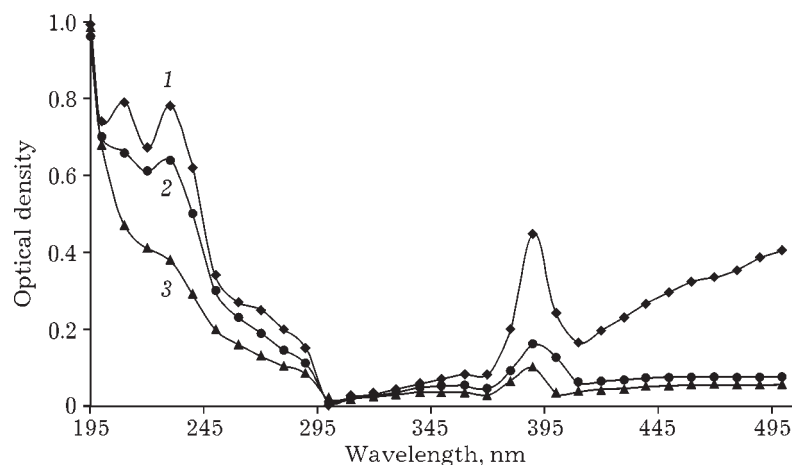


Fig. 4. Spectra of adsorption of sulphuric acid solutions in the process of indirect electrooxidation of zineb. Treatment time (min): 0 (1), 4 (2), 30 (3).

TABLE 5

Degree of destruction of zineb (α) at electrochemical processes

Processes	Time, h	C_z , mg/L	α , mass %
Electrocoagulation [4]	1	2.8	85
Electrochemical oxidation [4]	1	2.8	95
Indirect electrooxidation	0.5	100	90
Liquid-phase oxidation in 30 % H_2SO_4 solution	1.5	100	70

Note. C_z is zineb concentration.

the emulsion and suspension. Simultaneously with the isolation of the metal on the cathode, the process of deep oxidation of original organic components of the fungicide and their destruction products occurs, which is indicated by the data of physicochemical methods of research (see Table 3, Fig. 4).

The experimental data show (Table 5) that at indirect electrooxidation zineb is mineralized three times faster, than at liquid-phase oxidation and this occurs most intensively in the first 6–7 min of the process. Although the current yield based on the number of reduced zinc ions at the current strength of 1 A and time of 0.5 h is only 3 %, this method differs favourably from other, pure electrochemical processes by the possibility to perform deep oxidation of highly-concentrated sulphuric acid solutions of organic components of the pesticide up to simple compounds, with the same efficiency as at low original concentrations.

The qualitative analysis showed that the final gaseous products of the process were represented by ammonia; carbon sulphur and carbon dioxide that are absorbed by water after exiting the electrolyzer. The spent electrolyte containing simple organic and inorganic compounds undergo neutralization after several cycles of the use. The resulting waste relates to the 4th class of danger.

CONCLUSION

Thus, it has been shown that the use of the method of indirect electrooxidation provides the full mineralization of organic components of the pesticide zineb up to simple and non-toxic compounds in the bulk of the electrolyte and precipitation of forming zinc ions from the solution on the lead cathode.

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