

Effect of the Technological Parameters on the Liquid-Phase Electrochemical Oxidation of Pesticides

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Abstract

It was established that deep oxidation of such toxic strong compounds as organometallic pesticides occurs under the action of the system formed by passing the electric current through aqueous solutions of sulphuric acid. On the basis of experimental data, multiparametric equations characterizing the effect of the current density, temperature, concentration of sulphuric acid on the rate of oxidation of the organic fragments of pesticides and metal ion reduction on the cathode were obtained.

INTRODUCTION

Neutralization of toxic organic compounds with the expired use-by date or prohibited for use is a substantial problem at present. These compounds include ill-conditioned pharmaceutical preparations, pesticides, weapon chemical agents and other toxic wastes. These substances are stored at special ground in large amounts thus creating the danger in the aspect of ecology and fire. Therefore, it is necessary to neutralize these substances. The existing methods, such as burying [1], combustion [2], plasmachemical destruction [3] are imperfect, have a number of disadvantages and in many respects do not correspond to the ecological requirements. At present, intense development of other technologies and methods of ecotoxicant neutralization is carried out.

One of the promising methods of neutralization of highly concentrated toxic wastes is a combination of the liquid-phase and electrochemical oxidation, the so-called indirect electrooxidation. Previous investigations carried out with organometallic pesticides [4, 5] showed that this method may be used to perform deep destruction of strong toxicants (ST) with elec-

trochemically generated oxidizers to form non-toxic compounds; no secondary pollutants are formed. However, these works did not consider the effects of various factors on the rate of ST destruction.

The goal of the present work was to investigate the effect of the current density, temperature and concentration of sulphuric acid on the rate of oxidation of the organic components of ST and on the rate of metal ion reduction to the zero valence state at the cathode.

EXPERIMENTAL

The commercial forms of organometallic pesticides were investigated: Granosan (2 % Rhodamine C (RC), 2 % ethylmercurochloride, 96 % talc) and Zineb (reactant: the zinc salt of N,N'-ethylenebis(dithiocarbamic) acid).

The oxidative destruction of the pesticides was carried out in a set-up composed of a constant current source, diaphragm-free electrolyser with lead electrodes equipped with a jacket and a magnetic mixer [4].

Sulphuric acid of "kh. ch." (chemically pure) grade and distilled water were used to prepare the electrolyte.

The process of pesticide oxidation was monitored using the spectrophotometric technique. The concentrations of metal ions in solution were determined using stripping voltammetry.

The experimental data were processed using the data analysis package (regression analysis) Excel 2003.

RESULTS AND DISCUSSION

A number of peroxide compounds is synthesized during the electrolysis of the solutions of sulphuric acid; they form a mixture of strong oxidizers in solution [8]. At the anode, the oxidation of sulphuric acid into persulphuric acid and the formation of hydrogen peroxide take place; persulphate ion is also formed. Then persulphuric acid in the solution of concentrated sulphuric acid gets oxidized at first to form monopersulphuric and sulphuric acids, then to form sulphuric acid and hydrogen peroxide. This process is accompanied by the formation of ozone as an admixture.

The destruction of the chosen pesticides under the action of electrochemically generated oxidative system proceeds in several stages, both in the reaction volume and on the electrodes; carbon dioxide and water are formed as the final products [4, 5]. As a result of processing the experimental data, using the standard procedure of reaction order determination [6], it was established that the oxidation of these substances proceeds as the pseudo-first-order reactions because the concentrations of pesticides are much higher than the concentration of an oxidizer.

The most essential parameters governing the destruction of the organic components of

pesticides in the solution volume and at the anode, as well as the reduction of metal ions at the cathode, are the concentration of H_2SO_4 (C_{el} , %), current density (D_i , A/cm^2), and temperature (T , $^{\circ}C$).

The experimental data obtained (Fig. 1, a) provide evidence that an increase in the concentration of sulphuric acid promotes acceleration of pesticide destruction process.

At the same time, the use of concentrated acid (more than 50 mass %) leads to a decrease in the electric conductance of the solution, which results in a substantial increase in the amount of energy consumed for obtaining the oxidizer.

A decrease in the acidity of the electrolyte (less than 30 %) causes a decrease in the yield of the oxidizer, so the destruction of the pesticides under investigation proceeds mainly due to the electrochemical reduction-oxidation reactions.

It is known [7] that the efficiency of ST oxidation using the electric current depends on its density. The experimental data (see Fig. 1, b) provide evidence that the oxidation of the organic compounds and the reduction of metal ions formed during ST destruction proceed rather efficiently within the current density range 0.25–0.75 A/cm^2 because in this case the highest total concentration of the oxidizers formed as a result of the electrolysis of sulphuric acid.

For $D_i > 0.75 A/cm^2$, the rate of ST oxidation increases; however, this causes the formation of a large amount of gaseous products and, as a consequence, the loss of a part of the organic substances in the form of aerosol.

All these factors cause rapid wear of the electrode material (especially of the anode) due to its destruction, as well as contamination of the electrolyte with toxic lead in the form of Pb^{2+} (Table 1) and $PbSO_4$.

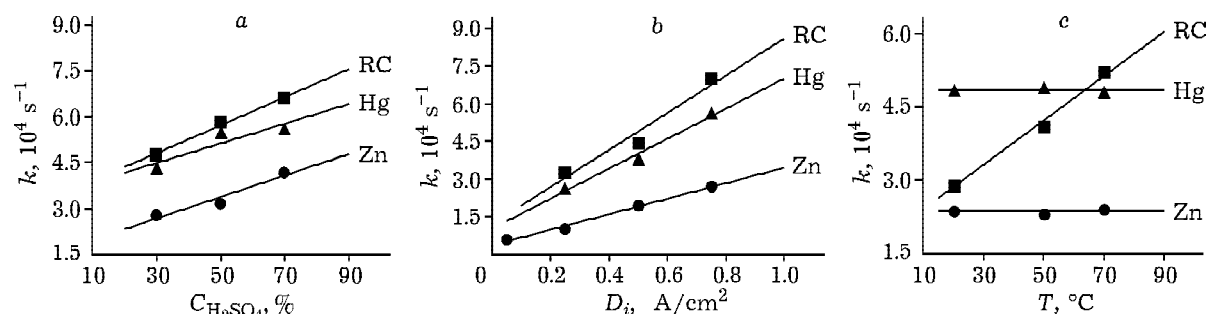


Fig. 1. Dependence of the rate constant of ST oxidation and reduction on the concentration of sulphuric acid (a), current density (b) and temperature (c).

TABLE 1

Changes in lead ion concentration in solution for granosan destruction ($C_{ef} = 40$ mass %, $T = 50$ °C, $\tau = 30$ min)

| | | | | |
|--|------|------|------|------|
| Current density, A/cm ² | 0.39 | 0.58 | 0.77 | 0.97 |
| Lead content in solution (calculated for Pb ²⁺), mg/l | 19.0 | 29.0 | 41.0 | 59.0 |

For current density less than 0.25 A/cm², the rate of metal ion deposition on the cathode decreases substantially.

An increase in the rate of ST destruction under the action of the electrochemically-generated oxidizer is possible due to an increase in the temperature of the oxidation reaction. According to the experimental data (see Fig. 1, c), with an increase in the process temperature from 20 to 70 °C, the rate of destruction of the organic substances in the volume of the electrolyte increases by a factor of 2–3 as a mean. However, at a temperature above 50 °C the reaction rate constant for difficultly oxidizable compounds is much smaller than that in the case of the oxidation of ordinary compounds. This is due to the fact that high temperatures promote destruction of a number of oxidizers (formed during the electrolysis of sulphuric acid); their lack causes slowing down of the ST oxidation process.

In this case, the reduction of metal ions is a purely electrochemical process, so temperature change (its rise or lowering) does not have any essential effect on the rate constant of metal ion reduction at the cathode, which is also in agreement with the literature data.

The experimental data were processed with the help of the statistical package of data analysis Microsoft Excel. We obtained the following

equations for the rate constant of oxidation of the organic components of Granosan and Zineb and reduction of mercury and zinc ions (k_T, s^{-1}):

$$k_T^{RC} = 8.451D_i - 0.058C_{el} + 0.059T - 3.799$$

$$k_T^{Hg^{2+}} = 5.387D_i + 0.033C_{el} + 0.046T - 1.136$$

$$k_T^{Zn^{2+}} = 3.383D_i + 0.124C_{el} - 3.546$$

These equations characterize the effect of H₂SO₄ concentration, current density and temperature on k_T . One can see that the most important part is played by the current density, similar to the case of the synthesis of oxidizers [8].

CONCLUSIONS

It may be concluded on the basis of the above considerations that the destruction of organo-metallic pesticides into non-toxic compounds proceeds with the highest intensity with the sulphuric acid concentration of 40 mass %, current density 0.75 A/cm² and temperature 50 °C.

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