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Oxidative detoxification of organomercury pesticides

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Abstract

A method of oxidative mineralization of the organomercury granozan pesticide commercial form under mild conditions was investigated. The product components of hazard class 1 were destructed to the low-toxic compounds in the electrolyte under the oxidants electrochemically formed in situ in sulphuric acid solutions of pesticide. Simultaneously, at the cathode, the mercury ions formed as a result of the pesticide organic component destruction process reduce up to more than 90%.

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1. Introduction

Pesticides are substances meant for protecting plant products from damaging influences of pests. Their application must be strictly regulated, as they are biologically active compounds. However, due to continuous development of new chemical pesticide types, discovery of their negative impact on human health, animals and plants, as well as detection of the products with modified physicochemical and application properties, being the part of other materials and/or substances, there are a lot of chemical pesticides accumulated in warehouses or unauthorised dumping grounds¹, which are often dilapidated and mostly in an emergency condition.

Since natural detoxification of chemical pesticides is much behind of their accumulation in the environment², it can result in serious biological imbalance and in some cases even in total mortality of various microorganisms³.

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Based on the DDT decomposition, taken as an example, it was revealed that the main morphological components of some toxic organics decompose for tens or even thousands of years.

Nevertheless, some types of chemical pesticides refer to the persistent organic pollutants, small quantities of which are very dangerous for human health and natural environments. Thus, chemical pesticides are considered to be one of the geo-ecological disruptors and must be recycled and/or detoxified. Due to the literature data the most common ways to recycle and/or detoxify these types of compounds are as follows: thermal, chemical, electrochemical, biological methods, as well as disposal^{3,7,8,9}. Global practice shows that liquid-phase oxidation, thermocatalytic oxidation or reduction, vapour-phase catalytic oxidation, gasification, pyrolysis reaction, plasma-chemical and flame treatment are used^{10,11}.

However, the above methods have their own disadvantages. Thermal detoxification methods are rather complicated and more expensive as high temperatures shall be used and the secondary pollutants generated shall be removed. Plasma-chemical technologies are limited in use due to their requirement of power-consumption, complex method implementation and purification of discharges. Thereby, combined liquid-phase oxidation, where high oxidation potential compounds as destructive agents are used, is of great interest.

In this regard, the purpose of the paper is to investigate liquid-phase process when detoxifying granozan pesticide with the oxidizing complex ($\text{H}_2\text{S}_2\text{O}_8$, H_2SO_5 , H_2O_2 , O_2 and O_3) that appear in situ on the lead electrode when the electric current passes through the sulphuric acid solution.

Nomenclature

HCH	hexachlorocyclohexane
COD	chemical oxygen demand
MAC	maximum allowable concentration
Di	density current

2. Experiment

Commercial form of granozan, consisting of ethylmercurchloride, colouring agent and talc, is taken as a subject of research. The chemical pesticide was mineralized to the non-toxic state in 30–70 % sulfuric acid solutions using the undivided cell (the volume of 30 dm³) with the lead electrodes (working area is 10 cm²) and the magnetic stir bar at the current density of 0.1–1 A/cm², the temperature of 20 °C, and the atmospheric pressure. Initial concentration of granozan was 10–1,000 mg/l.

Oxidation efficiency of the pesticide commercial form was estimated under laboratory conditions by the spectrophotometric measurements of the investigated sample solutions in visible and ultraviolet spectra, as well as by the determination of chemical oxygen demand (COD) using the Ecotest-120 microprocessor analyser.

3. Results and discussion

Granozan is a contact herbicide for dry chemical disinfection of wheat, oat, panicum and corn seeds, as well as for plant protection from phytopathogenic fungi and bacterial diseases. Granozan is a mixture of (Figure 1) 2 % of ethylmercurchloride (II), 1 % of rhodamine C (I) or purple K (III) colouring agent, 1 % of mineral oil and a filling agent.

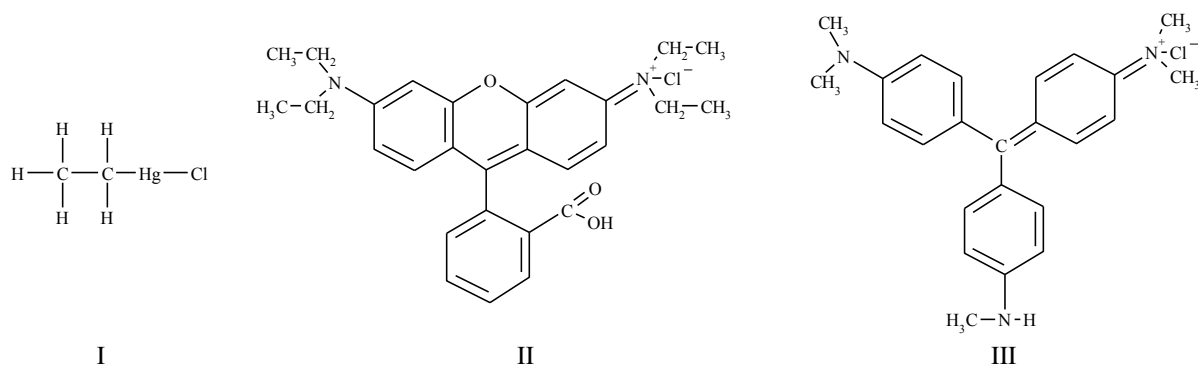


Fig. 1 – Organic components of granozan pesticide

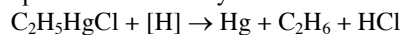
Russian industry produces some other hazardous chemicals containing ethylmercurchloride such as mercuran – it is a fixed combination of 2 % of ethylmercurchloride, gamma- hexachlorocyclohexane (γ -HCH) and talc, and mercurigexan – it is a fixed combination of 0.8–1 % of ethylmercurchloride, 20 % of hexachlorbenzene, up to 15–20 % of γ -HCH and 59 % of talc. Foreign industry produces harsh chemicals containing ethylmercurchloride as well.

Granozan is a highly toxic substance. Its maximum allowable concentration in the working zone air is 0.005 mg/m³ (by mercury). Occurrence of granozan in the environment is under strong control (Table 1).

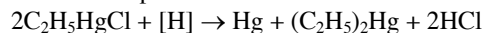
Table 1. Maximum allowable concentration (MAC) in waters of commercial fishing importance and the hazardous class of the granozan pesticides and their metabolites

Substance	MAC, mg/l	Hazardous Class
Purple K primary colouring agent	0.1	4
Rhodamine G colouring agent	0.1	4
Ethylmercurchloride	0.00001	1
Diethyl mercury	0.00001	1
Mercury	0.0005	1

The chemical is distinguished by the volatile properties even at low temperatures, thus, at improper storage, unconditional granozan pesticide become reactive and decompose with the formation of cancerogenic metabolites. Soil bacteria make mercury organic compounds reduce to hydrocarbon and metallic mercury:



Moreover, dialkyl mercury formation takes place as well:

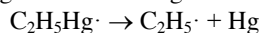


The above said products partially dissipate in the atmosphere, and non-volatile mercury derivatives remain in the soil, usually as mercury oxides or sulphides that are almost insoluble in water and cannot be taken up by the plants.

The photolysis results in the decomposition of organomercury salts into the radicals as follows:



which in its turn enter the reaction according to the following scheme:



All these factors result in permanent pollution that will affect the environment for a long time even after the main source of the pollution is eliminated. Thus, nowadays, recycling and detoxification of the useless or unconditional chemical pesticides are one of the important tasks. At present, combined methods of hazard substance recycling and/or detoxification become more and more popular^{9,12}, for example, liquid-stage disruptive oxidation of the

pesticides and similar toxicants using various oxidative systems. Oxygen, ozone, hydrogen peroxide and other active components generated as a result of electrochemical process interact with the organic components of the toxicant commercial forms and decompose them to non-toxic substances^{8,13,14}.

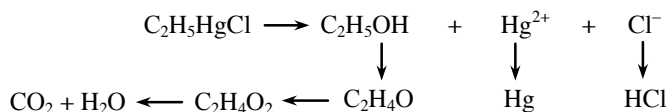
The amount of oxidants affects the decomposition rate of the chemicals, so this process can be forced by varying electrolyte composition that should be non-reactive to the electrode material (the cathode is made of lead, the anode is made of lead dioxide), able to generate peroxide compounds of maximum efficiency, non-toxic and non-volatile, as well as easily recycled. For the example, investigations provided below, individual solutions of KCl, NaOH, K₂SO₄, H₂SO₄, (NH₄)₂S₂O₈ in water and their mixtures were selected as electrolytes that are able to release oxidative particles. The experiments performed (Table 2) showed that when sodium hydroxide is added to the electrolyte, the amount of the generated oxidant is not enough for complete mineralization of all pesticide components among which there are colouring agents, surface-active agents and others. Thus, in these conditions, decomposition process goes due to electrochemical reactions and only at high-density current (Di) resulting in rapid electrode wear and considerable power consumption.

In industry, available chlorine, generated by chlorine-containing compounds anode oxidation, is often used for organic substance oxidation. The investigations show that the pesticide decomposition is effective only at the increased oxidant doses. However, in this case, a lot of gases are evolved, which take most of the unreacted chlorine.

Table 2. Effects of the electrolyte composition on the oxidation process of granozan pesticide: C_{gr}= 1 g/l, τ – 120 min, Di – 1 A/cm²

Electrolyte composition	NaOH	KCl	K ₂ SO ₄	(NH ₄) ₂ S ₂ O ₈ + H ₂ SO ₄	H ₂ SO ₄
Additive ratio, mole/dm ³	4	2.5	3.5	0.2+7.5	7.5
Pesticide decomposition degree, %	43	45	50	82	85

Some methods of electrochemical synthesis of the oxidants from the sulfate ion solutions are known. For example, electrolysis of the K₂SO₄ or (NH₄)₂S₂O₈ water solution results in formation of persulphates that have a high oxidation-reduction potential. However, detoxification of pesticides in the above systems is not effective due to low conductivity of neutral solutions. So, if the oxidation time exceeds 30 minutes, extreme heating of the reaction mass occurs (up to the solution boiling temperature). It results in destruction of peroxide compounds and the oxidative decomposition process transfers from the electrolyte layer to the electrodes. In this case, the electrode material wears out very quickly, the electrolyte is vaporized, and some unreacted pesticide components disappear from the unit of the equipment. Conductivity of a neutral solution can be increased when making the solution more acidic, for example, by means of adding sulphuric acid. However, the experimental data show the sulphuric acid-water solutions having the concentration of 30–70% (w/w) and able to form the oxidant complex like H₂S₂O₈, H₂SO₅, H₂O₂, O₂ and O₃ in situ during its electrolytic process are considered as the most effective electrolytes for this purpose. Due to the variety of oxidants formed, it is possible to carry out oxidation and reduction of the organic and inorganic optional components of the pesticide product simultaneously with oxidation of the active component of the product according to the following scheme:



According to the experimental data (Table 3), the sulphuric acid oxidation reserve is enough for multiple detoxification cycles of the pesticides in the same electrolyte solution.

Table 3. Total amount of organic substances contained in the electrolyte when detoxifying the commercial form of granozan pesticide

No. of loading Time, h	Organic substance content, %					
	1	2	3	4	5	6
0	100	100	100	100	100	100
1	40	54	63	75	88	97
2	26	29	47	56	67	75
3	14	17	26	32	39	45

When oxidizing individual substances, they can be loaded up to six or more times. However, the more cycles of the electrolyte are used, the lower pesticide organic components decomposition rate is, as water becomes one of the end products at deep oxidation. So, after six oxidation cycles, fresh sulphuric acid shall be added to activate the electrolyte.

4. Conclusion

Summing up the investigation results, it is clear that detoxification of hazardous chemicals occurs in the concentrated sulphuric acid-water solutions, in which at the same time, synthesis of the oxidants, oxidation of the pesticide organic components in the electrolyte and partially at anode, as well as electrochemical reduction of the high-density metal ions (in case of the metal-containing pesticides detoxification) at the cathode take place. According to the estimated data, having been neutralized by calcium hydroxide, the spent electrolyte can be qualified as the wastes of hazardous class 4. This method can be used to detoxify various solutions, emulsions and suspensions of hazardous chemicals, as well as the mixtures of unknown composition.

Acknowledgements

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