Mineralization of organophosphorous pesticides by electro-generated oxidants

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Abstract

In this study we have investigated organophosphorous pesticides destruction by oxidizing system, which was synthesized in the polluted aqueous sulfuric acidic solutions by constant current conducting. Bulk electrolyses with lead electrode were performed in an undivided cell under amperestatic conditions to study the oxidative cleavage of commercial pesticides and pure active ingredients. The pesticides were completely destroyed following pseudofirst-order kinetics estimated according to chemical oxygen demand (COD) data and phosphate ions accumulation. The assessment of decay rate constants shows the high mineralization degree. Moreover, the general current efficiency corresponds to high impact of chemical reactions in the bulk along with electrochemical interactions and defines the reasonable treatment process time as 120 min. The decay rate constants obtained by phosphate formation are higher for glyphosate than rate constants estimated by COD. It may be explained by P–C bond breaking and phosphate ions cleavage. For further study of organophosphorous pesticides oxidation pathways in detail by described process, the conditions of electrolysis should be milder.

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1. Introduction

Organophosphorous compounds are widely used as pesticides as well as chemical warfare agents. Undoubtedly such chemicals are highly toxic and dangerous to human and environment, chiefly by affecting the central nervous system. However, the pesticide wastes may be formed at the manufacturing, usage or storage of organophosphorous pesticides (OPs). In some publications, pesticide waste is also correctly referred to as *obsolete pesticides*. According to the inventory of Food and Agricultural Organization (FAO)[1], most developing countries have outdating and deteriorated stocks of obsolete pesticides. In whole world, around 300 kilotons of pesticides wastes were accumulated, and it is important to note that the third part belongs to the Russian Federation. These stocks are often stored in poor conditions and pose a threat to human health and the environment.

The hazardous nature of OPs and their wide usage has led to concerted efforts to develop methods for the destruction of these toxins[2,3].

An ideal treatment method for pesticide surplus should be non-selective, suitable for small-scale wastes, and achieve rapid and complete mineralization[4]. Today the main disposal method of obsolete pesticide stock is incineration, an impractical and expensive procedure[1]. The biological degradation of pesticides is generally difficult due to their high content in toxic matter[5].

To degrade OPs, diverse physical-chemical treatments such as granular activated carbon[6], wet air oxidation[7], photo-Fenton[7], UV/O$_3$ [8] or UV/H$_2$O$_2$ [9], and electro Fenton[10] were applied. Removal of phosphorus from pesticidal effluents can be achieved by combined chemical-biological treatment wherein additives are added into the aeration chamber[11,12]. The principle behind this technique is to convert soluble phosphorus into insoluble form by complexing with metallic ions coupled with microbial phosphorus assimilation and to transfer insoluble phosphorus into sludge mass, which can be removed efficiently by any conventional solid-liquid separation device. To maintain high efficiency, the combined process requires low sludge age, proper method of chemical addition, and effective solid-liquid separation in the final clarification step[12]. Also, among novel techniques, advanced oxidation processes (AOPs) have been widely used[13,15], due to the merits of rapid reaction rates and removals of non-degradable compounds. However, they need to be evaluated for effectiveness, costs, and possible side effects. It should be noticed that AOPs need not be very effective for treating highly concentrated effluents with the concentrations of organics several hundreds up to 1000 mg/l [14].

Therefore, development of new treatment technique for OPs is needed to overcome these problems. In this case the application of electrochemistry for the protection of the environment should be mentioned, since it offers promising approaches for the prevention of pollution problems in the process industry[16].

In the present work, we for the first time employed electro-generated oxidizing system for efficient mineralization of toxic OPs, such as glyphosate, malathion, bazudin, chlorophos and methaphos. For this aim, 100 mL of the aqueous sulfuric acidic polluted solutions have been electrolyzed with lead electrodes in an undivided electrolytic cell. There are serious difficulties in the analysis of intermediates due to very high acidity of the solutions. Thus, chemical oxygen demand (COD) was determined and it was compared to analysis of phosphate ions accumulation.

2. Experimental

2.1 Experimental setup

The main point of this method is the integration of the electrochemical generation of high-reactivity intermediates with their subsequent chemical reactions with substrates in an electrolytic solution. The construction of diaphragmless cell allows carrying out above mentioned processes (Fig. 1).
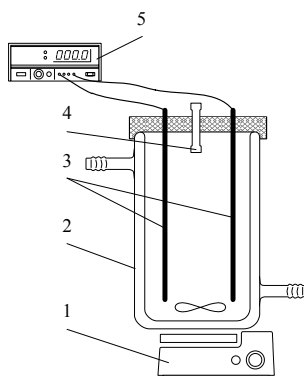
Fig. 1 Installation of organic compounds cleavage:
1. – magnetic stirrer; 2. – glass reactor with jacket; 3. – lead electrodes; 4. – outlet of gaseous products; 5. – constant–current source.

The lead cathode and anode are used in these processes, as this material is destructed in a fewer extent. Also anode is being covered by lead dioxide in an active sulfuric medium.

Intensive stirring is the great advantage for oxidation not only solutions but also suspensions and emulsions. Furthermore it is applied to increase an oxidation rate and prevent stagnant zones formation in a reactor.

2.2 Materials

To determine the limits of this method application a number of organophosphorous pesticides have been chosen (Table 1).

Table 1. The description of organophosphorous pesticides treated with electrogenerated oxidizing system.

Commercial pesticide	Active ingredient of pesticide	Structure	LD_{50} mg/kg	Product description
Glyphosate	N-phosphonomethylglycine $C_3H_8NO_5P$		5600	36 % e.c. 50 % w.p.
Karbofos, Malathion	O,O-dimethyl-S-1,2-dicarbeth-oxyethyl dithiophosphate $C_{10}H_{19}O_6S_2P$		400…1400	50 % e.c.
Bazudin, Diazinon	O,O-diethyl-O- 2-isopropyl-4-methyl-6-pyrimidil thiophosphate $C_{12}H_{21}N_2O_3SP$		76…130	60 % e.c.
Chlorophos	1-hydroxy-2,2,2-trichloroethyl-O,O-dimethyl phosphate $C_4H_2Cl_3O_4P$		225…1200	80 % w.p.
Metaphos	O,O-dimethyl-4-nitrophenyl thiophosphate $C_8H_{10}NO_5SP$		15…35	40 % e.c.

e.c. – emulsifiable concentrate;
w.p. –wettable powder.

They cover the wide variety of OPs. Firstly, some of these compounds have direct hydrocarbon chain, for example, karbofos and chlorophos, whereas some of them contain an aromatic ring, such as metaphos. Some of these pesticides are forbidden to use (for example, metaphos), but such chemicals are still kept in agricultural warehouses and they need to be destroyed. But as for glyphosate, also known as roundup, it has become the world's leading agrochemical[17], and its physical, chemical, environmental, and toxicological properties have been well-

documented[18,19].

The 10 % and 40 % (w.) sulfuric acid solutions were prepared from pure chemical reagent by dilution, controlled by density measurement, and used as a solvent and electrolyte.

To determine of orthophosphate ions concentration, the mixture of ammonium molybdate, sulfuric acid, sulfamic acid, antimony chloride and tartaric acid were used. All reagents satisfy the requirements of the Russian state standards.

2.3 Analysis

To quantify the pesticides mineralization the chemical oxygen demand (COD) as a function of time was carried out by ionomers voltammetric analyzers oximeters ("Ecotest-120", Russia).

Orthophosphate ions concentration was measured colorimetrically as the phosphomolybdate yellow complex using UV/VIS spectrophotometer (Evolution 60, USA) at 710 nm [20].

3. Results and Discussion

Basically, the electro-generated indirect cleavage proceeds under the action of strong oxidants, similar to the chemical incineration, moreover, *in-situ* electro-generation allows better efficiency of the organic substrates destruction and avoids the need for transportation and storage. Peroxydisulfuric acid and its salts electrogenerated by anodic oxidation of sulfuric acid and sulfates are hydrogen peroxide precursors. At the first stage of this process, the charge and adsorption of sulfate and hydrosulfate ions occur. The further vanishing of these intermediates occurs due to the reaction of recombination and electrochemical desorption.

Furthermore in acidic medium peroxydisulfate ions are hydrolyzed according to the following reactions:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-} \tag{1}$$

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \rightarrow HSO_4^- + SO_4^{\cdot} \tag{2}$$

$$SO_4^{\cdot} + H_2O \rightarrow H_2SO_5 \tag{3}$$

Also it has been demonstrated[21] that ozone can be formed during electrolyses with PbO_2 electrodes at high potentials:

$$PbO_2(^{\cdot}OH)_{ads} \rightarrow PbO_2(O^{\cdot})_{ads} + H^+ + e^- \tag{4}$$

$$PbO_2(O^{\cdot})_{ads} + O_2 \rightarrow PbO_2 + O_3 \tag{5}$$

Then, in the solution bulk, peroxydisulfuric acid is decomposed in two stages through formation of peroxymonosulfuric acid known as Caro's acid.

$$H_2S_2O_8 + H_2O \leftrightarrow H_2SO_5 + H_2SO_4 \tag{6}$$

$$H_2SO_5 + H_2O \leftrightarrow H_2O_2 + H_2SO_4 \tag{7}$$

The hydrolysis of peroxymonosulfuric acid is the reversible process. And the rate-determining step is hydrogen peroxide formation due to peroxymonosulfuric acid hydrolysis by the reaction (7).

The decomposition of persulfate in aqueous solutions with wide range of pH value is first order reaction. And in strongly acid solutions Caro's acid is an intermediate in the decomposition of persulfuric acid to form hydrogen peroxide.

So in a bulk of solution the following mediators are formed: $H_2S_2O_8$, H_2SO_5, H_2O_2, also a little quantity of O_3 and products of their cleavage, possessing high oxidative potential. The same oxidizing system was successfully applied to salicylic and sulfosalicylic acids cleavage[22].

3.1 Mineralization of Pesticides

To estimate pesticides mineralization we have measured COD concentration and then calculated the conversion

of COD, X_{COD}, according the following equation:

$$X_{COD}(\%) = \frac{[COD]_0 - [COD]_t}{[COD]_0} \cdot 100\% \tag{8}$$

where $[COD]_0$ is the initial COD concentration of the pesticides solutions (mgO_2/dm^3), and $[COD]_t$ is the residual COD concentration at time *t* of treated pesticides solutions. The reduction of COD estimated by (8) is widely used for destruction measuring of different pesticides and other organic pollutants[23] as well. The data are shown in Table 2.

Table 2. The conversion of chemical oxygen demand obtained for OPs oxidation during electrolysis: initial concentration of pesticides – 0.1 M in 10 % (w.) aquatic sulfuric solution, current density – 0.12 A/cm^2.

Pesticide	The time of electrolysis, min								
	15	30	60	90	120	150	180	210	240
	COD conversion, %								
Glyphosate	9.4	23.7	35.8	59.6	73.3	83.4	91.4	99.0	–
Karbofos	46.3	78.4	86.5	95.2	97.8	98.0	98.3	98.4	99.8
Bazudin/ Diazinon	3.9	8.3	16.7	56.2	83.3	87.6	91.7	96.1	99.8
Metaphos	2.8	8.5	29.0	42.7	43.4	56.8	79.9	89.4	99.1

Thus, the total mineralization of four commercial OPs was achieved till 240 min of treatment time. But it was known[24] that diazinon was treated with an electrolysis system using Ti/Pt as anode and stainless steel as cathode and the achieved reduction was more than 50%.

At the same time, these data are related to removal of not only active ingredients of pesticides but also bulkier materials, e.g. dyestuffs, surface active agents and talc, which are contained in commercial products. Also the bulkier materials may influence detoxication treatment as foam is shortly formed at the beginning of electrolysis of commercial pesticides. So we have treated pure active ingredients of metaphos and chlorophos (Table 3).

Table 3. The conversion of chemical oxygen demand obtained for active ingredients of OPs oxidation during electrolysis in 40 % (w.) aquatic sulfuric solution, current density – 1.2 A/cm^2.

Pesticide	Initial concentration g/l	The time of electrolysis, min					
		30	60	90	120	180	240
		COD conversion, %					
Chlorophos	3.7	16.95	37.14	51.67	73.25	95.63	100
Metaphos	9.4	22.94	54.75	81.68	95.02	96.89	99.57

These data also confirmed the complete mineralization of pesticides, but the conditions of electrolysis were more severe. Even if the initial concentrates increase two times, the total removal time rises to a very little degree (Fig. 2).
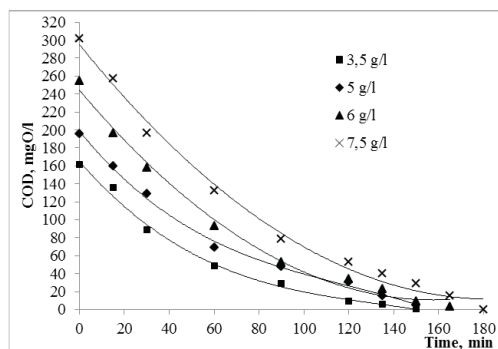
Fig. 2 Decay of glyphosate with electrolysis time, determined by COD, for the treatment solutions of 100 ml containing herbicide in 40 % (w.) of H_2SO_4 solution at 0.9 A/cm^2.

3.2 COD current efficiency

Current efficiency is generally defined as the ratio of the charge used for the oxidation of each compound to the total charge passed during electrolysis[25]. In this work we used general current efficiency (GCE) represented as an average value of current efficiency, between the initial time $t = 0$ and t. It can be determined with COD using the following relationship:

$$GCE = F \cdot V \cdot \frac{(COD_0 - COD_t)}{8 \cdot I \cdot t} \qquad (9)$$

where COD_0 and COD_t are chemical oxygen demands (gO$_2$/dm^3) at times $t = 0$ (initial) and t (min), respectively; I is the current (A), F is Faraday's constant (96485 mol^{-1}), V is the electrolyte volume (dm^3), and 8 is the oxygen equivalent mass (g eq^{-1}).

Table 4 shows the values calculated for 120 min and 210 min of process treatment.

Table 4. The general current efficiency (GCE, relative unit) of organophosphorous pesticides mineralization during electrolysis treatment.

Pesticide	The time of electrolysis, min	
	120	210
Glyphosate	8.2	6.3
Karbofos	14.7	8.4
Bazudin/ Diazinon	8.7	5.7
Metaphos	9.7	7.8

When the COD current efficiency is 1, the theoretical COD reduction is equivalent to the value of $8 \cdot I \cdot t/(F \cdot V)$. GCE (COD) of more than 1 might be caused by impact of chemical oxidation in the bulk solution. At the same time, the GCE values are higher at 120 min of electrolysis time, than at 210 min. Thus, the reasonable treatment process time is 120 min, that is confirmed the data from Fig. 2 as well.

3.3 Assessment of decay rate constants

Theoretically, the concentrations of mineralization products (PO_4^{3-}) in solution bulk will stoichiometrically increase according to eq (10) (1 mol PO_4^{3-} per mol OPs), which is given here only to its most oxidized state during the degradation.

$$C_xH_yO_zP + [Oxd] \rightarrow CO_2 + H_3PO_4 + H_2O \qquad (10)$$

For this reason, PO_4^{3-} was chosen as the examination product to ensure that no pesticide is lost during the electrolysis treatment. The kinetic analysis the OPs treatment by electro-generated oxidizing system was carried out according to a pseudo-first-order reaction. We have evaluated the decomposition of organic matter (COD concentration) in comparison with phosphate formation rate, which are given in Table 5.

Table 5. Estimated rate constants for organophosphorous pesticides degradation based on COD and phosphate ions concentration.

Pesticide	The rate constants determined by COD, min^{-1}	The rate constants of phosphate formation, min^{-1}
Glyphosate	0.97 ± 0.02	1.14 ± 0.05
Karbofos	2.40 ± 0.04	1.26 ± 0.08
Bazudin	1.44 ± 0.07	1.098 ± 0.02

Rather controversial values of rate constants may be explained by different degradation pathways of OPs. In case of karbofos and bazudin, the phosphate ions accumulation proceeds slower than the destruction of organic matter and vice versa for glyphosate. As for glyphosate, phosphate ions first cleave and then the destruction of organic intermediates proceeds. We assume that glyphosate destruction begins with breaking the P–C bond, phosphate ions cleavage. The organic matter of karbofos and bazudin is destructively oxidized and phosphate ions slowly cleave. Also these pesticides contain sulphur, the compounds of which increase the COD values.

Decontamination of aqueous glyphosate solutions by electro-Fenton-like process was represented in [10] and the calculated psuedofirst-order rate constants for glyphosate decay have the following values: 0.086 min^{-1} (0.1 mM), 0.039 min^{-1} (0.2 mM), and 0.010 min^{-1} (0.4 mM), that are much lower than the rate constant of glyphosate degradation by electro-generated oxidizers.

Conclusion

We have demonstrated that the complex of oxidizing intermediates synthesized by conducting direct current through sulfuric acid solution contained OPs can be successfully employed for efficient mineralization of these pesticides. The process leads to the complete destruction of commercial pesticides and pure active ingredients. According to analysis of pseudofirst-order decay kinetics and values of general current efficiency, the chemical oxidation prevails over electrochemical reactions. Also it was shown that the reasonable treatment process time is 120 min. In addition, it should be noted that to study the organophosphorous pesticides oxidation pathways in detail by described process the conditions of electrolysis should be milder.

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