DESTRUCTION OF CHLORINE-CONTAINING ORGANIC AGENTS IN A SYSTEM PLASMA – LIQUID

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The plasmachemical destruction of persistent toxic agent 1,1-di(4-chlorophenol)-2,2,2-threechlorethane (DDT) in water solutions is researched in this work. The destruction of agricultural pesticide containing DDT was carried out in water solution at atmospheric pressure with usage of plasma treatment on the basis of secondary discharges with a "liquid" electrode, and of combination of a plasma method with reagent method. The comparative analysis of results of the physical-chemical analysis and biological test of toxicity of solutions is carried out and the optimum regimes for destruction and detoxication of DDT in water are determined.
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1. INTRODUCTION

At present the huge amount of anthropogenous contaminants are accumulated in the world. The most dangerous contaminants on international standards are dioxins, polychlorbiphenyls and pesticides [1]. The basic migration of these contaminants to bio objects occurs through waste and ground waters. Therefore the major attention is given now to development of new advanced oxidative technologies (AOT) of water purification to which the different plasma technologies belong.

The usually plasma technologies of water purification create on the basis of self-maintained electric discharges which ones generate non-equilibrium plasma: corona discharge, barrier discharge, combination of corona and barrier discharge, diaphragm discharg, gliding arc.

The numerous investigations of plasma treatment of water with an organic pollutants have shown effective degradation of an initial pollutant. However physical-chemical analysis has shown an appearance of high-molecular substances in water after plasma treatment.

Interest to investigation of toxicity of output products of plasma chemical processes also is bound with necessity of the solution of a problem of feed-backs for ecological plasmachemical technologies such as water purification and destruction of a toxic waste. The real opportunities (physical and economical) of modern methods of the physical-chemical analysis of multi-component solutions of high-molecular compounds do not allow to hope for their usage for a primary signal of feed-backs. But today some biological tests of toxicity are rapid and cheap [2].

2. METHODS

The choice of the schema of plasmachemical treatment of water was bound with necessity of realisation of the following requirements:

- Operation at atmospheric pressure;
- Big contact area of plasma with liquid;
- Permanency and uniformity of plasma parameters near an interaction range of plasma with liquid;
- Flexibility of control of plasma chemical action on liquid.

The first requirement ensures a simplicity and low cost price of technology. The second requirement ensures a high productivity of treatment. The third and fourth requirements should ensure minimisation of spectrum of waste products. The confrontation of these requirements and physical properties of such classic electric discharges as barrier, corona and spark show their feeble compatibility. As the plasma of these discharges is non-stationary or heterogeneous.

Besides the peculiarity of this gas-discharged systems on the basis of self-maintained discharges is a relative coherence between various plasma parameters. Independent control by energy, concentration and composition of charged particles is impossible in an interaction range of plasma with the liquid, as practically one external factor (electric field) determines an existence of plasma.

Therefore treatment of water with pesticide containing DDT was conducted in plasmachemical reactors on the basis of secondary discharge with a "liquid" electrode. The key peculiarity of such secondary discharges is an independent control of plasma parameters in an interaction range "plasma - liquid" and stream of charged particles through an interaction range.

The flowing plasma chemical reactor for treatment of solution (Fig. 1) consisted from the glass cylinder (1), a diameter of 120 cm, which was closed by the cover (3). A free jet of atmospheric air ran from the nozzle (4) across two opposite electrodes (5) and formed a bright crescent-shaped electric arc. We used the rod graphite electrodes with diameter d = 5 mm. A nominal gap between the electrodes from which we started usually was δ = 1 mm. The air nozzle (4) was axisymmetric, with inner diameter $\varnothing$ = 1 mm, made from stainless steel. It was maintained vertically in a plain of the electrodes (5) at the length L = 5 mm and was centered strictly between the electrodes. The exhaust gases came out of a reactor through two holes (6) with diameter 6 mm in the cover (3). The current of secondary discharge rans through a plasma (7) of arc discharge, a transition layer (8) and a liquid. The

distance between electrodes of arc discharge (5) and an electrode of secondary discharge (2) was h_1 = 1 cm.

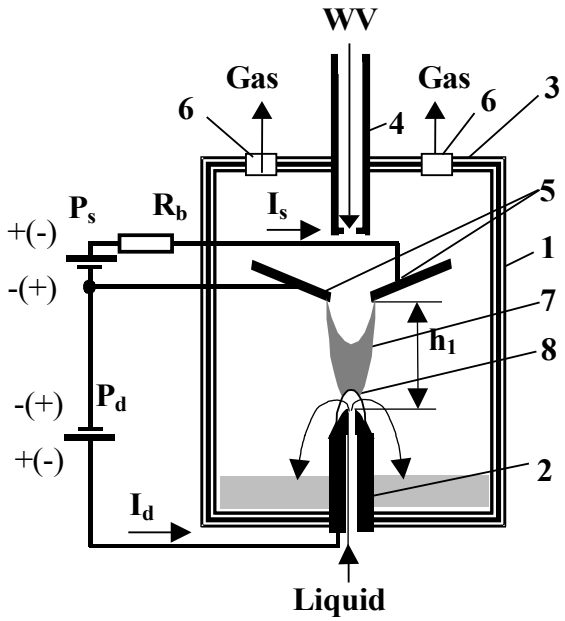

Fig.1. Experimental system for water treatment in flowing regimes

The power supply (P_d) of the secondary discharge connected to one of electrodes of arc discharge (5) and to an electrode (2). The source of alternating current (50 Hz) or of DC was a power supply (P_s) of arc discharge. The secondary discharge is powered by the DC source. The secondary discharge was with the "liquid" cathode or with the "liquid" anode depending on polarity of the electrode (2).

Distinctive peculiarity of the flowing plasma chemical reactor was a continuous input of the solution by the axial channel, a diameter of 1.5 mm, of duralumin conic electrode of the secondary discharge (2), a diameter of 1.5 mm and a taper angle of 60°. The electrode (2) was submerged in a plasma of the arc discharge.

The stream of air was 80 cm^3/s in all investigated regimes. Exhaust gas bubbled through a column of the satiated solution of alkali (NaOH), a height of 5 cm, before emission in an atmosphere.

The toxic agent 1,1-di(4-chlorophenol)-2,2,2-threechloroethane ($(C_6H_4Cl)_2CHCCl_3$) (DDT) in form as agricultural chlorine-containing pesticide (superfine clay / non-ionic surfactant / DDT: 0.65/0.05/0.3) were used as objects of research. Technical agricultural pesticide contains 30% DDT at weight. It dissolves in a water because of presence of the surfactants. The water emulsion with a pesticide had a DDT concentration $1kg/m^3$.

UV absorption spectroscopy method was applied for analysis of the destruction of DDT in water emulsion. The light source used in this analysis is a deuterium lamp.

The dependence of an absorption coefficient of solutions at λ = 270 nm was applied for a quantitative assessment of concentration of pesticide in a solution after plasma treatment. The strong absorption of water after plasma treatment was watched in the area of wave lengths smaller 250 nm because of occurrence of hydrogen dioxide in it. The standard ion-metrical procedure was used for a measurement of pH of solutions.

The toxicity of solutions was determined on their influence on habitability of biological objects. As objects the microorganisms *Daphnia magna* were used, as the study of habitability such organisms underlies the standard biological tests on the toxicity [3].

This bio-test of the toxicity are based on the measurements of the life time of such organisms in tested solutions. Distilled water at room temperature was a control solution at examination of solutions on toxicity.

3. RESULTS AND DISCUSSIONS

The typical absorption spectrums of solutions after plasma treatment with the "liquid" cathode and anode are shown in Fig. 2 for currents of auxiliary discharge I_s = 400 mA and secondary discharge I_d = +200 mA (curve 2) and -200 mA (3), initial solution (curve 1).

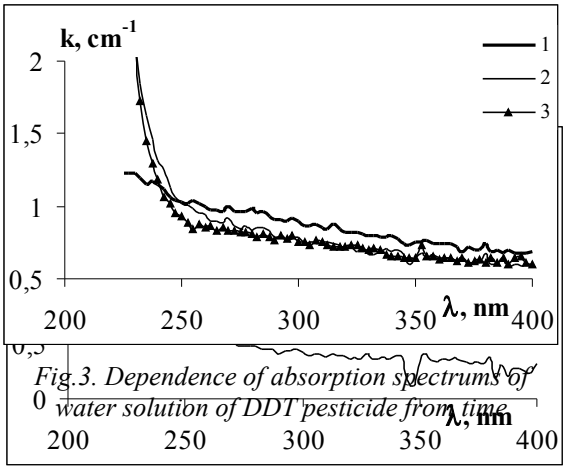

Fig.3. Dependence of absorption spectrums of water solution of DDT pesticide from time

Fig.2. Absorption spectrums of water solution of DDT pesticide

As it is visible from Fig.2 destruction has place. The output products are chemical steady in time, about which testify spectra of absorption shown on Fig. 3 (curve 1 - initial solution of pesticide; 2 - after treatment; 3 - in day after treatment). However it is impossible to identify output products on spectra of absorption.

The essential question is the toxicity of output products. It was checked up with measurement of life time of population *Daphnia magna* and has shown, that it has decreased in 2.5 times in comparison with an initial solution (Fig. 4).

It was shown earlier [4], after plasma treatment of distilled water the oxidizing agents, such as hydrogen peroxide and oxides of nitrogen (H_2O_2, HNO_2, HNO_3) were formed. This fact well illustrates by absorption spectra of water after plasma treatment (Fig. 5). Possibly

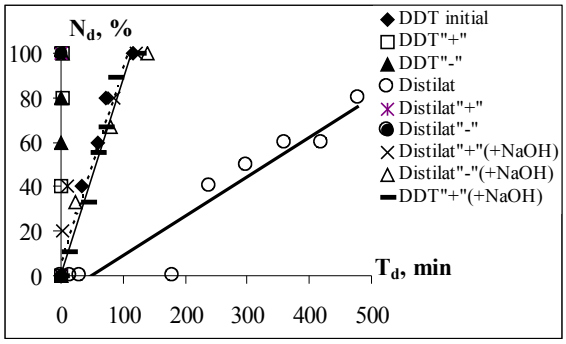

Fig.4. Dependence of life time of Daphnia magna population

the presence of these oxidizers decreased the life time of population *Daphnia magna* (Fig. 4). More that and standard ion-metrical procedure has shown a decreasing of pH from pH = 6.8 in an initial solution of pesticide to pH = 3.35 in these solutions after plasma treatment. It indicates on appearance of acid properties of treated

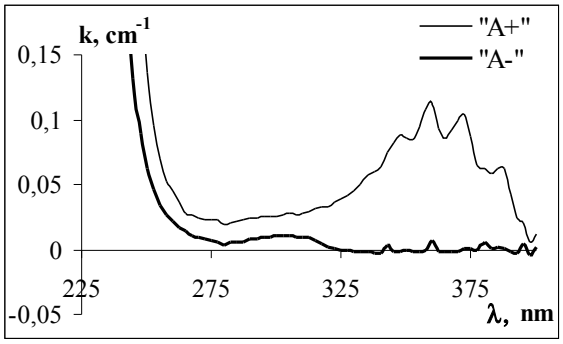

Fig.5. Absorption spectrums of distilled water after plasma treatment

solutions. Therefore was logical to add in the treatment solutions alkali for neutralization of oxidizers. Results of such researches on Fig. 4. From these results it is visible, that by adding of alkali the toxicity of solutions is decreased.

4. CONCLUSION

The present study reveals that the destruction of persistent toxic agricultural pesticide containing DDT in plasma-liquid system of secondary discharges with a "liquid" electrode is a reliable and effective process.

The plasmachemical treatment on the basis of secondary discharge with a “liquid” electrode can provide effective destruction of chlorine-containing pesticide in water. However growth of destruction of DDT is tracked by growth of toxicity of solutions from appearance of oxidizing agents in water after plasma treatment (H_2O_2, HNO_2, HNO_3).

The usage of complex plasma + reagent (NaOH) treatment can guarantee not only pesticide destruction in water, but also the small toxicity of output products.

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УНИЧТОЖЕНИЕ ХЛОР–СОДЕРЖАЩИХ ОРГАНИЧЕСКИХ ВЕЩЕСТВ В СИСТЕМЕ ПЛАЗМА-ЖИДКОСТЬ

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В работе исследовалась плазмохимическая деструкция устойчивого токсичного вещества 1,1-ди(4-хлорфенол)-2,2,2-трихлорэтан (ДДТ) в водных растворах. Деструкция сельскохозяйственного пестицида содержащего ДДТ проводилась в водном растворе при атмосферном давлении с использованием как плазменной методики на основе вторичных разрядов с «жидким» электродом, так и комбинации плазменного метода с реагентным методом. Проведен сравнительный анализ результатов физико-химического анализа и биологического контроля токсичности растворов и на его основе определены оптимальные режимы для деструкции и детоксикации ДДТ в воде.

ЗНЕШКОДЖЕННЯ ОРГАНИЧНИХ РЕЧОВИН, ЩО МІСТЯТЬ ХЛОР, У СИСТЕМІ ПЛАЗМА-РІДИНА

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В роботі досліджувалась плазмохімічна деструкція стійкої токсичної речовини 1,1-ді(4-хлорфенол)-2,2,2-трихлоретан (ДДТ) у водних розчинах. Деструкція сільскогосподарського пестициду, що містить ДДТ, проводилась у водному розчині при атмосферному тиску з використанням як плазмової методики на базі вторинних розрядів з «рідим» електродом, так і комбінації плазмового методу з реагентним методом. Проведено порівняльний аналіз результатів фізико-хімічного аналізу та біологічного контролю за токсичністю розчинів та на його базі визначені оптимальні режими для деструкції та детоксикації ДДТ у воді.