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MODELLING OF KINETICS PLASMA-CHEMICAL DISPOSAL OF PERSISTENT ORGANIC POLLUTANTS IN WATER SOLUTIONS BY HIGH-VOLTAGE PULSED DISCHARGE

Summary. The problem of disposal of persistent organic pollutants arose in 1972 and did not lose relevance to the present day. Modern technologies for waste disposal for example the high-temperature incineration or pyrolysis can't produce satisfactory results, because any from these methods transforms target toxic compounds to some other harmful compounds. For example, incineration of organochlorine compounds and polychlorinated biphenyls intensively produces dioxins. This work represents materials of experimental and theoretical research that can be the basis for creating plasma-chemical technologies for the full destruction of persistent organochlorine toxicants in water solutions.

Keywords: spark, long streamer, persistent organochlorine toxicants.

Introduction

Analysis of the proposed internationally efforts to ensure environmental safety, gives reason to believe the low level of industrial technology utilization persistent organic pollutants (POPs) on the list established by the Protocol on Persistent Organic Pollutants Stockholm and other conventions 1979-2001 years [1-4]. At the same time this very list updated with new items. The difficulty creating such technologies associated with extraordinary chemical resistance under normal conditions these substances and not only [5]. Typically, destructive ways of recycling materials associated with the use of high temperature combustion, pyrolysis, electric burning, and so on. However, in a reactor, where the following processes, there is always a transition zone between the area where intensive decomposition precedes target compounds and the environment under normal conditions. So these reactors contain essentially the area in which a high probability of the reverse process can occur, leading to the synthesis of toxic substances. For example, the destruction of organochlorine POPs in pyrolysis furnaces is intense produsing of dioxins due to fundamental thermodynamic properties of pyrolytic decomposition of PCBs [6]. That is, there is no general disposal but only converting one kind of pops into another. It is even harder to achieve the required result during the destruction of toxic pollutants that exist in the form of water solutions. The problem is that the presence of water molecules, hydroxyl and hydrogen in the reaction zone by quite a wide range of temperature conditions causes a cascade of fast processes of synthesis of toxic

substances - such as phosgene [7].

One of the most effective and safest directions of plasma-chemical treatment of POPs can be using of high-chemically active particles, that are generated in electrical discharges, as the main factor of degradation of toxic molecules. From the results of experiments it is known that plasma discharge treatment of water solutions of stable macromolecular compounds can lead to total destruction of their [8]. However, the question of the composition of the end products of this process remains open.

The proposed work is devoted to experimental and theoretical investigation of the possibilities of using plasma-liquid systems atmospheric pressure for removal of certain kinds of POPs in water solutions by their complete decomposition and clarify of possible mechanisms of degradation of toxic molecules under the influence of physical and chemical factors generated in plasma.

Experiment technique

Discharge system to implement a pulsed discharge in a long streamer mode [9] is shown schematically in Figure 1. To compare the effects of electrode material for chemical processes in the working solution a system was created in two versions: with liquid - a) and metal - b) base electrode. Liquid base electrode consisted of a cylindrical quartz insulator - 1.a), hermetically sealing silicone injected through - 4 in nickel camera to supply current – 2.a). Working solution - 6 was placed in a glass vessel conical shape, which served as the working liquid electrode – 7. This glass vessel is tightly connected with the nickel camera to supply current – 8 similar to the camera – 2. Defensive liquid filled electrode with distilled water – 3.a). The metal base electrode – 1.b) were placed in a teflon insulator – 2 so as to form its recording surface liquid meniscus shape repeated electrode. To test the spark discharge between the reference and working electrodes were served a series of high-voltage pulse of 75 kV repetition rate of 200 Hz.The plasma channel – 5 formed between the surface of the working fluid – 6 and the meniscus surface of distillate– 3or working surface of the metal electrode. Breakdown voltage level at the beginning of exposure was ~ 60 kV. In the process of changing the chemical composition of the working fluid under the plasma influence this voltage decreased in some cases up to 30 kV. The average pulse energy was ~ 200 mJ. Pulse duration equal to 150 microseconds.

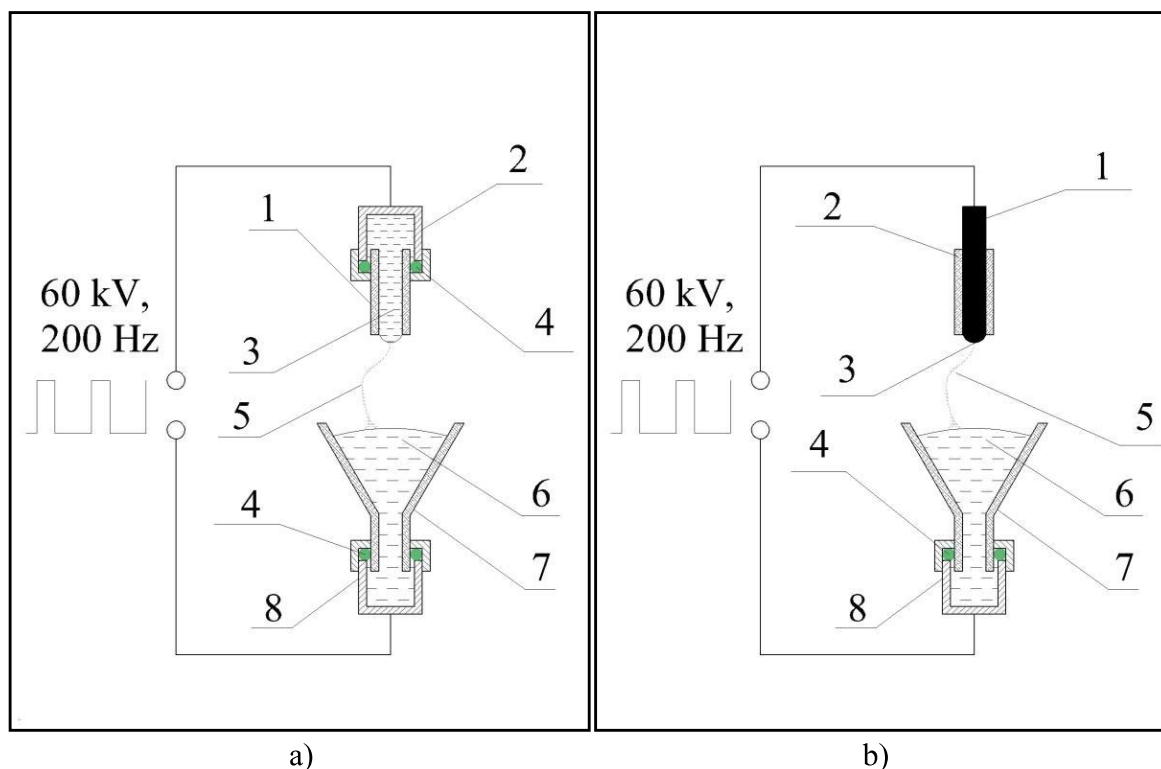a)   b)

Figure 1 – High-voltage pulse-periodic discharge system with liquid -
a) and metal - b) bas electrode.

Electrical characteristics of the investigated discharges were recorded direct measurement with capacitive sensors and high-voltage current transformers using high-speed digital oscilloscope «Regol DS1102M». Plasma parameters were recorded emission spectroscopy methods whith using CCD-spectrometer «OceanOptics S2000». Registration composition of working solutions was performed by liquid-gas chromatography and gas chromatography-mass spectrometry. Qualitative and quantitative chromatographic analysis was performed using a gas chromatograph "KrystalLyuks 4000m" produced by MetaHrom and chromatography-mass spectrometer «Clarus 600" manufactured by PerkinElmer.

The destruction of POPs in water solutions by high-voltage pulsed discharge

Experiments for the disposal of some of the most persistent and widespread POPs have been held for water solutions of p,p'-DDT, DDE and aldrine. The concentration of substances in the solution was ~ 1 mg/l. We used the following modes of solutions processing: positive and negative potential on the solution for the case of liquid reference electrode - Fig. 1 a), and positive and negative potential on the solution in the case of metallic reference electrode - Fig. 1 b). Solution was processed with pulsed-periodic discharge frequency of 200 Hz for 60 min.

The chemical composition of organic compounds in solution before and after processing was recorded by liquid-gas chromatography and gas chromatography-mass spectrometry. The results of chemical analysis of processed solution p,p'-DDT, are shown Table 1. The complete destruction of the substance tested for all modes. In similar experiments, it was found that the DDE and aldrine for 60 min. destroyed completely too.

Table 1

The products of destruction p,p'-DDT ($C_{14}H_9Cl_5$) under the influence of plasma high-pulse-periodic dischargee. Presence of the substance marked in gray.

Compound	Initial solution	Liquid electrode		Metal electrode	
		On solution +	On solution −	On solution +	On solution −
$C_{10}H_{18}O_2$		gray	gray	gray	gray
$C_{22}H_{44}$		gray	gray	gray	
$C_{19}H_{34}O_2$					gray
$C_{22}H_{42}O_4$				gray	gray
$C_{19}H_{38}O_2$		gray			gray
$C_{16}H_{34}O$		gray	gray		
$C_{27}H_{56}$		gray	gray		
$C_{14}H_9Cl_5$	gray				
$C_{22}H_{42}O_4$		gray	gray		

To enable the kinetic model of the mechanism of plasma-chemical destruction of macromolecular compounds the experimental studies of spark electrophysical characteristics at plasma-liquid system were held. Studies have shown that the shape of the pulse voltage to discharge that breaks between two water surfaces or between the metal and the water surface, somehow evolves during exposure solution by plasma (Fig.2.).
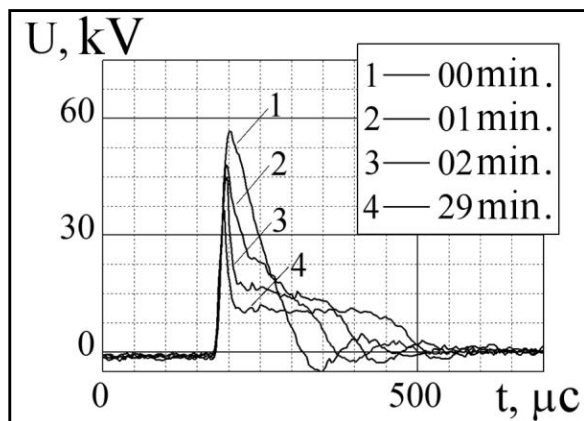
Figure 2 – Evolution of the shape of the pulse voltage during plasma exposure solution. Curve – 1 corresponds to the solution state at the beginning of processing 2 – Exposure for 1 min., 3 – 2 min., 4 – 29 min.

Form voltage pulse consists of relatively sharp peak amplitude from 30 to 60 kV and duration of ~ 10 − 50 μs, and trapezoidal pulse amplitude of 10 − 20 kV and duration of ~ 50 − 100 μs. The high-voltage sharp peak corresponds to capacitive discharge combustion mode, trapezoid − inductive. The evolution of the discharge pulse was increasing steepness Ξ_C falling edge of «capacitive» peak and decreasing inclination angle Θ_L «plateau» of inductive mode.

The experiment showed that the evolution of the pulse form is mostly in the first 120 seconds of exposure of working solution by plasma. Comparison of evolution curves for pulse form to the working fluid and metal electrodes (Figure 3) provide grounds to consider that this evolution is related to the changing of the conductivity solution due chemical modification of working liquid under the influence of plasma.

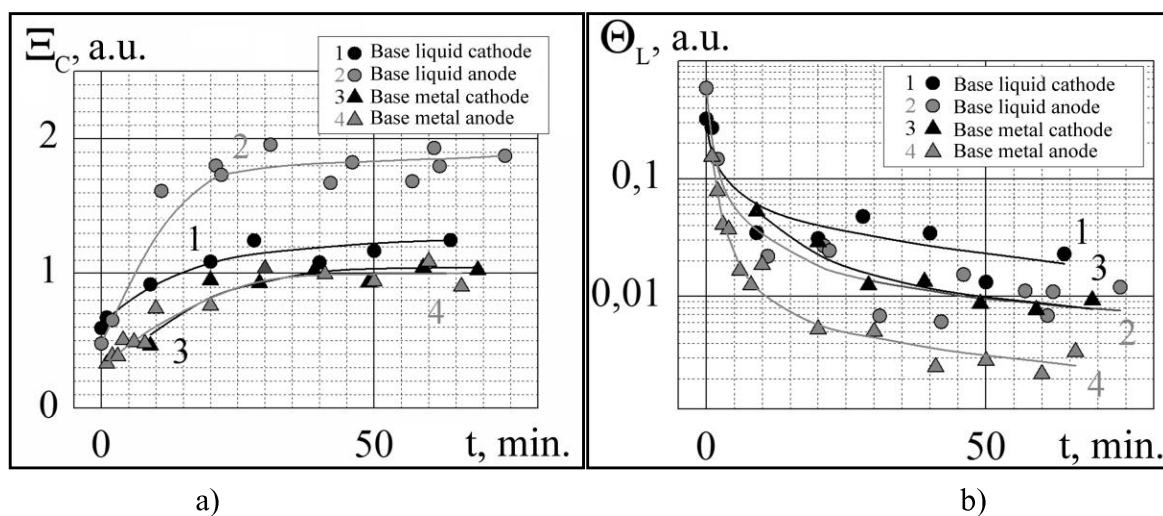a)   b)

Figure 3 – The time dependence of the falling edge steepness Ξ_C of the high peak discharge pulse – a) and inclination angle Θ_L «plateau» inductive discharge mode – b) for various configurations discharge system. Round markers correspond to the liquid base electrode, triangular – to the metal electrode. Black color corresponds to the case of a positive potential on the solution, gray – negative.

Results of modeling the kinetics of plasma-chemical degradation of p,p'-DDT

Kinetic model of spark discharge between the liquid surfaces was built as the development of long streamers classical model [10] in conditions of liquid electrodes. The ultimate aim of the simulation was to calculate the number of particles in the liquid phase that are born during one high-voltage impulse, to calculate the solutions' relative conductivity time dependans, and comparison of simulation results with experimentally obtained curves. According to [10], the classic basic physical model of long streamers includes continuity equation for electrons, positive and negative ions of different sort and electron-excited molecules based on photoionization sources:

$$\left(n_e \vec{v}_e\right) = \left(k_i N + k_i^* n^*\right) n_e - \left(k_a' + k_a'' N\right) N_e n_e +$$
$$+ \left(k_d N + k_d^* n^*\right) n_- - \beta_{ei}\, n_+ n_e + S_\phi \tag{1}$$

$$\frac{\partial n_+}{\partial t} + \nabla \cdot \left(n_+ \vec{v}_+\right) = \left(k_i N + k_i^* n^*\right) n_e - \beta_{ei}\, n_+ n_e - \beta_{ii}\, n_- n_+ + S_\phi \tag{2}$$

$$\frac{\partial n_-}{\partial t} + \nabla \cdot \left(n_- \vec{v}_-\right) = \left(k_a' + k_a'' N\right) N_e n_e - \left(k_d N + k_d^* n^*\right) n_- - \beta_{ii}\, n_- n_e \tag{3}$$

$$\frac{\partial n^*}{\partial t} = k^* N n_e - k_i^* n^* n_e - k_q N n^* \tag{4}$$

$$\vec{v}_k = \vec{v}_{äð.k} - D_k \nabla \left(\ln\left(n_k\right)\right) \tag{5}$$

Where N, n^*, n_e, n_+, n_- $\left(abbreviated: n_k\right)$ - are the concentration of neutrals, excited molecules, electrons, positive and negative ions - respectively. $\vec{v}_k$, $\vec{v}_{äð.k}$ - are velocity and drift velocity of kth component of the plasma. D_k - is the diffusion coefficient of kth component of the plasma. S_ϕ - is the photoionization source. β_{ei}, β_{ii} - are the coefficients of electron-ion and ion-ion recombination.

Poisson equation for electric field:

$$\Delta\varphi = e\frac{n_e + n_+ - n_-}{\varepsilon_0}, \quad E = -\nabla\varphi \qquad (6).$$

Energy balance equation for the gas temperature:

$$c_V N \frac{\partial T}{\partial t} = \lambda_{rt} j E + Q_{vT} + Q_{eT} \qquad (7),$$

and relaxation equation:

$$\frac{\partial E_v}{\partial t} = \lambda_v j E - Q_{vT}, \quad Q_{vT} = \frac{E_v - E_v(T)}{\tau_v(T)} \qquad (8).$$

Where j - is a current density, E - is a longitudinal field in the channel, c_V -is a heat capacity of one molecule, λ_x - is a part of energy that was spent on excitation of xth internal degree of freedom. Q_{vT}, Q_{eT} - are the contributions of heat from the vibrational and electronic states of molecules de-exitation, $E_v(T)$ - is the equilibrium vibration energy, $\lambda_{vT}(T)$ - is a time of vT - relaxation.

Extending the classical model in case of liquid electrodes was to neglect the surface effects, in particular - the photoemission from the surface. The source of photoionization was only volume isotropic processes. The disappearance of particles on the liquid surface was considered as a gradual loss of particles' kinetic energy acquired in plasma during the inelastic collisions between molecules in the solution. In case of a liquid phase the excitation of all internal degrees of freedom and striking dissociation of molecules were considered. The constants of elementary processes were taken mostly from the database NIST. Those constants that were absent in the database, were calculated from the quantum-mechanical principles using the notorious package Gaussian 09W. For plasma-forming gas the mixture of air with water molecules was chosen, excluding from consideration the processes with atomic metal ions. In the region of gas phase, the component mixture was considered as inhomogeneous along the axial axis of the system. The axial profiles of the water molecules' concentration and air components were calculated using the analytical theory that was developed in [11] and based on the conditions of heat - mass - transfer through the liquid-gas boundary with diffuse evaporation.

Simulation results presented in Fig. 4 show that the behavior of conductivity in time qualitatively agrees with the experimental dependences on Ξ_C and Θ_L. This fact is illustrated by calculateddependenceof high-voltage peaks' falling edge ξ in exponential approximation overlayed with experimental data Ξ_C. However, the quantitative agreement of the experimental data with the model was not observed. The calculated time-to-saturation was three times lower than the experimental, while the level of induced conductivity was approximately 2-times lower than the experimentally obtained for all test solutions. The best quantitative agreement of the experimental results and the calculations took place for the case of distilled water. Calculated characteristic time within the error limits coincided with the experiment, and calculated saturation level was lower than the experiments in about 1.3 times. Disagreements of calculation and experiment can be explained by the fact that in the model was not taken into account that the shock dissociation products of complex organic molecules are also non-stable, and the gradual disintegration of complex fragments is taking place [12]. The latter leads to a significant increase of the solutions' conductivity as a result of current carriers generation in a volume comparing to the calculated number of acts of shock dissociation.
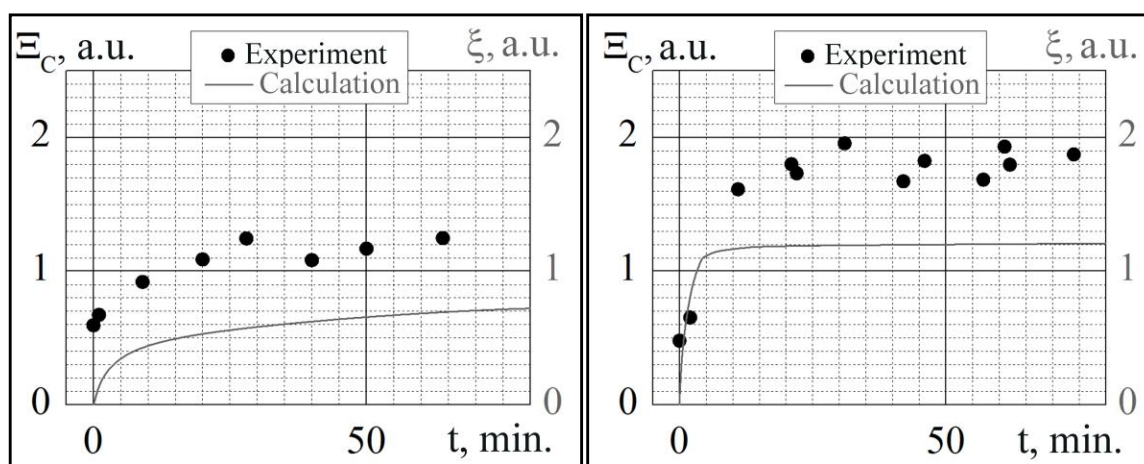
a) b)

Figure 4 – The calculated time dependence of the falling edge steepness ξ of the high peak discharge pulse for spark discharge between liquid electrodes compering with experiment ΞC. – a) illustrates the case of a positive potential on the working solution b) – negative potential. The solid gray curve – is a calculation, black markers – experiment.

Conclusions

• By means of gas chromatography, it was shown that treatment of the p,p'-DDT, DDE, and aldrinu water solutionswith the plasma of high-voltage pulse-periodic discharge leads to their complete decomposition.

• The proposed model of the spark discharge between the liquid surfacesshow that the evolution of electrophysical discharges' parameters is determined by the change of electro conductivity of a liquid phase with increasing of organic molecules' degradation products' concentration in the solution.

REFERENCES

1. Convention on Long-Range Trans-boundary Air Pollution, Geneva, 1979.

2. The 1998 Aarhus Protocol on Persistent Organic Pollutants (POPs).

3. Basel Convention on the Control of Transboundary Movement of Hazardous Wastes and their Disposal, Basel, 1989.

4. Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade, Rotterdam, 1998.

5. Donnelly J.R., Dupuy E.A., McDaniel D.D. et al// Chlorinated dioxins and dibenzofurans in the total environment/Eds. L.H.Keith, C.Rappe, G.Choundhary. Stoneham. MA:Butterworth Publ., 1985. P.339.

6. В.Г. Петров Исследование термодинамики реакций полибромированных дибензо-п-диоксинов и дибензофуранов в установках по сжиганию отходов // Вестник удмуртского университета 2013. вып. 1 физика.химия с.22.

7. Касимов А.М., Семенов В.Т., Щербань Н.Г., Мясоедов В.В. Современные проблемы и решения в системе управления опасными отходами. - Харьков: ХНАГХ, 2008. - 510 с.

8. Sergij Olszewski, Valeriy Chernyak, Evgen Martysh, Oleg Nedybalyuk`, Vitalij Yukhymenko, Sergij Sidoruk, Iryna Prysyazhnevich, Olena Solomenko PLASMA ASSISTED DISTRUCTION OF ORGANIC MOLECULS IN DYNAMIC PLASMA-LIQUID SYSTEMS // 7th International Conference "Electromagnetic Devices and Processes in Environment Protection" ELMECO- 7, September 28

9. Лозанский Э.Д., Фирсов О.Б. Теория искры. М., Атомиздат, 1975, 272 с.

10. БАЗЕЛЯН Э.М. РАЙЗЕР Ю.П. Искровой разряд: Учеб.пособие: Для вузов. М.:Изд-во МФТИ.1997.-320с.

11. В. В.Кузнецов Условия переноса тепла и массы на границе раздела жидкость-газ при диффузионном испарении //Journal of Siberian Federal University. Mathematics & Physics 2010, 3(2), 216-227с.

12. Зенкевич И.Г., Иоффе Б.В. Интерпретация масс-спектров органических соединений.– Л.: Химия, 1986.–176 с.