

# DESTRUCTION OF TOXIC AGENTS IN PLASMA OF SECONDARY DISCHARGES WITH DIFFERENT PLASMA CREATION GASES

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## INTRODUCTION

The secondary discharges in a plasma stream with a "liquid" electrode are the perspective generators of non-equilibrium plasma for destruction of the toxic agents. The given discharges allow not only to supply a stationary of conditions in zone of interaction of plasma with liquid but also to supply the new mechanism of destruction: the destruction with the participation of charged particles with a controlled energy (10 - n100 eV) [1]. The positive results on use of similar systems for disinfecting of water and some preliminary results on a comparison of plasma destruction of organic substances in barrier discharge and secondary discharge were reported earlier [2].

The given work is devoted to discuss of last results of experimental researches of the influences of a choice of plasma creation gas, the polarity of a "liquid" electrode and the concentration of the initial toxic organic agent (phenol and cation-active surfactants (tetradecyl piridinium bromide (TDP):  $C_{14}H_{29}NC_5H_5Br$ ) in a water solution on effectiveness of destruction stimulated by plasma of a secondary discharge in a plasma stream with a liquid electrode.

## Experiments

The plasma chemical reactor (Fig. 1) for treatment of solution represented the glass cylinder - 1, the copper electrode - 2 is built in a floor of this glass cylinder. The reactor is hermetically closed by a dielectric cover - 3. The relative system of graphite (cooper) electrodes - 4, the systems of a gas injection - 5 and gas exhaust - 6 are built in a cover. The system of a gas injection (5) allowed to control the gas consumption.

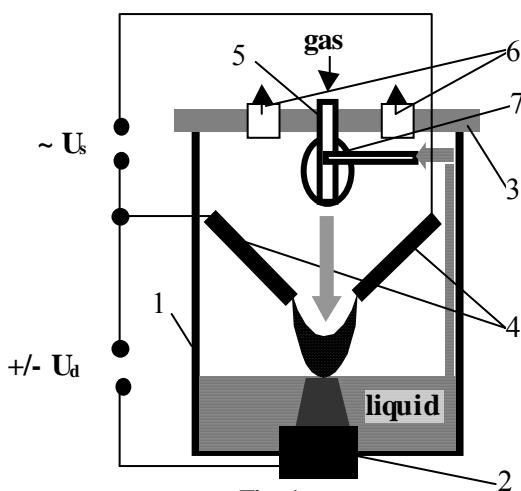


Fig. 1

The sprayer - 7 could be installed on the extremity of gas canal. The construction of the sprayer allowed to inject the liquid, treated in a reactor, and to give it to the discharge zone by the way of aerosol. The hardware of a reactor allowed to vary a voltage and current of the auxiliary discharge and secondary discharge with a liquid electrode. The reactor worked at atmospheric pressure of air.

The plasma treatment of the water solutions of the organic agents was carried out in the plasma reactor in the conditions with a constants current (400 mA) of auxiliary arc discharge in a transversal stream of plasma creation gas of atmospheric pressure and modification of a current of a secondary discharge with a liquid electrode in a range of 0 - 200 mA. The

cheapest substances: a dry air ("A"), a water vapour ("WV") and a mixture of an air with an aerosol of a treated solution ("S") were used as plasma creation gases. The cation-active surfactants (teradecyl piridinium bromide (TDP):  $C_{14}H_{29}NC_5H_5Br$ ) were used of model organic substances at plasma destruction. The volume of solution was 250 ml in the plasma reactor; the time of plasma treatment was 3 min in all experiments.

The measurements of pH of a solution were carried out with use the universal ionometer EV 74. The TDP-detection in solution after plasma treatment was carried out by the new chemical analytical method (c.m) and the UV absorption spectroscopies. The chemical method is based on the reactions of surfactants with special dyes on the silica gel surface. The detection limit of this chemical method is  $5\mu\text{g/l}$ ; the accuracy of determination is 1-3%.

## Results and Discussions

The preliminary researches of a distillate water after plasma treatment in the reactor have shown an essential influence of a choice of plasma creation gas and a polarity ("+"/"-") of a "liquid" electrode both on absorption spectra and on a character of a behaviour of pH of solutions. The treatment of solutions by plasma only of auxiliary discharge of an arc in a transversal stream of plasma creation gas reduced in a drop of pH on  $\sim 2.5$ .

The character of a pH modification depends on polarity "liquid" electrode at switching of a secondary discharge: pH insignificantly decreased under the linear law for  $\sim 0,5$  irrespective of a choice of plasma creation gas at magnification of a discharge current at the "liquid" cathode. The magnification of a current of a secondary discharge reduced in increase pH at the "liquid" anode. However the pH modification depend essential from a choice of plasma creation gas: a maximum modification pH ( $\Delta \text{pH}$ ) did not exceed 0.5 at a dry air,  $\Delta \text{pH} = 0.8$  for a mixture of an air with an aerosol of a solution,  $\Delta \text{pH} = 5$  for a water vapour.

Spectrophotometric research have shown that the adding of water in a dry air reduces in a diminution of a degree of oxidation of nitrogen in treated water ( $\text{NO}_3^- \rightarrow \text{HNO}_2, \text{NO}_2^-$ ). The passage to a water vapour practically eliminates emerging oxides of nitrogen in treated water.

The dependence of phenol and TDP concentration from a current of secondary discharge are represented in a Fig. 2, 3 respectively. The concentration of organic agents have been detected by UV-absorption spectrums in this case. As it is visible from Fig. 2,3 in an investigated range of parameters of a secondary discharge the more effective conditions of destruction are the "liquid" cathode and use of a water vapour in quality of plasma creation gas as the nitrogen oxides is observed less in treated solutions.

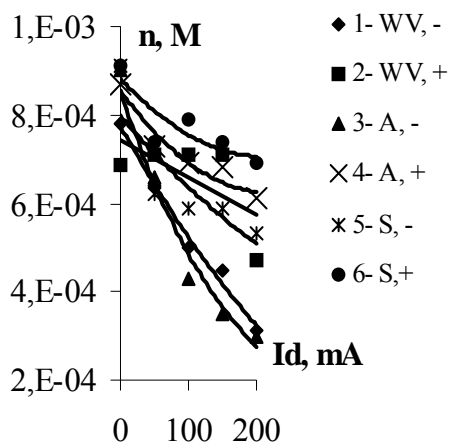


Fig. 2

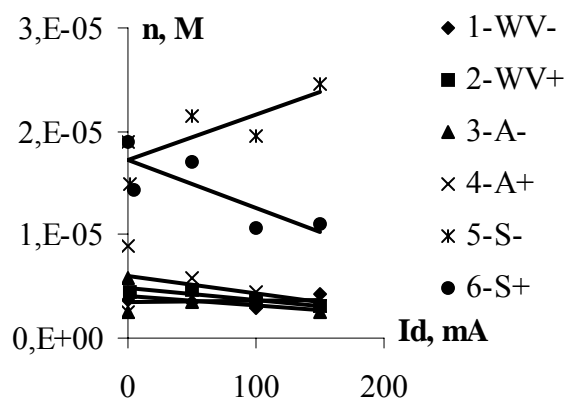


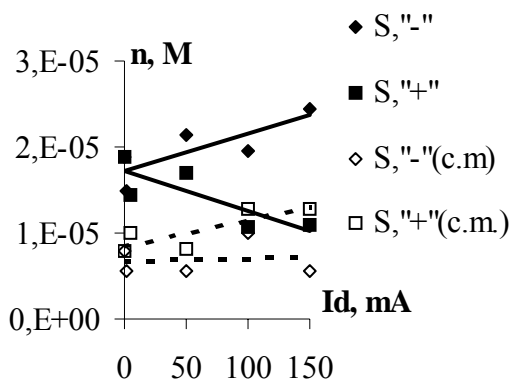
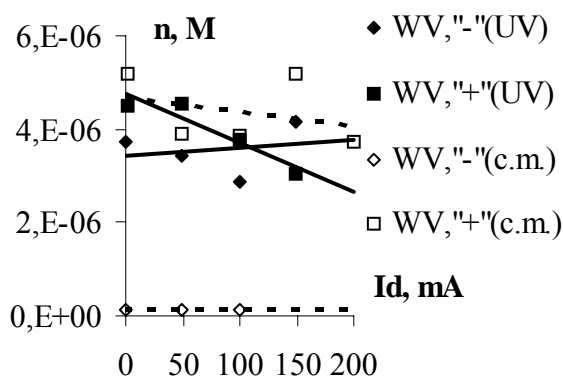
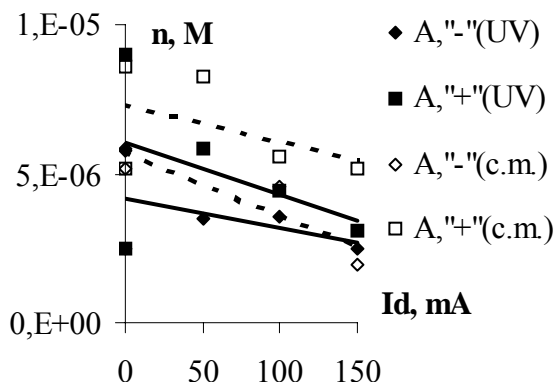
Fig. 3

The absorption spectrums confirm that the rate of plasma destruction of surfactant and phenol and the kind of final products depend on the "liquid" electrode charge.

The surfactant destruction products have been detected by UV-absorption spectrums (1) and by chemical method with silica gel and special dyes (2).

- (1) method allows to display the  $\pi$  - bonds in the piridinium cycle of the surfactant molecule ( phenol cycle of the phenol molecule)
- (2) method detects cationic charge and hydrophobic part of cationic surfactant molecule.

The dependences of TDP concentration from a current of secondary discharge are represented in a Fig. 4 (continuous curves are the dependences obtained with use of the UV-absorption spectrums, dashed curves - chemical method). As it is visible from datas in a Fig. 4 there are essential differences between the results of both methods.



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radicals and active destruction of a phenol cycle.

As the bond energy C-C of atoms of carbon in phenol cycle (477 kJ/mol) is more than C-N in piridinium, also degree of phenol molecules destruction will be less than surfactant molecules. It is confirmed by experimental data.

In a condition + the destruction degree of phenol molecules is less, than in a condition -, as the basic active agents in this case are the radicals  $^*O_2^-$ ,  $^*OH^-$ , and coulone forces hinder with their coming together with ionized phenol molecules.

Also researches have shown, that the solutions do not remain stable after an extinction of plasma treatment. Their stability depends on polarity of a "liquid" electrode. The solutions of

That is why the results of both methods are not the sameness:

in case WV- and S- the destruction rate detecting by (1) method is less than results by (2) method for each treatment solution;

in case WV+ and A+ the destruction rate by (2) method is less than detecting by (1) method for each treatment solution too.

We suppose that the carbonic part is destroyed more efficiently than piridinium cycle at WV-, A- and AS-. The piridinium cycle is destroyed effectively ar WV+ and A+.

As the energy of C-N bond of a piridinium cycle with a carbon group (285 kJ/mol) is less, than the connection C-N in the piridinium cycle of a surfactant molecule (450 kJ/mol), also action energy of active radicals  $^*O^+$ ,  $^*NO^+$ ,  $^*NO^{+2}$  in conditions WV- and A- (and in plasma as a whole) is less than the energy of radicals  $^*O^{2-}$ ,  $^*OH^-$  in conditions WV+ and A+.

Best destruction ability of radicals  $^*O^{2-}$ ,  $^*OH^-$  in relation to cationic surfactant is explained by availability of a positive charge at a dissociated surfactant molecule, thus coulone interaction strengthens of oxidation destruction.

The yields of phenol destruction detected only (1) method. It is visible from UV-absorption spectrums that phenol destroys better in conditions WV- and A-, that completely confirms the offered mechanism of plasma action on phenol molecules:

In a condition - the radicals  $^*O^+$ ,  $^*NO^+$ ,  $^*NO^{+2}$  actively operate and deeply go to treatment solution and phenol molecule in an outcome of ionization (separation of atom of hydrogen) gains a the negative charge. The coulone interaction promotes coming together of

phenol had the greatest instability after plasma treatment with the "liquid" anode. The chemical processes proceeded on stretch of several tens hours in these solutions.

### Conclusions

The results of work by plasma destruction of phenol and tetradecyl piridinium bromide indicate that the more effective conditions of destruction are the using of a water vapour in quality of plasma creation gas as the nitrogen oxides is observed less in treated solutions.

Effectiveness of the plasma destruction will increase under the linear law at growth of concentration of agents in an initial solution in a range of concentration  $10^{-3}$  -  $5 \cdot 10^{-1}$  N and it exceeds 5 % at concentration  $5 \cdot 10^{-1}$  N.

The velocity of plasma destruction for a tetradecyl piridinium bromide is essentially higher than for a phenol. The rate of molecular destroy is 99% at "liquid" cathode, use of a water vapour and a dry air in quality of plasma creation gas.

The chemical processes proceed in the treated solutions during several tens hours after an extinction of plasma treatment in the plasma reactor. The character of a modification of organic agents in solutions essentially depends after plasma treatment from polarity of the "liquid" electrode of the plasma reactor.

### REFERENCES

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