# 79. NEW ADVANCED OXIDATION TECHNOLOGIES FOR DESTRUCTION OF POLLUTANTS IN WATER

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## ABSTRACT

The use of the set of advanced oxidation technologies (plasma, bio- and photochemical) for the purification and desinfaction of the heavy contaminated water is proposed. The plasma and photochemical techniques are used for the destruction of complicated organic molecules such as phenols and cation-active surfactants (cetylpiridinium bromides) as well as for the inactivation of pathogenic microorganisms such as Pseodomonas fluorescens, Bacillus cereus B 4388 and Escherichia coli. The gram-negative bacteria and gram-positive spore cultures are used for the biological desinfection of water from the secondary toxic substances after the plasmachemical treatment. The pulse UV treatment is applied for the inactivation of mutant microorganisms after the biotechnological treatment. The efficiency of a complex approach to the wastewater treatment is demonstrated.

## INTRODUCTION

The advanced oxidizing technologies (AOT's) are necessary for using, if pollutant is toxic substance. Destruction of high active and toxic substances (HATS) in AOT's occurs under action of advanced oxidizing processes (AOP's). Basic AOT's are radiochemical, plasmachemical, ozonization, and photochemical technologies. Apparently, radiochemical and plasmachemical technologies are represented by most perspective, as allow to achieve the greatest speeds destruction of substances at the expense of high energy concentration.

However, it is necessary to take into account, that toxic substances are, frequently, the complex high-molecular compounds. Therefore destruction of HATS results in occurrence not only products of disintegration, but also wide spectrum more complex high molecular of compounds /1,2/. The chemical reactions both in radiochemical and in plasmachemical systems can proceed with participation of the electronic-exited particles, which practically are not investigated today. It is specified that by high probability of occurrence unknown before substances at the data AOP's. Therefore now the transition to complex technologies on a basis AOP's begin. The opportunities of plasma-bio technology were considered at water clearing from chlorophenols in work /1/ and was shown, that the transition to complex technology of water clearing results to synergism.

However, the destruction of toxic components by microorganisms can result in occurrence the mutants. It means, that after biochemical destruction of high active products of preliminary plasma water clearing from initial toxic pollution it is necessary to provide inactivation of microorganisms in water. The given work is devoted to development of similar multistage technology on base AOP's (plasma-bio-photochemical).

## EXPERIMENTS

The base scheme of the proposed technology includes the plasma module for the preliminary treatment of initial wastewater, the biochemical modules (biodestruction, biosorption and biosedimentation) and the modules for photochemical or plasma inactivation of microorganisms in water. The sources of plasma in experimental plasma modules of preliminary HATS destruction were the secondary discharge with a liquid electrode /3/ and the barrier discharge (Fig. 1). The barrier discharge glowed between two quartz cylinders - 1, which divided metal electrodes - 2. water - 3 flowed between quartz cylinders.

## RESULTS AND DISCUSSIONS

1. The surfactant and phenol destruction in water solutions by plasma treatment

The surfactants are the dangerous and widespread contaminations in the environmental. Their stable molecules are not distracted upon the natural factors influence. It is important to explore the new methods of the surfactant breaking and neutralization. The plasma influence on the molecular structure of the surfactants in water solution was studied.

The alcylpiridinium salts (pentadecyl piridinium bromide, cetyl piridinium bromide, tetradecyl piridinium bromide) and quaternary ammonium salts (tetradecyl three ethyl ammonium bromide, cetyl threemethyl ammonium bromide) have used as cationic surfactant models in the present work. The reference solutions with $10^{-3}$ M concentration were prepared by distillate water solution of the purity crystal matters. Other solutions were prepared by water diluting. The sensitive and selective sorption-photometric method has been using for surfactant detection in solutions after plasma treatment. This method permits to determine less than 1 μg/l cationic surfactants for all types of it.

The power of barrier discharge system is 10 W during all experiments, but the speed of treatment. The destruction rate of the surfactant molecules as function of plasma treatment time is submitted in Table 1. The all solutions before treatment: 200 μg cationic surfactant was added in the 60 ml of water.

Phenol destruction in water solutions was investigated in a range of concentration $10^{-6}$ - $2\ 10^{-3}$ M with use the spectrophotometer analysis in UF area of a spectrum (200 - 500 nm). The typical absorption spectra of water solutions of phenol measured during 10 mines after their processing by barrier discharge plasma are given in a fig. 2 (curves 2 - 4) at initial concentration: 2 - $2\ 10^{-3}$ M, 3 -5 $10^{-4}$ M, 4 - $2\ 10^{-6}$ M, curve 1 - spectrum of the raw solution $2\ 10^{-3}$.

Was noticed that the phenol solutions begin to darken after plasma processing. Therefore absorption spectra of solutions investigated after end of plasma processing within several day. Some of these spectra are given in a fig. 3 for a solution with initial concentration $2.10^{-3}$ M - curve 2 (spectrum is measured at once after processing), 3 - in day after plasma processing, 4 - two day, 5 - three day (1 - raw solution $2\ 10^{-3}$ M). Pays on itself attention, that the absorption spectra for the solutions processed by secondary and barrier discharges plasma and measured at once after processing are very similar. There is also wide band in long of wave area at these spectra except for a phenol band with a maximum on 275 nm.

The absorption spectra of the processed solutions very strongly change within the first day that is connected to course with oxidation and polymerization processes after the discontinuance of plasma processing.

2. Photochemical and plasma

The cultures of Bacillus cereus B4368 and Pseudomonas fluorescens B894 were used as test cultures for study of opportunities of the developed photochemical section on

inactivation of micro-organisms. The influence of suspensions UV - processing on survival of cultures was investigated. $D_{540}$ of initial suspensions was 0.07 in dB.

The survival degree - N after UV - radiation processing of bacteria suspensions estimated by sowing of control and photochemical processed tests on rich agared environment. The Luria-Bestani environments (LB, Scotland) were used. The influence of specificity of each of cultures on them survival at photochemical processing is not revealed. It is doubtless advantage of the developed UV-module of microorganisms inactivation at last stages of complex treatment of water.

Escherichia coli was used as test culture at study of decontamination action of plasma processing. The plasma processing was carried out in the experimental module with the secondary discharge with a liquid electrode at low pressure ~ 10 torr /3/.

As have shown researches the degassing of a solution as a result of an exposition it at the lowered pressure (10 - 30 torr), the burning of the auxiliary independent discharge above a surface of a solution did not influence on vital functions of Escherichia coli culture. The essential influence of thickness of a solution above an electrode shipped in a solution was not noticed also on vital functions of Escherichia coli culture. Last is connected to effective mixing of a solution at gas bubbling that to evolve on shipped in a solution electrode.

Some results on plasma decontamination are given in the table 2, where $U_d$ - secondary discharge voltage, Id - secondary discharge current, P - gas pressure in system, H - height of solution pole above the shipped in a solution electrode, t - exposition time of a solution, N - share of inactivation micro-organisms.

The complete inactivation can occur at low enough power inputs ~ 6 kW hour $м^{-3}$, as follows from experimental results of plasma inactivation with use of the secondary discharge at low pressure with a liquid electrode in optimum modes: at negative polarity of a liquid electrode.

3. Growth of cultures in water after plasma treatment

Cultures cultivated within 18 hours on nutritious environment № 284 containing 5 g/l gluconate. Then these cultures accommodated in distillate water past plasma processing and investigated intensity of their growth. The various secondary discharges of low and high pressure with a liquid electrode used at plasma treatment. The spore culture of Bacillus cereus B4368 and the Gram-negative culture Pseudomonas fluorescens B5040 were used as test cultures.

The results of experiments have shown: Gram-negative culture more intensively cultivates in water after low-pressure plasma treatment, spore culture - after plasma treatment of atmospheric pressure.

4. UV-radiation influence on the surfactants in water solutions

The UV-radiation influence on the surfactant molecules in water was explored with using the impulse UV-radiation system. It was detected that the impulse UV-radiation breaks down the cationic surfactant molecules and the destruction rate is a function of the treatment time and the initial concentration of surfactant solutions before treatment. UV-radiation influences equally on any type of the cationic surfactants. The surfactant solutions (V=500 ml) are on the rest state during the treatment by UV-impulses. If the initial solution has $10^{-3}$M concentration of cationic surfactant the all molecules of this matter are distracted after treatment during10 minutes. They lose the ability for ion associating with sulfophthtalein reagent and for adsorption on the silica gel surface. But the radical fragments of surfactant molecules are complexing with the reagent and detecting by spectrometry. The radical concentration dilutes the maximum after treatment during 20 min. The destruction rate of the surfactant molecules as function of the initial surfactant concentration before UV-radiation treatment is submitted in Table 3 (V=500 ml, treatment time is 20 min).

## CONCLUSIONS

The results of our investigation indicate the efficiency of plasma destruction of phenol and surfactants, inactivation of micro-organisms at plasma and pulse photochemical treatment of water and allow to make a choice of cultures for designing of biodestructeres of products of preliminary plasma treatment in complex plasma - bio - photochemical technology of waste water treatment.

## REFERENCES


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## KEYWORDS

Pollution, water, purification, desinfection, plasma, UV radiation, bio-technology


## FIGURES AND TABLES

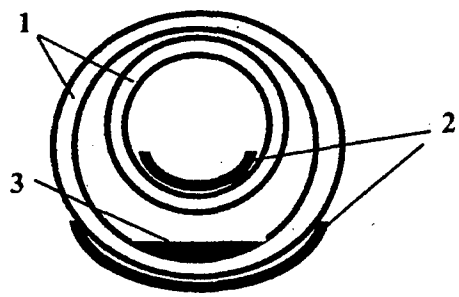


Fig. 1. Cross-section of an interelectrode interval of the barrier discharge.

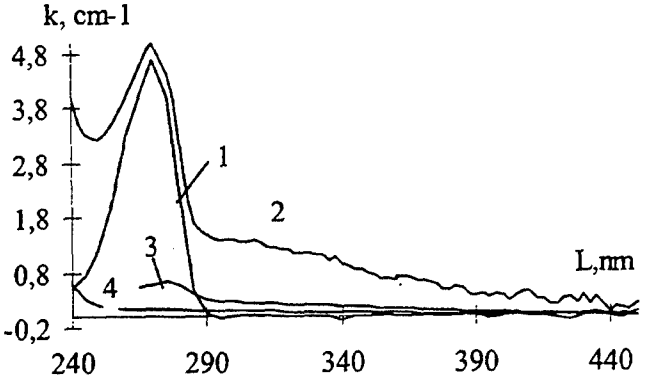


Fig. 2. The absorption spectra of water solutions of phenol measured during 10 mines after their processing by barrier discharge plasma at initial concentration: 2 - 2 $10^{-3}$ M, 3 -5 $10^{-4}$ M, 4 - 2 $10^{-6}$ M, curve 1 - spectrum of the raw solution 2 $10^{-3}$.

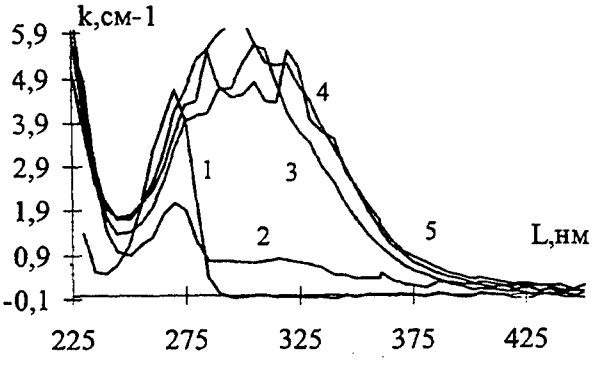


Fig. 3. The absorption spectra of solutions with initial concentration 2 $10^{-3}$ M - curve 2 spectrum is measured at once after processing, 3 - in day after plasma processing, 4 - two day, 5 - three day (1 - raw solution 2 $10^{-3}$ M).

| Find after plasma reatment, m | Stream speed, ml/min | Time treatment, min | Destruction rate, % |
|---|---|---|---|
| 200 | 0,87 | 0 | 0 |
| 90 | 5.00 | 12 | 55 |
| 40 | 2,40 | 25 | 80 |
| 20 | 1,80 | 32 | 90 |
| 0 | 0,87 | 70 | 100 |

Table 1. The destruction rate of the surfactant molecules as function of plasma treatment time.

| № | Ud, V | Id, mA | P, torr | H, mm | t, s | N, % |
|---|---|---|---|---|---|---|
| 1 | 400 | 100 | 10,8 | 10 | 300 | 99,99 |
| 2 | 400 | 100 | 10,8 | 19 | 300 | 99,99 |
| 3 | 400 | 100 | 10,8 | 25 | 300 | 99,99 |
| 4 | -400 | 100 | 10,8 | 10 | 300 | 100,00 |
| 5 | -550 | 100 | 14,4 | 19 | 5 | 100,00 |
| 6 | -550 | 100 | 14,4 | 19 | 300 | 100,00 |
| 7 | -700 | 100 | 14,4 | 25 | 300 | 100,00 |

Table 2. Results on plasma decontamination.

| Add surfactant, mkg | Find, mkg | Distract, mkg |
|---|---|---|
| 183 | 0 | 183 |
| 910 | 800 | 110 |
| 1830 | 1750 | 80 |

Table 3. The destruction rate of the surfactant molecules as function of the initial surfactant concentration before UV-radiation treatment (V=500 ml, treatment time is 20).