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## PHYSICOCHEMICAL PROPERTIES OF A PLASMA—LIQUID SYSTEM WITH AN ELECTRIC DISCHARGE IN A GAS CHANNEL WITH A LIQUID WALL

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Physicochemical properties of a plasma-liquid system with the electric discharge in the gas channel with a liquid wall have been studied. The opportunity to apply such a plasma for stimulating the destruction of an organic pollutant in water has been demonstrated. Phenol was used as a contaminator for simulating the destruction process. The optimal conditions for carrying on the destruction of organic pollutants and obtaining the low toxicity of decay products have been studied. It is revealed that the treatment with the air plasma results in both a deeper destruction of phenol and a lower toxicity of the solutions of decay products than the argon plasma does.

### 1. Introduction

Nowadays, new oxidizing technologies for preserving water and air are developed intensively. This is confirmed, in particular, by a plenty of articles and elaborations dealing with this subject. Amongst them, we mention the radiative-chemical treatment of water and sewage, the photochemical treatment of water and air, the application of ozone, hydrogen peroxide, ultrasound, etc.

A substantial attention is paid to the application of plasma-chemical methods for treating the gaseous, liquid, and solid wastes. For example, under investigation are the efficiency of treating the polluted water by diaphragm discharges [1], the destruction of phenol in an aqueous solution by subjecting it to a high-voltage pulse discharge in the presence of hydrogen peroxide [2], oxidation of phenol in an aqueous solution under the action of a corona discharge with the formation of ozone [3], application of a valve discharge

for the nonchemical water decontamination from dissolved organic impurities [4], ecological application of the barrier discharge for the sewage disinfection and treatment, application of the secondary discharge stimulated by a plasma flow [5], as well as a number of other elaborations.

Electric discharges, when occurring in air, transform oxygen to ozone. In addition, they generate various chemically active particles such as  $O\cdot$ ,  $N\cdot$ ,  $O_3^*$ ,  $N_2^*$ ,  $N^*$ ,  $OH^-$ ,  $O_2^-$ ,  $O^-$ ,  $O_2^+$ ,  $N_2^+$ ,  $O^+$ ,  $N^+$ , etc. These particles are short-lived and decay prior to the ozone-enriched air penetrates into water. However, if a reactor is designed in such a way that the discharge plasma directly contacts with the surface of water, some of those particles can penetrate into water and destroy the contaminant. Moreover, a strong electric field which is necessary for electric discharges to happen is also fatal to some forms of microorganisms that live in water and, being combined with traditional disinfectants such as  $O_3$  and  $H_2O_2$ , demonstrates the synergistic lethal result. Electric discharges in water are also able to generate ultraviolet radiation and shock waves which assist in destroying contaminants [6]. For these reasons, the application of controlled electric discharges in water undoubtedly belongs to a new generation of technologies for the water purification which are favorable for the environment and can ensure a much higher efficiency than traditional oxidizers and disinfectants do. The technologies of electric discharges immediately in water or being short-circuited on the water surface are quickly developed and are commercially tested for the purification of drinking and contaminated water.

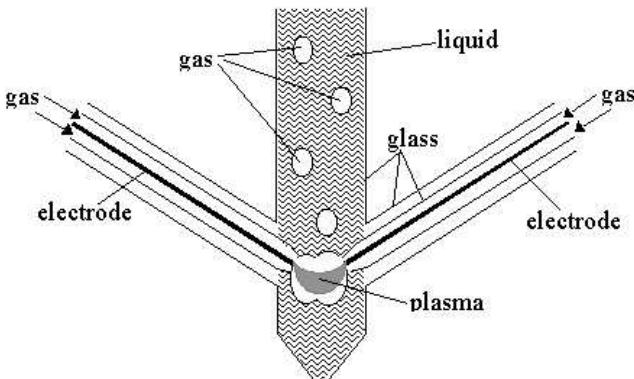


Fig. 1. Plasma-liquid reactor

In this work, we describe a substantially new low-power plasma-liquid reactor with small dimensions and high destructive efficiency of a discharge which is designed for purifying water from toxic contaminants and is suitable for the use in the individual systems of water purification.

## 2. Experimental Installation

The reactor consists of a narrow high glass working chamber with soldered-in thin glass tubes that contain nickel electrodes. At the bottom of the chamber, there is a faucet to pour out a solution; and at the top of the chamber, there is the system to withdraw the worked-out gas.

Through the tubes with electrodes, gas enters the chamber volume filled with a solution. By merging, the gas streams form a stable gas channel in the interelectrode gap, where a discharge is burning. From it, the gas blows off chemically active particles into the liquid (Fig. 1).

The plasma-liquid reactor of such a geometry accomplishes the following main tasks:

- total immersing of a discharge channel into the liquid,
- blowing-off chemically active particles from the plasma into the liquid,
- ensuring the maximal ratio between the plasma surface and the plasma volume,
- ensuring the stability of the plasma-solution contact,
- a substantial increase of the interaction time between active plasma particles and solution molecules.

We may also expect a high degree of nonisothermality in the system at the expense of the intense energy and mass exchange between the plasma and the liquid. Since all the walls of the channel are now in contact with a solution, the interaction area between the plasma and the liquid respectively increases, as well as the discharge efficiency. A bubble of the activated-by-plasma gas, having broken away from the channel, makes a long way to the liquid surface by carrying active particles and stirring a solution. As the height of a liquid column increased, the efficiency of the discharge grew (the amount of synthesized oxidizers in the solution increased). However, the growth of a liquid column leads to the increase of the pressure in the chamber and, therefore, to the instability of the gas channel. Hence, it is necessary to optimize the height of a column of the solution according to the dimensions of the working chamber in order to get the maximal efficiency of discharges.

Gas was supplied to the installation through an SNA-1 gas intake system. In the case where air served as a plasma-forming agent, we used a compressor. In the case of argon, we attached a gas balloon. The discharge was energized through a high-voltage transformer, a power amplifier, and a GZ-109 standard generator of low-frequency signals. The parameters of the standard mode of a discharge in the experiment were as follows: the generator frequency  $f = 7$  kHz, and the power  $P \approx 30$  W.

The solution temperature was not stabilized. In the discharge region, it can reach 50 °C, and, at long exposures for tens of minutes, the average temperature of the solution can increase by ten centigrade degrees.

In order to determine the chemical composition of the solutions obtained, we applied the spectrophotometric method. The variations of the structural and chemical contents of the liquid after its treatment in the reactor were determined by the absorption spectra of the waste solutions.

## 3. Experimental Method

To study the destruction of toxic substances, we used aqueous solutions of phenol as working substances. To elucidate the mechanism of reactions which prevail in a solution, plasma-forming gases of two types – inert argon and air – were selected.

In order to monitor the processes that run in the reactor, both physical and chemical methods

were used. The quantitative and qualitative variations in the solutions were studied by optical methods: the registration of emission spectrograms of the gas discharge plasma and the measurement of the absorption spectra of solutions at various stages of their treatment. The treated liquid specimens were tested for toxicity, and the change of pH in them was studied.

At the opening stage of researches, the main task was to find what factors govern the reactions in the solution during its plasma treatment. Therefore, all studies were firstly carried with an ordinary distillate. Some amount of distillate (about 8 ml) was poured into the reactor and treated for a definite time interval (10, 20, 30, or 40 min) with air or argon, being used as a plasma-forming gas. The treated specimens were poured out into quartz flasks, and their absorption spectra, as well as the variation of pH, were measured relative to those of the untreated distillate. The revealed absorption peaks were identified using optical tables [7], while the obtained amount of a substance was determined on the basis of the known or plotted calibration dependences. The next step comprised the insertion of a toxic substance, a pollutant, into the system and the study of the level and the character of its destruction after the treatment.

Aqueous solutions of phenol ( $C_6H_5OH$ ) with concentrations in the range  $10^{-3} - 10^{-2}$  M were used as model pollutants, and the distillate served as the standard substance. After the specimens of solutions having been treated in the reactor for 40 min, the variation of their parameters with respect to the characteristics of untreated specimens was studied.

In the course of the experiment, the solution acquired yellowish coloring, the intensity of which increased with the concentration; the phenomenon being especially noticeable if air served as a plasma-forming gas. After the treatment, the solution was cooled down to room temperature, its pH was measured, and the investigation of its toxicity was carried out following the standard method (the death time of 50% of the population of living test organisms [8]). For this purpose, flasks were filled with a portion of the treated solution, some ten living organisms *Daphnia magna* were placed in it, and the duration of their life in the medium under investigation was registered. In the mean time, the electrodes of a pH-meter were immersed again into the remaining portion of the solution, and a 0.01 M alkaline solution of KOH was added drop-by-drop under the continuous stirring. In so doing, the dilution was insignificant and did not exceed 3%. In such a way, the pH of the treated solution was brought to a natural, usual for those *Crustacea*, value

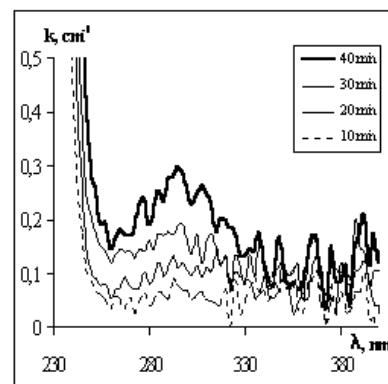


Fig. 2. Absorption spectra of the distillate after various durations of its treatment in the reactor. Air is a plasma-forming gas

of 8.6. Then, the toxicity of the obtained solution with  $pH = 8.6$  was tested again following the same method.

Concurrently, the absorption spectra of the phenol solutions were measured before and after their treatment. A solution specimen was placed into a quartz flask 1 cm in thickness, which was rigidly fixed in a flask chamber and irradiated with a deuterium tube. The absorption spectrum of the treated phenol was calculated relative to the transmission spectrum of distillate and was compared with the absorption spectrum of the untreated specimen. Such an operation has been carried on for ten days (with the immovable flask) in order to determine the temporal dynamics of redox reactions and to monitor possible variations of the liquid parameters. This time interval turned out sufficient for the solution to become stabilized.

#### 4. Results

At the first stage of the researches, liquid distillate served as a working substance, and air as a plasma-forming gas. In Fig. 2, the typical absorption spectra of distillate at various durations of its treatment are presented. The emergence of the diffusion peak at a wavelength of 300 nm evidences for the formation of nitric acid  $HNO_3$  [7] in the liquid, the concentration of which increases in the course of the treatment. The appearance and growth of the characteristic rise in the ultra-violet range of the spectrum testify to the synthesis of a noticeable amount of hydrogen peroxide  $H_2O_2$ . The generation of oxidizers is confirmed by pH-measurements: the pH value decreases proportionally to the amount of the acid synthesized during the treatment of distillate in the reactor (Fig. 3). In so doing, the

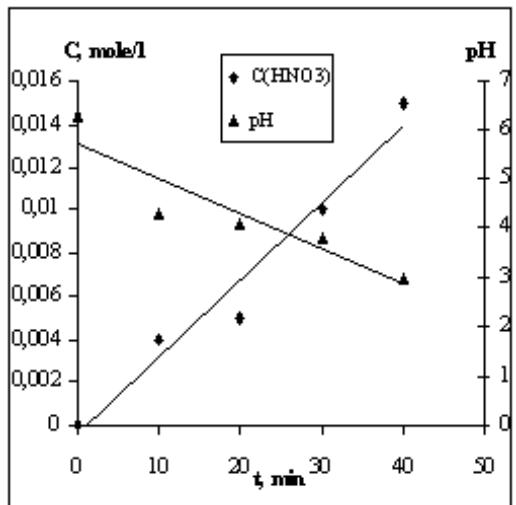


Fig. 3. Variations of the treated distillate parameters with the treatment duration

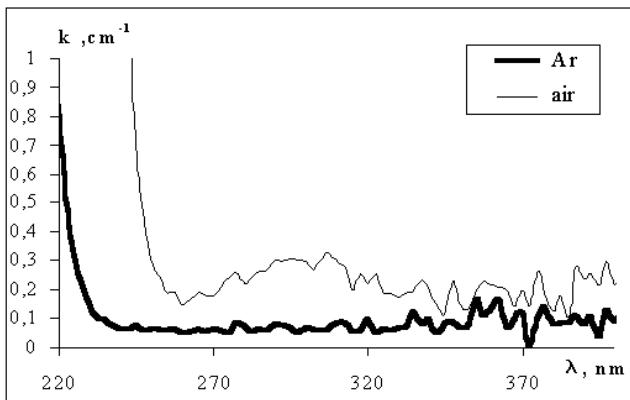


Fig. 4. Absorption spectra of distillate treated with the argon or air plasma for 40 min

spectrum does not reveal the absorption bands of  $\text{HNO}_2$  which may also arise, but probably becomes oxidized to  $\text{HNO}_3$ .

Other active particles —  $e$ ,  $h\nu$ ,  $\text{N}^*$ ,  $\text{N}_2^*$ ,  $\text{O}^*$ ,  $\text{O}_2^*$ ,  $\text{O}_2^+$ , and so on — are also present in plasma. In fact, the high oxidizing properties of the plasma are caused by a wide spectrum of active particles which are formed.

While using argon as a plasma-forming gas, the number of chemically active components of the plasma considerably decreases. Therefore, there is an opportunity to elucidate the role of just the physical processes in plasma-liquid systems. In order to compare the results of the interaction between distillate and the air or argon plasma, Fig. 4 exposes the absorption

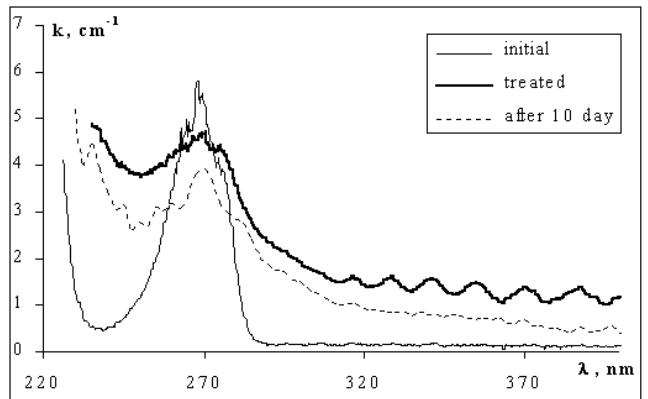


Fig. 5. Absorption spectra of the phenol solution before and after its treatment with argon plasma

spectra of the solution after its 40-min treatment in both modes. One can see that nitric acid is not formed in the system with the argon plasma, and hydrogen peroxide appears in a much smaller quantity. This means that the oxidizing properties of the air plasma are considerably stronger, but oxidizers are also synthesized in the liquid in the case of an inert plasma-forming gas owing to the physical processes that engage high-energy particles of the discharge.

The following stage of the experiment, which was directed at solving the problem of the purification of water from contaminants, consisted in studying the destructive capabilities of the plasma-liquid reactor in question. Aqueous solutions of phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) with concentrations in the range  $10^{-3} - 10^{-2}$  M stood for model pollutants, while the distillate played the role of a standard. Air or argon was passed through those solutions. The solution specimens had been treated in the reactor for 40 min, then the variations of their parameters relative to the characteristics of untreated specimens were researched.

Early works indicated the instability of solutions during several days after their treatment with plasma [9]. Therefore, the absorption spectra were measured before, just after, and within the following ten days after the treatment. The absorption spectrum of a  $0.0015$  M phenol solution, which was recorded 40 min after the solution had been treated with argon plasma, is exposed in Fig. 5; its analysis evidences for a 70% destruction of the contaminant. Within 10 days of monitoring, no substantial variations in the spectrum and the pH value have been noticed. Therefore, we may suggest that, in this case, the main oxidizing factors of the plasma are physical ones ( $e$ ,  $h\nu$ ,  $A^*$ ,  $A_n^+$ ) in combination with

elevated temperature in the reaction region. The general rise of the signal caused by the intermediate products of destruction, which become more oxidized and decay, decreases in time; and, respectively, the synthesized oxidizer (hydrogen peroxide) disappears.

Since it was very difficult to identify the obtained products of the destruction, we studied their total toxicity making use of living organisms – *Daphnia magna* (*Crustacea*) — as testing ones.

The experiments showed that the maximum permissible concentration (MPC) of phenol in water, which does not affect the vital functions of testing organisms appreciably, amounts to 0.003 M. At the same time, concentrations above 0.005 M, resulted in an almost instant death of the whole population.

The obtained values of pH in the treated phenol solutions allowed us to find that their acidity does not depend on the initial concentration, being 2.7 after air and 3.7 after argon plasma treatment. The corresponding pH values for the treated distillate are 3.2 and 4.2, respectively. Such a difference is probably explained by the synthesis of  $H^+$  ions not only from water, but with a direct participation of phenol molecules (hydroxybenzoic acid may be formed).

The research of the treated solutions demonstrated that their toxicity also does not depend on the initial concentration of phenol in the investigated range of concentrations of the initial solution both for the air and argon plasmas; the death time of 50% of the *Crustacea* population was 8 and 35 min, respectively. This brought us to the idea that, in this case, the governing factor of the toxicity is the level of the acidity of a solution.

After diluting the treated specimens up to pH = 8.6, being a natural value for those microorganisms, the dependence of the solution toxicity on the initial phenol concentration is restored (Fig. 6). But now, in contrast to the solutions without KOH, the toxicity of the solutions treated with the air plasma decreases, while the toxicity of the solutions treated with the argon plasma, on the contrary, increases. This fact can indicate that the destruction of phenol by the air plasma is more complete and the products of decay are less toxic than those in the case of the treatment with the argon plasma. Whence, it follows that the presence of the destruction products is the main reason for the toxicity of solutions after their neutralization. It is evident from the figure that the toxicity of the destruction products in the treated solutions with the initial concentrations of phenol higher than the MPC is lower; at the same time, the solutions with concentrations of phenol lower than the MPC are more toxic. This can be explained by the fact that, in all

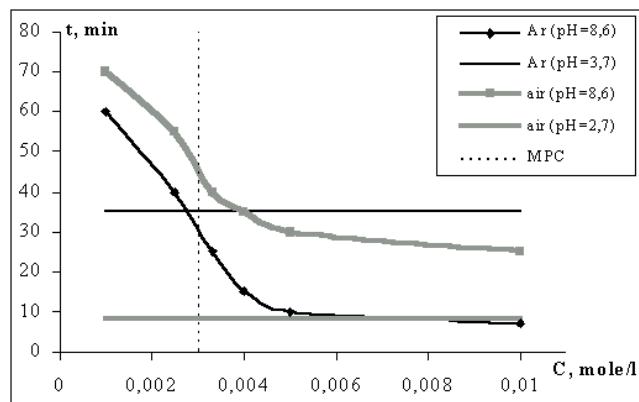


Fig. 6. Dependences of the lifetime of living organisms on the initial concentration of the treated phenol solutions with the induced and natural values of pH

cases, the amount of synthesized oxidizers turns out approximately identical, while their spending is proportional to the pollutant concentration. Therefore, if the concentration of phenol is low, the remaining excess of oxidizers induces the enhancement of the solution toxicity.

## 5. Conclusions

Thus, our research of the plasma treatment of distilled water and aqueous solutions of phenol with concentrations in the range  $10^{-3} - 10^{-2}$  M in a plasma-liquid system, making use of a discharge in the gas channel with a liquid wall, showed the following:

1. Oxidizing destruction of organic substances in water is characterized by a high efficiency.
2. The basic oxidizers are  $H_2O_2$  in the case of the air plasma and  $HNO_3$  in the case of the argon one; they enhance the distillate toxicity after the plasma treatment.
3. Provided the destruction of phenol of 70% at the air or argon plasma treatment, the toxicity of treated solutions does not depend on the initial concentration of phenol. In this case, the governing factor of toxicity is the acidity level of the solution.

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ФІЗИКО-ХІМІЧНІ  
ВЛАСТИВОСТІ ПЛАЗМОВО-РІДИННОЇ  
СИСТЕМИ З ЕЛЕКТРИЧНИМ РОЗРЯДОМ  
У ГАЗОВОМУ КАНАЛІ З РІДКОЮ СТІНКОЮ

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Р е з ю м е

Досліджено фізико-хімічні властивості плазмово-рідинної системи з електричним розрядом в газовому каналі з рідкою стінкою. Показано можливість стимулювання плазмою цього розряду деструкції органічного забрудника у воді. У ролі модельного забрудника в роботі використано фенол. Вивчено оптимальні умови не тільки для руйнування органічних забрудників, але й для досягнення низької токсичності продуктів розпаду. Виявлено, що повітряна плазма приводить до глибшої деструкції фенолу з меншою залишковою токсичністю розчинів порівняно з аргоновою.