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Plasma assisted destruction of organic molecules in dynamic plasma–liquid systems

Abstract. *The processes of organic compound (phenol and cation-active surfactants) destruction in water solutions, which occur under the influence of plasma treatment was investigated in different dynamic plasma-liquid systems (PLS). The breakdown products of phenol and cation-active surfactants detected with absorption spectroscopy. The most effective system for phenol plasmolytic destruction in water solutions are the secondary discharge with a liquid electrode at atmospheric pressure and PLS, based on the impulse discharge in the gas channel with liquid wall.*

Streszczenie. *W artykule prezentowane są metody plazmowej destrukcji związków organicznych (fenole oraz powierzchniowo czynne kationy) w środowisku ciekłym (PLS – plasma-liquid systems). Do detekcji produktów rozpadu fenolu stosowane są metody spektroskopii absorpcyjnej. Autorzy wskazują, że system plazmowy z podwójnym wyładowaniem na wodnej elektrodzie, pracujący przy ciśnieniu atmosferycznym, cechuje się największą skutecznością destrukcji fenolu spośród systemów z wyładowaniem impulsowym. (**Plazmowo wspomagana destrukcja związków organicznych w dynamicznych systemach wodno-plazmowych**)*

Keywords: dynamic plasma-liquid system, plasma-chemical processing, ultrasonic nebulization.
Słowa kluczowe: systemy wodno-plazmowe, procesy plazmo-chemiczne, nebulizacja ultradźwiękowa.

Introduction

Water is a valuable natural resource. With metabolic processes forming the base of human living, water plays an exclusive role in every aspect. The everyday human need for it is known to all. At the UN World Economic Forum (January 2008) held in Switzerland), has been claimed that the population of more than half of the world population will experience a shortage of clean water by 2025, and 75% by 2050. Methods based on plasma-chemical processes in the liquid-gas environments for water treatment and purification of highly polluted wastewater are among the most promising. Unlike the regenerative methods which remove the impurities from the water into the solid (adsorption), gas (desorption) or non-aqueous liquid (extraction) phase, the destructive method (technology of water and industrial waste plasma-chemical processing) is based on changing the chemical structure of molecules and impurities.

The problem of complete cleaning for the industrial wastewaters from organic high active and toxic substances (HATS) is important enough and simultaneously difficult to decide. However this problem can not be considered as decided. Apparently, plasmachemical technologies are represented by most perspective, as allow to achieve high velocity of substances destruction 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 compounds [1]. The chemical reactions both in plasmachemical systems can proceed with participation of the electronic-exited particles, which practically are not investigated today. It is specified that high probability of unknown earlier substances occurrence at the data technologies. Therefore now the transition starts to complex technologies on a basis of plasmachemical processes.

Discharge systems for plasma stimulation of physical and chemical processes, peculiarities of oxidation and reduction reactions and the applicability issues, caused by contact between plasma and the liquid solution, were studied in the present work.

Experimental technique

The process of organic compound destruction in water solutions, which occurs under the influence of plasma, was investigated in different plasma-liquid systems (PLS).

The organic solutions in distillated water was treated by plasma of secondary discharge stimulated by transverse arc at atmospheric pressure [2, 3] of DC discharge in the gas channel with liquid wall and the additional excitation of ultrasonic field in liquid [4]. Pulse discharge in gas channel with liquid wall [5] and the discharge in reverse-vortex gas flow of “tornado” type with “liquid” electrode [6].

The studies were with various plasma-forming gases: dry air (mode A), water vapor (WV), a mixture of air and aerosol solution, which is handled by (S).

The scheme of experimental setup for studying of plasma of secondary discharge stimulated by transverse arc at atmospheric pressure is shown in fig.1.

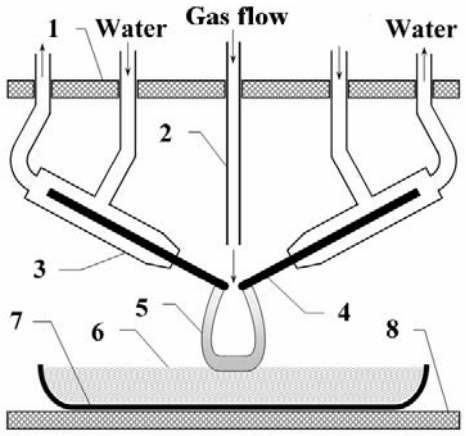


Fig.1. Scheme experimental device to study the properties of the plasma-liquid system based on secondary discharge stimulated by plasma of transverse arc.

It consists of two copper electrodes - 4, between which the DC arc burns. Electrodes are cylindrical with hemispherical ends, directed to the region discharge gap. Electrode diameter equal to 6 mm, length - 70 mm. Shells of water cooling - 3 used to prevent excessive heating of transverse arc electrodes. The length of the electrode part is not immersed in the shell is 25 mm. The discharge gap size in the narrowest part is 1.5 mm.

The flow of air-droplet mixture was directed in a transverse arc discharge gap through tubes - 2, made of stainless steel. Outlet diameter of this tube was 4 mm. Air-droplet mixture was created by the ultrasonic spraying of

distilled water in the air. The generator of air-droplet mixture used ultrasound at a frequency 800 kHz. Ultrasound field was created by three piezoelectric transducers total capacity of 150 watts. Drip air mixture derived from the generator and served in the discharge system through PVC hose length 1.5 m and internal diameter of 15 mm.

The system of electrodes, shells of the water cooling, the feeding system of air-drip mixture into the transverse arc and electrical power supply system were mounted on the dielectric platform – 1, forming the auxiliary discharge assembly.

The working electrode of the secondary discharge – 7 was a thin-walled vessel for holding working liquid – 6. This vessel was a made of stainless steel. The diameter of the side walls of the vessels was 120 mm. Height of vessels amounted to 20 mm. Vessel with electric power supply system of secondary discharge was mounted on the dielectric platform - 8. Platforms - 1 and 8 can move relative to each other along the vertical axis system, which gave the opportunity to change the discharge gap of the secondary discharge.

The characteristic size of transverse arc torch - 5 along the axial coordinate was ~ 20 mm. The distance between the plane of minimum cross-sectional arc discharge gap and surface of liquid was taking as discharge gap of the secondary discharge. In a study of this distance was equal to 20 mm.

The fig.2 is represented the photo of this device during work.

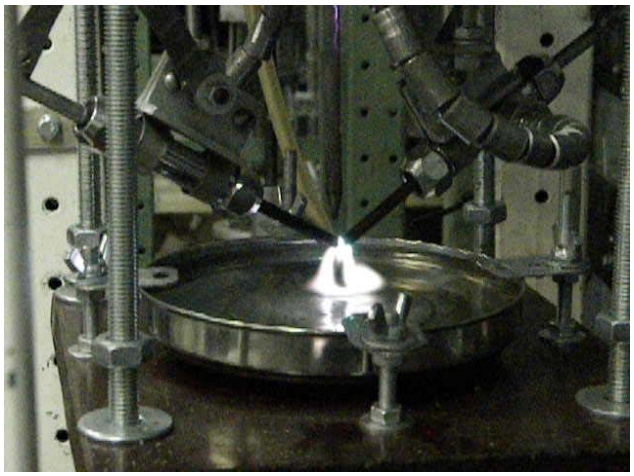
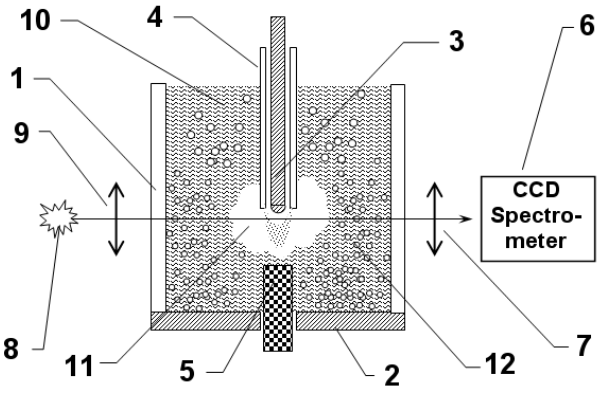


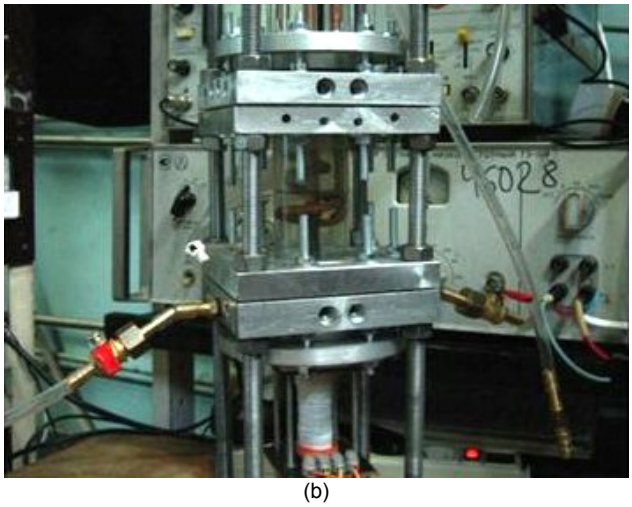
Fig.2. Photo of the plasma-liquid system based on secondary discharge stimulated by plasma of transverse arc during work.

The experimental installation for studying a plasma-liquid system, which is based on the gas discharge immersed into a liquid with an ultrasonic field, is depicted in Fig.3.

It consists of quartz cylinder –1 hermetically sealed at its end faces with metal flanges. Cylindrical metal electrode – 3 in quartz insulator – 4 is introduced through an aperture in the upper flange into liquid layer – 10, being directed along the geometrical axis of the cylinder. In order to create gas channel – 11 in the liquid, a gas is supplied through the space between the external lateral surface of the electrode and the internal lateral surface of the cylindrical quartz insulator. Lower metal flange – 2 is immersed in the liquid and serves for the second electrode, which the discharge potential is applied to. In this work, we considered a regime, when the negative potential is applied to the liquid. Hence, the gas discharge breakdown takes place between metal electrode – 3 and the surface of the liquid surrounding the dynamic gas channel. Magnetostriction ultrasonic projector – 5 is introduced through a rubber seal in the central aperture of flange – 2 into the liquid layer. The resonance frequency of projector was 17 kHz. The ultrasonic projector was excited with the help of a laboratory generator of sound frequency and a 100-W amplifier. Distilled water was a liquid to study. In the course of researches, the discharge current was maintained at a constant level of about 300 mA. The electro-conductance of distillate increased with the plasma exposure time. Therefore, the voltage between electrodes 2 and 3 changed within the interval 2.5-1.8 kV. The ultrasonic radiation intensity during experiments was maintained above the cavitation threshold. Air was used to create the gas channel.



(a)



(b)

Fig.3. Scheme (a) and photo (b) of the experimental installation for studying a plasma-liquid system based on the DC discharge in the gas channel with liquid wall and the additional excitation of ultrasonic field in liquid.

The plasma parameters were studied taking advantage of the emission spectroscopy method. The optical axis of the emission spectrum registration system passed through the midpoint of the gap between electrode – 2 and ultrasonic transducer – 5. The plasma radiation passed along the optical axis of the system through the working liquid layer and, with the help of a quartz lens – 7, was focused on entrance slit – 6 of a spectrometer.

Another PLS reactor used with the discharge TORNADO-LE is shown in Fig.4.

It consists of a cylindrical quartz vessel 1 with diameter of 9 cm and height of 5 cm, sealed by the flanges at the top 2 and at the bottom 3. The vessel was fueled by the work liquid 4 via the inlet pipe 5; the level of liquid was controlled by the spray pump. The basic water-cooled T-shaped 2.5 cm-diameter cylindrical electrode 6 on the bottom flange

3 made from stainless steel was fully immersed in the liquid. The second electrode on the top flange 2 made from duralumin had the copper hub 11 with the axial nozzle 7 of 2 mm inner diameter and 6 mm length. The gas was fed into the reactor chamber through the orifice 8 in the top flange 2 tangentially to the wall 1 and formed a vortex flow of tornado type. The swirling gas went down to the liquid surface and moved to the center of the system, where it flowed out through the nozzle 7 in the form of jet 10 into the upper quartz camera 12. Since the area of minimal static pressure above the liquid surface during the vortex gas flow was located near the central axis, it created the column of liquid at the gas-liquid interface in the form of the cone of ~1 cm height above the liquid surface as is shown in Fig. 3.

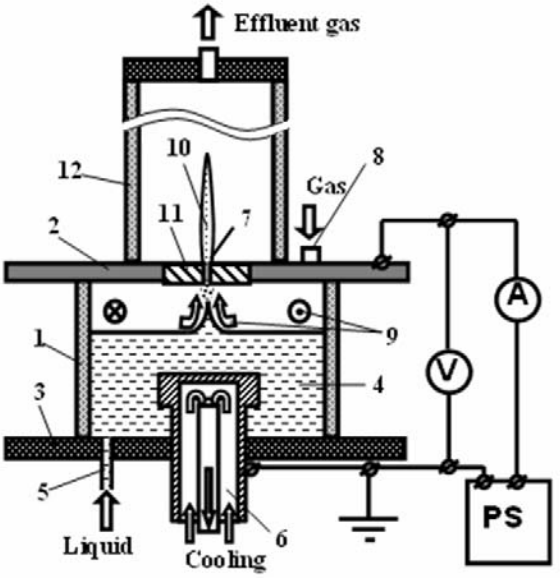


Fig.4. Schematic of the PLS reactor with the DC discharge in a reverse vortex gas flow of tornado type with a "liquid" electrode.

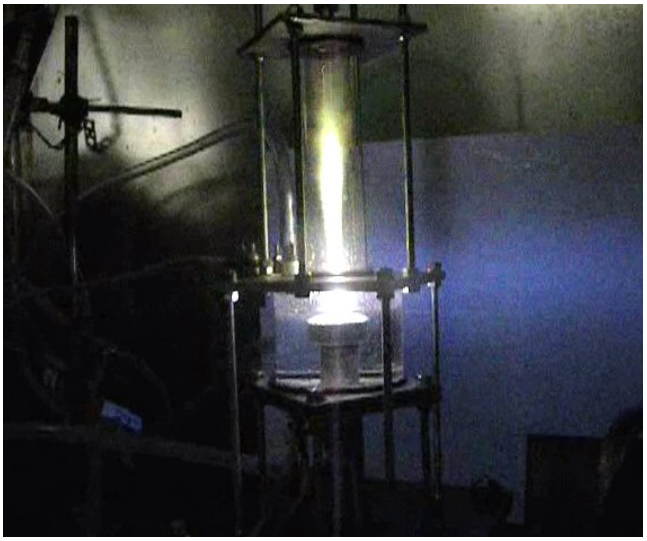


Fig.5. Photo of the PLS reactor with the DC discharge in a reverse vortex gas flow of tornado type with a "liquid" electrode during work. The ges flow G =55 cm^3/s. Discharge current I_d=300 mA.

The plasma torch 10 of ~5 cm long was formed during the discharge in the chamber. The voltage was applied between the top flange 2 and the electrode 6 in the liquid 4 from the DC source powered up to 10 kV. In experiments, two basic modes of discharge were studied: 1) with “liquid” cathode (LC), and 2) with “solid” cathode (SC), using “+” on the flange 2 in the LC mode, and “-” on the flange 2 in the SC mode. The conditions of breakdown were regulated by three parameters: by the level of working liquid; by the gas flow rate G; and by the applied voltage U. The discharge ignition began with the appearance of axial streamer. Time for establishing a self-sustained discharge burning was ~1-2 s after the first streamer. The discharge current varied within the range 100-400 mA. The pressure in the discharge chamber during the discharge was ~1.2 atm, the static pressure outside the reactor was ~1 atm. Fig. 5 shows the TORNADO-LE during work.

Experimental results

Examples of experimental results that were obtained by emission spectroscopic method in UV region ((200 – 400 nm) are shown in Fig.5. The flow of plasma gas was stable - 0,13 $l \cdot s^{-1}$.

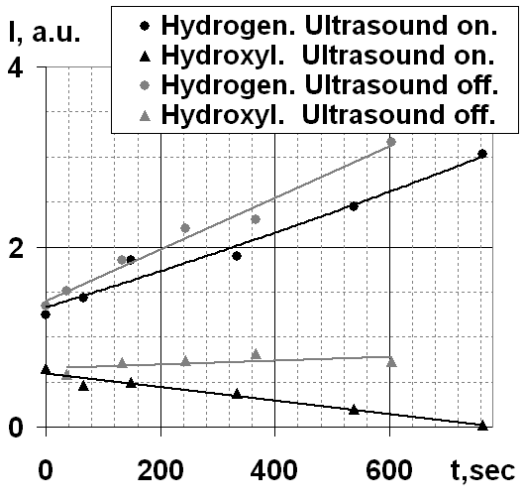


Fig.5. Dependences of the relative intensity of the hydroxyl molecular band – trigonal points and hydrogen – round points in the emission spectra of DGCLW plasma on the distilled water treatment time. The black lines correspond to ultrasound in liquid is present. The grey lines – to ultrasound is absent. All spectral components are normalized on intensity of respective atomic lines of copper (electrodes material).

As follows from the analysis of aggregated data that there is always a strong absorption at λ (wavelength) < 250 nm for the spectra of hydrogen peroxide H_2O_2 and formic acid HCOOH. These compounds are formed during the plasma chemical processing regardless of the type of orifice gas, electrode material and polarity of the “liquid electrode”. During the plasma chemical processing, it was noted that there is a significant disruption of copper and graphite electrodes. “Liquid electrode” with a positive polarity is the most bright example. Bands of nitrogen compounds, typical for the absorption spectra are: NO_3^- (broad band with maximum 300 nm) and NO_2^- (broad band with maximum 355 nm). So, investigated discharges produce very powerful oxidizing species and can essentially change the acidity of our samples. The quantitative responses presented at Fig.6.

Examples of experimental results that were obtained by spectrophotometric method in UV region ((200 - 400 nm) are shown in Fig.7. In here set out results of plasma assisted destructions of phenol molecules in water solution 0,0003 mol/l. Solutions were treatment by plasma of secondary discharge stimulated by transverse arc with air flow and air-droplet flow. The air-droplet flow was generated by ultrasonic nebulization of initial solution. The total discharge power was ~ 800 W. The flow of plasma gas was stable - 0,13 $l \cdot s^{-1}$.

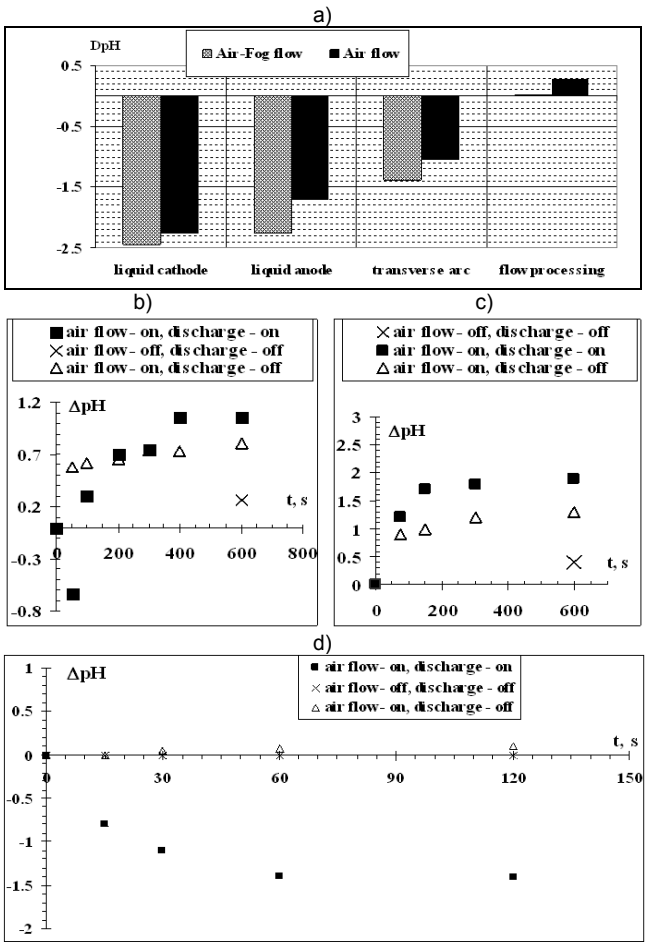


Fig.6. Variation of pH value from airflow with and without plasma treatment. a) - PLS with secondary discharge; b), c) - with DC and Pulse discharges in the gas channel with liquid wall; d) - with the discharge in reverse-vortex gas flow of "tornado" type with liquid electrode.

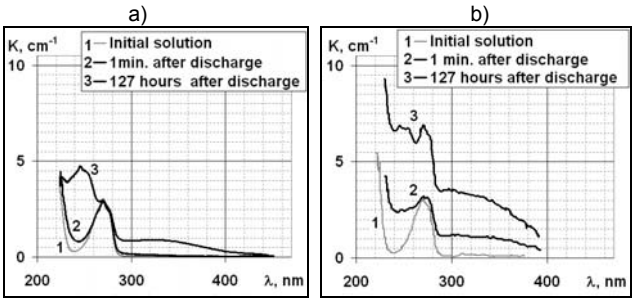


Fig.7. Evolution of phenol-water solutions after plasma assisted destruction of phenol molecules. Chart -a) correspond to secondary discharge stimulated by transverse arc with air flow; chart -b) – with air-droplet flow. The plasma exposition time is 30 sec. The total discharge power ~ 800 W. The grey curve #1 correspond to initial solution, the black #2 – to processing solution in 60 sec after plasma treatment and the black #3 – to processing solution in 127 hours after plasma treatment.

Conclusions

It has been established that the water processing by plasma leads to destruction of toxic phenylic compounds in water solutions.

Analysing the received experimental data, it is possible to conclude that the cleaning of water occurs basically at the expense of oxidizing destruction of phenylic compounds. It is a result of hydrogen peroxide influence, nitric and nitrogenous acids, which are formed in water under influence of plasma secondary discharge, and also of others chemically active particles.

Plasma-chemical factors, which cause the compound destruction:

a) forming the active particles, which activate cascade chemical reactions with molecules of phenylic compounds (free radicals and active oxygen);

b) changing of water structure under plasma-radiolysis and as a consequence - displacement of equilibrium to destruction of molecules of phenylic compounds.

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