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Contact Nonequilibrium Plasma as a Tool for Treatment of Water and Aqueous Solutions: Theory and Practice

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Abstract—Theoretical and practical results of the treatment of water and aqueous solutions by low-temperature nonequilibrium contact plasma are considered. It is shown that the liquid medium in the process of plasma treatment or thereafter undergoes significant structural and physical-chemical transformations, the use of which opens up new horizons in the modernization or improvement of technological processes to replace out-of-dated or obsolete ones.

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INTRODUCTION

Contact nonequilibrium low-temperature plasma with its unique ability to modify the physicochemical properties of water and aqueous solutions is gaining increasing popularity among researchers and practitioners. Plasma treatment is useful for disinfection and detoxification of water media, for sample preparation in atomic absorption analysis, for making bactericidal, antiseptic, and sterilizing water solutions [1–4] , for organic and inorganic synthesis, and it is just the beginning of applying scientific achievements in high-energy chemistry.

The interaction of a gas discharge with solutions can be arranged in several significantly different ways [5] using: (1) pulse breakdown of the liquid phase; (2) liquid-contacting discharge between electrodes in the gas phase; (3) steady or quasisteady discharge, where the electrolyte solution acts as one or both electrodes.

Of most interest is the third mode in which the discharge current goes through the electrolyte substantially modifying the properties of the plasma–liquid interface. Therewith, plasma may be formed in the initial plasma-forming gas containing solvent vapors or in the vapor shell produced inside the liquid phase as a result of temperature instability. The physicochemical properties of the plasma–solution interface and the activation pattern of chemical processes in the bulk of the solution depend significantly on the polarity of the electrode placed in the gas phase. In case of an electrolytic cathode, the voltage drop at the solution surface is higher, and oxidative processes proceed more effectively.

For an appreciable length of time, researchers at the USUCE studied, with the aim of solving certain manufacturing and environmental problems, the phenomena and processes associated with contact exposure of water and aqueous solutions to non-equilibrium plasma. The studies were both theoretical and experimental, and the results obtained provided the basis for the development of plasma chemical manufacturing machinery. Special emphasis was placed on creating a new generation of mathematical models describing the plasma–aqueous solution system, as well as examining physical and chemical transformations in aqueous solutions at the atomic molecular and quantum chemical levels.

When modeling plasma chemical processes in a gas–liquid system, a number of problems arising from the necessity to, concurrently, take into account all the processes, had to be overcome. First of all, it concerns the use of the liquid surface as a bipolar electrode contacting with the plasma discharge [6]. In this context, plasma is a tool for treating the liquid medium which, in its turn, serves as a source of charged species facilitating ionization of low-density gas and formation of a plasma discharge.

The plasma chemical treatment process relies on a variety of factors: temperature of the solution, pressure, diffusion processes at the phase interace, and change in the system volume due to a partial loss of matter. Because it is virtually impossible to take into account all the factors acting in real conditions, certain simplifications are inevitable. Therefore, in building the model, it was taken that the following three effects were involved in the process of the plasma contact treatment of liquid: The first one is UV radiation which facilitates formation of high-reactivity hydrated electrons. The second one is the physical and chemical transformations at the gas–liquid interface, caused by the transfer of charged species from the discharge zone. And the third effect is the electrochemical processes within the liquid layer; in this case, the electrochemical stage, unlike traditional electrochemical processes, proceeds in more favorable conditions due to lower diffusion limitations and lower activation energies.

With the aforesaid effects, a mathematical model for plasma treatment of liquid media, beginning with distilled water and up to solutions containing chemical compounds of polyvalent metals, was proposed. The model is based on: chemical reactions in the gas and liquid phases; plasma chemical yields equivalent to those produced by radiolysis; electrochemical processes on the surface of an electrode immersed in liquid; and reactions induced by plasma discharge. The resulting differential equation system is solved using the Rosenbrock pattern search implemented through built-in Mathcad Professional function. The model results are given both in matrix and graphic formats.

Peculiarities of the Mathematical Modeling of Processes in the Plasma Discharge-Phase Boundary System

Processes leading to the formation of charged particles in liquid are mostly the result of the action of an electrode immersed in the solution. Usually, a cathode serves this purpose. The key criterion enabling to evaluate the number of charged species emitted from the electrode to the liquid is current density.

Generally, the simplified equation including most of the physical and chemical processes involved in the plasma chemical treatment of water and aqueous solutions [7, 8] enables to define, reasonably well, the kinetic changes and to identify more precisely the quantitative yields of target components in the plasma-treated liquid medium. However, the capabilities of the existing mathematical apparatus to solve systems consisting of 16 plus differential equations with a wide scatter of coefficients at variables (e.g. for an aqueous solution, such scatter in values is from 10^{-5} to 10^{18}) are limited. The widely known Adams and Gear methods and their derivatives [9, 10] are sufficiently accurate but require certain factors to be taken into consideration, such as the absence of the positivity property (non-negativity constraints should be imposed on the solutions in the software). An increase in the number of steps (h) in the process of kinetic computations will naturally be accompanied by an accumulation of errors. For example, when calculating changes in solution concentration in the course of its plasma chemical treatment for 5–10 min with the prescribed accuracy $E = 10^{-12}$, the number of steps may far exceed $h = 10^6$, which will result in a substantial error accumulation in the subsequent calculations.

In the numerical study prior to the laboratory tests it is essential to define the possible occurrence and route of the process, as well as the way to control it. For this purpose, it is preferable to make calculations at the level of clusters and particles interaction rather than at the macro level. Using the multiscale simulation method [11, 12], the system may be referred to as a body of interacting particles.

Polyatomic systems and processes are commonly modeled in terms of methods of classical (empirical) potentials, semiempirical and ab initio approaches, and the quantum Monte Carlo method [13–17]. However, in computational modeling of polyatomic systems and processes, none of these methods and approaches allow us to take into account large quantities of particles (molecules, atoms, clusters), ranging usually from 1000 to 5000, involved in chemical transformations both in the gas and liquid phases. Therefore, using such methods one can derive only qualitative characteristics of the process.

Software products implementing methods and approaches for the description of multicomponent systems, such as the Gaussian [18], GAMESS [19], or SageMD2 [20] suites, allow one to simulate the properties of different materials at constant temperature or pressure and to compute the radial distribution function of atoms and their mean square deviations in order to determine the diffusion coefficient. The softwares can apply various boundary conditions, e.g., periodic boundary conditions, free surface, or movable walls. To simulate chemical compounds with covalent bonds, a charge equilibration algorithm was integrated in the software. For ab initio interatomic force field computations using SageMD2, this code was integrated with commercial quantum chemical codes. The SageMD2 suite includes modules that interwork with the widely known quantum mechanical programs, such as Abinit and Gaussian, using standard input and output formats for the results of the interatomic forces calculations.

Among the variety of the existing software packages, there are no program products that can simulate sufficiently, at the polymolecular level, the plasma chemical liquid treatment process. Currently, only the behavior of clusters in liquid can be sufficiently traced and only in a simplified mode [21, 22].

Therefore, new methods are needed to simulate the plasma–liquid interaction, for which purpose we have to develop new application software suites or to enhance the capabilities of existing ones. If we are to take into account as many atoms in a system as possible, we need to have enhanced computation capacity of the supercomputer-based multiprocessing systems or other types of simulation tools.

Thermodynamic Analysis of the Formation of Hydrogen Polyoxides in Water under the Action of Contact Nonequilibrium Plasma

Processes at the liquid–gas interface induced by contact nonequilibrium plasma are most easily expressed in terms of the classical scheme adopted for chain reactions [23]. At the chain initiation step in aqueous media, hydrogen and hydroxyl radicals are formed [24]:

$$H_2O + e_c^- \rightarrow H_2O^* \rightarrow H^{\cdot} + {}^{\cdot}OH. \qquad (1)$$

At the following chain propagation steps, the main products are the hydrodioxyl radical and atomic oxygen [25, 26]:

$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O + O, \qquad (2)$$

$${}^{\cdot}OH + O_2 \rightarrow HO_2^{\cdot} + O, \qquad (3)$$

$${}^{\cdot}OH + O \rightarrow HO_2^{\cdot}, \qquad (4)$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}, \qquad (5)$$

$$H^{\cdot} + O \rightarrow HO^{\cdot}. \qquad (6)$$

Chain termination steps may occur, yielding stable molecular species part of which may then react with radicals:

$$H^{\cdot} + H^{\cdot} \rightarrow H_2, \qquad (7)$$

$$O + O \rightarrow O_2, \qquad (8)$$

$$HO_2^{\cdot} + {}^{\cdot}OH \rightarrow H_2O + O_2. \qquad (9)$$

The formation of hydrogen peroxide as a final product can also be ranged as a chain termination step:

$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2, \qquad (10)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2, \qquad (11)$$

$$HO_2^{\cdot} + \cdot H \rightarrow H_2O_2. \qquad (12)$$

Hydrogen peroxide accumulating in the course of chemical transformations tends to polymerize to form hydrogen polyoxides. In general, the process can be described by the following overall equation:

$$(n - 1)H_2O_2 \rightarrow HO_nH + (n - 2)H_2O. \qquad (13)$$

The 3D structure of such compounds with up to 10 oxygen atoms is shown in Fig. 1 [27].

The probability of various pathways of formation of hydrogen peroxide and its polymerization products was estimated using the thermodynamic approach.

The heats of the reactions were calculated from the heats of formation at the standard thermodynamic temperature of 298 K:

$$\Delta H^0 = \Sigma(v_i \Delta H^0_{f,i})_{\text{prod}} - \Sigma(v_i \Delta H^0_{f,i})_{\text{reag}}.$$

The Gibbs free energies were calculated using the corresponding values for the reaction products and starting reagents [28]. When for some of the compounds there were no such data, the Gibbs free energies was calculated using the enthalpies and entropies of formation.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0.$$

Thermodynamic data for the synthesis of hydrogen peroxide by reactions (10)–(12) are given in Table 1.

From the data obtained it follows that all the reactions involved are exothermic with a minimal heat release. The negative Gibbs energies suggest the possibility of spontaneous formation of hydrogen peroxide by reactions (10)–(12). However, according to [23, 24], the main reagent involved in the formation of hydrogen peroxide is deemed to be the hydrodioxyl radical.

This radical forms a water-bonded complex, thereby facilitating hydrogen peroxide formation:

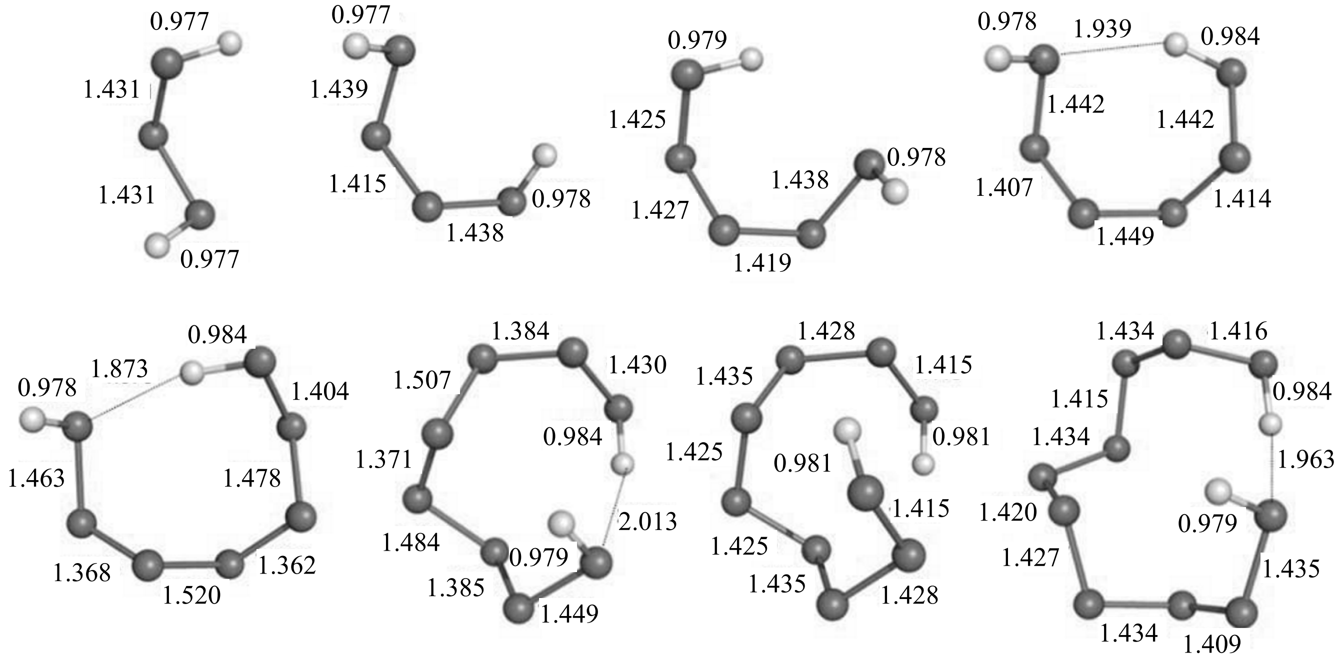

Fig. 1. Structure of hydrogen polyoxides.

$$HO_2^{\cdot} + H_2O \rightarrow (HO_2^{\cdot} \cdot H_2O), \quad (14)$$

$$HO_2^{\cdot} + (HO_2^{\cdot} \cdot H_2O) \rightarrow H_2O_2 + O_2 + H_2O, \quad (15)$$

$$2(HO_2^{\cdot} \cdot H_2O) \rightarrow H_2O_2 + O_2 + 2H_2O. \quad (16)$$

The hydrodioxyl radical is a weak acid and dissociates to form the superoxide radical ion [29, 30]:

$$HO_2^{\cdot} \leftrightarrow H^+ + (O_2^{\cdot})^-, \ pK_a = 4.9. \quad (17)$$

With increasing pH, this radical ion undergoes chemical transformations resulting in hydrogen peroxide:

$$2(O_2^{\cdot})^- + H_2O \rightarrow HO_2^- + O_2 + HO^-, \quad (18)$$

$$(O_2^{\cdot})^- + HO_2^{\cdot} \rightarrow HO_2^- + O_2, \quad (19)$$

$$HO_2^- + H^+ \rightarrow H_2O_2. \quad (20)$$

The distribution of molecular and ionic radical species in solutions at various pH values was calculated from the dissociation constant of $HO_2^{\cdot}$ (Fig. 2).

As follows from the resulting data, up to pH = 4, the prevailing radical species is $HO_2^{\cdot}$ (no less than 90%), and dominating contributors to the formation of hydrogen peroxide are reactions (14)–(16). However, at pH > 6 prevailing is the ionic radical species $O_2^{\cdot -}$ and the reactions are (18)–(20).

Table 1. Heat effects and Gibbs free energies of the reactions forming hydrogen peroxide at 298 K

Reaction	ΔH^0, kJ/mol	ΔG^0, kJ/mol
$\cdot OH + \cdot OH \rightarrow H_2O_2$	–262.4	–188.8
$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$	–208.8	–165.6
$HO_2^{\cdot} + H^{\cdot} \rightarrow H_2O_2$	–416.3	–363.3

In the pH range 4 to 6, the quantities of molecular and ionic radical species are comparable and both hydrogen peroxide formation mechanisms can operate concurrently.

On the basis of thermodynamic data in [28], we calculated the heat effects of hydrogen peroxide formation reactions and, to evaluate the probability of such reactions, the Gibbs free energies were calculated (Table 2).

According to data obtained, hydrogen polyoxides are formed with heat release, and the more oxygen atoms there are in a molecule, the more heat is released. The fact that in all the cases the change of Gibbs free energy was negative suggests spontaneous hydrogen peroxide polymerization in aqueous solutions, resulting in formation of hydrogen polyoxides of various compositions. Apparently, an increase in the number of oxygen atoms in the polymer molecule brings about major kinetic hindrances to the polymerization process due to increasing number of steric forms and increasing entropy contribution aspect.

Results of experimental verification of the thermodynamic analysis are presented in [31].

Kinetic Model of Chemical Transformations in Aqueous Solutions, Induced by Contact Low-Temperature Plasma (on an Example of a NaCl Solution)

One of the promising applications of contact low-temperature plasma is plasma chemical treatment of NaCl solutions. Plasma-treated NaCl solutions contain oxygenated chlorine compounds which endow the treated solutions with oxidizing properties. Such plasma chemically "activated" solutions are useful for bleaching textiles and cellulose, disinfecting and cleansing food production equipment, etc. In [32–34] we demonstrated, theoretically and experimentally, that under the action of contact plasma, hydrogen peroxide and hypochlorite ions are generated in NaCl solutions, and then they fast react to form chlorite ions. The possibility of further oxidation of chlorites and chlorates to perchlorates was also established. Defining the kinetic model of such plasma chemical process is of academic and practical interest.

Mathematical kinetic description of the chemical and electrochemical processes in a gas–liquid plasma-chemical reactor is hindered by the lack of knowledge on the mass transfer in each of the phases and on the hydrodynamic conditions near the phase boundary. The simplest film model of mass transfer in a gas–liquid system suggests that the aggregate resistance to mass transfer is additive, i.e., consists of all the phases' resistances and of the chemical reaction resistance [34]:

$$K_H = \left[\frac{1}{\beta_\mathrm{l}} + \frac{1}{\beta_\mathrm{g}} + \frac{1}{k}\right]^{-1},$$

where K_H is the apparent rate constant of the process; β_g and β_l, mass transfer coefficients at near-surface layers of the gas and liquid phases; and k, chemical reaction rate constant.

It has been proved that a virtually instantaneous plasma chemical process ($k >> \beta_\mathrm{g}$ and β_l) occurs in the diffusion zone. The rate of the process does not depend on the concentrations of substances involved in the reaction and is expressed in terms of a zero-order kinetic equation. For fast (though not instantaneous) reactions the process zone expands and may occupy a part of the flow core volume. In this case, the plasma chemical process occurs in a mixed diffusion/kinetic control zone. With an excess of one of the reagents, the rate of the plasma chemical process is well fitted by a pseudofirst-order equation.

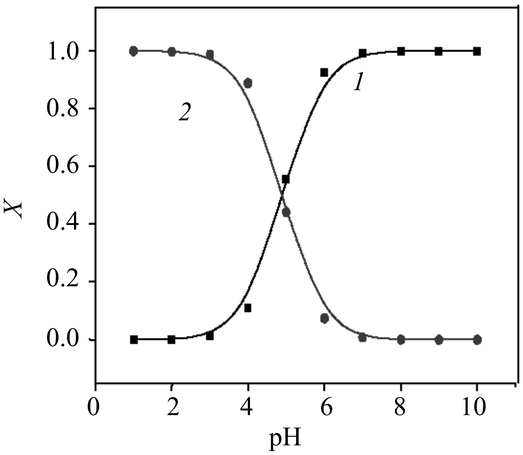

Fig. 2. Distribution of the (*1*) ionic $O_2^{\bullet-}$ and (*2*) molecular $HO_2^{\bullet}$ radical species at varied pH of the solution.

The application of the film model of mass transfer model to the description of chemical processes in a plasma chemical reactor requires taking account of the "activation" of molecules in the plasma medium and their transfer to the liquid surface. Let us examine the activation stages in more detail.

Continuous "Activation" of Gaseous Molecules in the Plasma Medium is Caused by an Electron Flux

Along with changes in the kinetic energy and internal degrees of freedom, the molecules undergo ionization processes, e.g.:

$$H_2O(\mathrm{gas}) \rightarrow H_2O^{+}(\mathrm{gas}) + e^{-}, \tag{21}$$

$$O_2(\mathrm{gas}) \rightarrow O_2^{+\bullet}(\mathrm{gas}) + e^{-}, \tag{22}$$

$$H_2(\mathrm{gas}) \rightarrow H^{+}(\mathrm{gas}) + H^{\cdot}(\mathrm{gas}) + e^{-}. \tag{23}$$

Table 2. Heat effects and Gibbs free energies of the reactions forming hydrogen polyoxides at 298 K

Reaction	ΔH^0, kJ/mol	ΔG^0, kJ/mol
$2H_2O_2 \rightarrow HO_3H + H_2O$	–4.10	–122.83
$3H_2O_2 \rightarrow HO_4H + 2H_2O$	–55.34	–192.74
$4H_2O_2 \rightarrow HO_5H + 3H_2O$	–102.8	–258.87
$5H_2O_2 \rightarrow HO_6H + 4H_2O$	–156.65	–331.92
$6H_2O_2 \rightarrow HO_7H + 5H_2O$	–196.75	–390.16
$7H_2O_2 \rightarrow HO_8H + 6H_2O$	–248.80	–460.88
$8H_2O_2 \rightarrow HO_9H + 7H_2O$	–295.34	–526.09
$9H_2O_2 \rightarrow HO_{10}H + 8H_2O$	–347.51	–596.93

To simplify the model, we neglect the reversibility of these processes, as well as the possibility of chemical reactions in the gas phase, e.g.,

$$H_2O^{+\bullet}(\text{gas}) + H_2O(\text{gas}) \rightarrow HO^{\bullet} + H_3O^{+},$$

as the aim of the work is to examine chemical transformations only in the liquid phase. We also assume that the concentration of ionized water molecules in the gas phase is higher than the concentrations of any other ionized species. The assumption is based on the fact that, with the plasma chemical reactor being continuously evacuated, the main component of the gas phase is water vapor, the concentration of which is several orders magnitude higher compared to other components of the reaction mixture. According to the law of mass action, the quantity of water molecules transforming into radical cations will depend on their total content:

$$\frac{dN(H_2O^{+\cdot})}{V_P dt} = k_i p(H_2O), \qquad \text{(I)}$$

where k_i is the ionization rate constant; $p(H_2O)$, water vapor pressure (or pressure inside the reactor); and V_P, plasma volume.

Considering that the anode diameter is much smaller than the plasma plume base, the volume of the plasma discharge is taken to be that of a cone the base of which is the cathode spot on the surface of the solution and its height h equals the distance S_P between the anode and the solution surface:

$$V_P = 1/3 S_P h.$$

Whereas the activation of molecules in the plasma discharge is induced by electron impact, its properties, such as electron flux density, electron velocity, probability of ionization in direct particle collisions, etc., should have been taken into account. In Eq. (I) all the above-listed electron flux parameters are “concealed” in the ionization rate constant k_i.

The second stage of the plasma-chemical process is $H_2O^{+\cdot}$ transfer from the gas phase to the solution surface. In view of the low concentration of these species (with the pressure in the reactor maintained within the range of 20 to 50 kPa) and their positive charge, we assume that the driving force of mass transfer is particle migration between the cathode and anode. The ion flux in the electrostatic field through an imaginary unit area per unit time is described by the equation:

$$j_m = -DC\frac{zF}{RT}\,\text{grad}\,\varphi.$$

Combining all constants, the expression for $H_2O^{+\cdot}$ migration rate can be written in the form:

$$\frac{dN(H_2O^{+\bullet})}{S_P dt} = -DC^{\text{g.p.}}_{H_2O^{+\cdot}}\frac{zF}{RT}\,\text{grad}\,\varphi = -k_m C^{\text{g.p.}}_{H_2O^{+\cdot}}, \qquad \text{(II)}$$

where S_P is surface area of the plasma cathode spot; D, diffusion coefficient, $C^{\text{g.p.}}H_2O^{+}$, concentration of ionized water molecules in the gas phase; z, ionic charge; F, Faraday constant; R, gas constant; T, temperature; grad φ, potential gradient; and k_m, migration rate constant.

At the third stage of the plasma-chemical process, chemical transformations induced by cation radicals $H_2O^{+\cdot}$ occur on the surface of the solution and perhaps in its near-surface layer. As already stated, even in fast (though not instantaneous) reactions the process zone expands and may occupy a part of the liquid phase volume. If the trigger of the oxidizing reactions of water molecules and chloride ions is only $H_2O^{+\cdot}$ particles, then their concentration in the liquid phase (that is, at solution’s surface and near-surface layer) will be a factor that control the rate of the entire process. From Eqs. (I) and (II) we obtain the H_2O^{+} concentration in the solution at equilibrium condition, i.e., when the rates of all the stages equalize being limited by the slowest one:

$$\frac{dN(H_2O^{+\bullet})}{dt} = -k_i p(H_2O)V_P = -k_m C^{\text{g.p.}}_{H_2O^{+\cdot}} S_P.$$

The concentrations of H_2O^{+} particles in the gas and liquid phases can be represented as the ratios:

$$C^{\text{g.p.}}_{H_2O^{+\cdot}} = \frac{N(H_2O^{+\bullet})}{V_P} = \frac{N(H_2O^{+\bullet})}{1/3 S_P h}$$

and

$$C^{\text{g.p.}}_{H_2O^{+\cdot}} = \frac{N(H_2O^{+\bullet})}{V_{\text{g.p.}}}.$$

Substituting these ratios into the above equation we get:

$$C^{\text{l.p.}}_{H_2O^{+\cdot}} = \frac{k_i}{k_m}\frac{p(H_2O)V_P^2}{V_{\text{l.p.}}S_P} = \frac{k_i}{k_m}p(H_2O)S_P, \qquad \text{(III)}$$

where $k_P = (h^2/9V_{\text{l.p.}})$ is the constant for the given plasma chemical reactor depending on the distance between the anode and the solution surface, as well as on the solution volume.

Equation (III) relates the concentration of ionized species in the liquid phase and key parameters of both stages of the process, ionization and migration, and such parameters as pressure in the reactor, surface of the cathode spot, and dimensions of the reactor.

To build a kinetic model for chemical transformations occurring in the liquid phase in a plasma chemical reactor we have to define kinetic equations for each stage of the chemical reaction. The sequence in which these stages occur determines the pathways of chemical transformations. Experimental study of such chemical transformations is a challenging task. Due to the low activation energies the rates of radical reactions are very high, and after the contact action of the plasma discharge on the solution is terminated, the concentration of radical species decreases rapidly. The problem becomes much easier to solve if only relatively stable reagents are included in the kinetic model and if the summing up of stages of chemical interactions is carried out in a way where the resulting stoichiometric equations do not include radical intermediates.

In aqueous solutions of sodium chloride, the possible chemical reactions are oxidation of water molecules (and OH^- ions), chloride ions and of intermediate products of their oxidation, as well as reduction of water molecules (and H^+ ions) and of oxidation products of chloride ions:

$$2H_2O \xrightarrow{-2e} H_2O_2 \xrightarrow{-2e} O_2,$$

and also

$$2OH^- \xrightarrow{-2e} H_2O_2, \tag{24}$$

$$Cl^- \xrightarrow{-2e} ClO^- \xrightarrow{-2e} ClO_2^- \xrightarrow{-2e} ClO_3^- \xrightarrow{-2e} ClO_4^-, \tag{25}$$

$$ClO_x^- \xrightarrow{+ne} Cl^- \text{ (where } x = 1, 2, 3 \text{ or } 4), \tag{26}$$

$$H_2O \xrightarrow{+2e} H_2 \text{ (and also } 2H^+ \xrightarrow{+2e} H_2). \tag{27}$$

Oxygen-containing chlorine compounds can undergo self-oxidation and self-reduction reactions known as disproportionation and decomposition:

$$2NaClO \rightarrow NaCl + NaClO_2, \tag{28}$$

$$3NaClO_2 \rightarrow NaCl + 2NaClO_3, \tag{29}$$

$$NaClO_2 \rightarrow NaCl + O_2, \text{ etc.} \tag{30}$$

In these reactions, chlorine or oxygen oxidation degrees change but the mechanism of such transformations does not necessarily involve electron transfer, which is the case in electrolysis. It has been proved, e.g., in [32], that oxidation with hypochlorite is the result of oxygenrather than electron transfer:

$$HClO + NO_2^- \rightarrow [H(Cl)O{\cdots}NO_2^-]^\# \rightarrow [H^+(Cl^-){\cdots}ONO_2^-]^\# \rightarrow H^+ + Cl^- + NO_3^-. \tag{31}$$

In parentheses, likely compositions of the transition states (activated complexes) are shown, while the three dots mean a new bond formed on Cl–O bond cleavage.

Similarly, the disproportionation of hypochlorites, chlorites, and chlorates can be described by the following schemes of oxygen transfer:

$$2ClO^- \rightarrow [^-OCl{\cdots}O\text{–}Cl^-]^\# \rightarrow [^-OClO{\cdots}Cl^-]^\# \rightarrow ClO_2^- + Cl^-, \tag{32}$$

$$2ClO_2^- \rightarrow [^-O_2Cl{\cdots}O\text{–}ClO^-]^\# \rightarrow [^-O_2ClO{\cdots}ClO^-]^\# \rightarrow ClO_3^- + ClO^-, \tag{33}$$

$$2ClO_3^- \rightarrow [^-O_3Cl{\cdots}O\text{–}ClO_2^-]^\# \rightarrow [^-O_3ClO{\cdots}ClO_2^-]^\# \rightarrow ClO_4^- + ClO_2^-. \tag{34}$$

Such compositions of activated complexes are due to the HOMO–LUMO interaction of the reacting species.

Clearly, the charged atoms of oxygen and chlorine in the activated complex will be under significant Coulomb repulsion, and, therefore, more probable are reactions involving molecular reacting species. For example, the disproportionation of hypochlorites can be represented as a sequence of two stages, the protonation of the ClO^- anion and reaction between HClO and ClO^-:

$$ClO^- + H^+ \rightarrow HClO, \tag{35}$$

$$HClO + ClO^- \rightarrow [HOCl{\cdots}O\text{–}Cl^-]^\# \rightarrow [HOClO{\cdots}Cl^-]^\# \rightarrow H^+ + ClO_2^- + Cl^-. \tag{36}$$

In this representation of the disproportionation mechanism its rate at a constant pH of the solution can be described in terms of first-order kinetics in ClO^- ions (both for the first and the second stages of the reaction). Similar conclusions apply to other oxidation and reduction reactions of oxygenous chlorine compounds. Therefore, in the building of a kinetic model of plasma chemical reactions in the liquid phase we used first-order rate equations for each reagent. The possibility of this kind of mechanism, even for bimolecular reactions, is conditioned by the excess of one of the reagents as compared with the concentration of the other one.

To maximally simplify the kinetic model, the scheme of water and chloride transformations was built without specifying the concrete form of the oxidizer reagent which can be $H_2O^{+\cdot}$ or $OH^{\cdot}$, or any other species with unpaired electrons. It was assumed that at an equilibrium condition their concentration in the solution does not change [see Eq. (III)], hence it can be included in the rate constant of the process stage under consideration. With this approximation, the scheme of chemical transformations induced by plasma in aqueous solution of sodium chloride can be written as follows:

(1) Oxidation of water induced by plasma:

$$H_2O \xrightarrow{k_1} H_2O_2$$

(2) Decomposition of hydrogen peroxide:

$$H_2O_2 \xrightarrow{k_2} O_2$$

(3) Plasma-induced oxidation[1] of chloride ions:

$$Cl^- \xrightarrow{k_3} ClO^-$$

(4) Chemical reaction:

$$ClO^- + H_2O_2 \xrightarrow{k_4} ClO_2^-$$

(5) Plasma-induced oxidation of hypochlorite ions:

$$ClO^- \xrightarrow{k_5} ClO_2^-$$

(6) Reduction[2] of hypochlorite ions:

$$ClO^- \xrightarrow{k_6} Cl^-$$

(7) Plasma-induced oxidation of chlorite ions:

$$ClO_2^- \xrightarrow{k_7} ClO_3^-$$

(8) Reduction of chlorite ions:

$$ClO_2^- \xrightarrow{k_8} ClO^-$$

(9) Plasma-induced oxidation of chlorate ions:

$$ClO_3^- \xrightarrow{k_9} ClO_4^-$$

(10) Reduction of chlorate ions:

$$ClO_3^- \xrightarrow{k_{10}} ClO_2^-$$

(11) Reduction of perchlorate ions:

$$ClO_4^- \xrightarrow{k_{11}} ClO_3^-$$

Apart from the above reactions, reduction of water molecules and hydrogen ions may proceed in the plasma chemical reactor:

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-,\ 2H^+ + 2e^- \rightarrow H_2\uparrow.$$

The decomposition of hydrogen peroxide may result not only in oxygen but also in water formation:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O.$$

As the concentrations of hydrogen and oxygen in the plasma chemical reactor had not been measured, the rate of these stages were not studied.

In the above scheme of transformations, instead of disproportionation of hypochlorites, chlorites, and chlorates, only their reduction reactions are written. Reactions of their decomposition with the release of oxygen were not included either. It was presumed that during the period of plasma-chemical treatment of sodium chloride solutions (from 2 to 20 min) these reactions do not affect materially the composition of the solutions: disproportionation reactions are rather slow, while decomposition with oxygen release proceed only when there is a significant rise in temperature.

Given the aforesaid assumptions and according to the law of mass action, the mathematical model of the process kinetics in the plasma chemical reactor can be represented as a differential equation system:

$$(d/dt)C_A = -k_1C_A, \tag{IV}$$

$$(d/dt)C_B = k_1C_A - k_2C_B - k_4C_BC_E, \tag{V}$$

$$(d/dt)C_C = k_2C_B, \tag{VI}$$

$$(d/dt)C_D = k_6C_E - k_3C_D, \tag{VII}$$

$$(d/dt)C_E = k_3C_D + k_8C_F - k_6C_E - k_5C_E - k_4C_BC_E, \tag{VIII}$$

$$(d/dt)C_F = k_5C_E + k_{10}C_G - k_8C_F - k_7C_F + k_4C_BC_E, \tag{IX}$$

$$(d/dt)C_G = k_7C_f - k_9C_G - k_{10}C_G + k_{11}C_H, \tag{X}$$

$$(d/dt)C_H = k_9C_G - k_{11}C_H, \tag{XI}$$

where (*A*) H_2O; (*B*) H_2O_2; (*C*) O_2; (*D*) Cl^-; (*E*) ClO^-; (*F*) ClO_2^-; (*G*) ClO_3^-; (*H*) ClO_4^-.

The following initial concentrations were taken as boundary conditions:

$C_A = 55.6$ M, $C_D = 0{,}05$ M, $C_B = C_C = C_E = C_F = C_G = C_H = 0$.

The results of experimental verification of the plasma chemical treatment model of the sodium chloride solution are shown in Fig. 3. Sodium chloride solutions of 3 g/L initial concentration were used in the experiments. Solutions were preliminarily alkalinized

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[1] In the description of the first stage of chloride oxidation, the possibility of formation of Cl_2 was disregarded. In aqueous solutions with pH > 3, chlorine undergoes fast disproportionation to form hypochlorite and chloride ions

[2] The reduction processes in the scheme of transformations under consideration can be homogeneous or heterogeneous, that is, proceed either in the bulk of the solution, involving solvated electrons, or directly on the surface of the cathode.

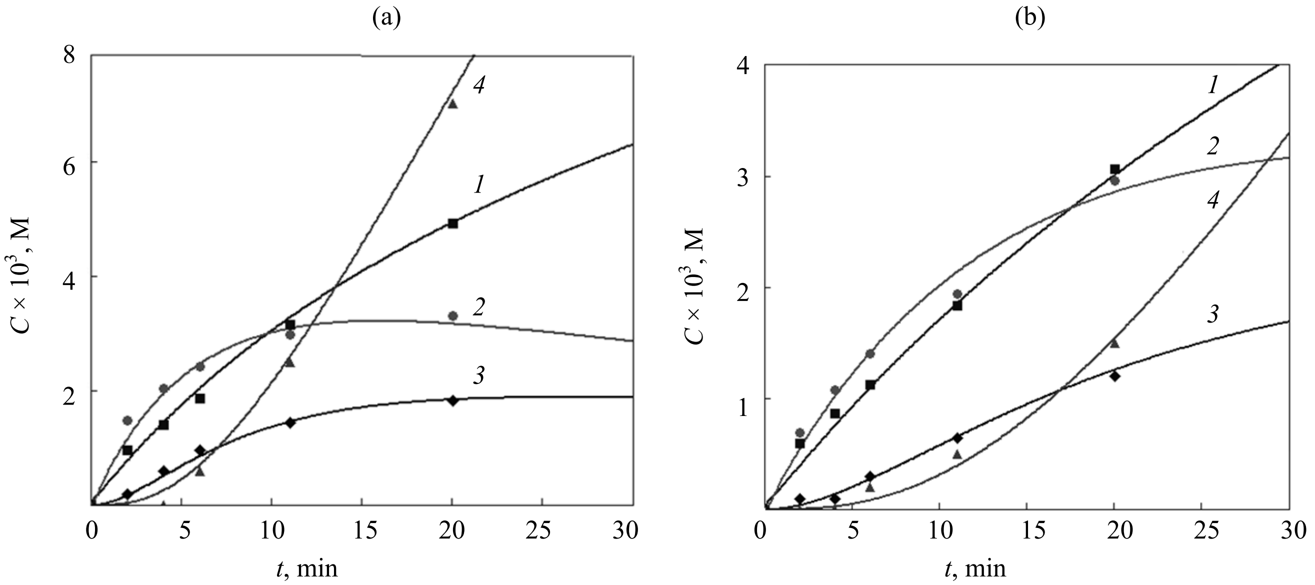

Fig. 3. Dependences of the concentrations of (*1*) H_2O_2, (*2*) ClO_2^-, (*3*) ClO_3^-, and (*4*) ClO_4^- in NaCl solution (concentration 3.0 g/L, pH = 11.7) on the time of its treatment with contact plasma. Plasma conditions: current 140 mA, pressure in the reactor (a) 45.1 and (b) 19.6 kPa. (Dots) Experimental data; the curves are plotted according to the mathematical model.

to prevent a likely loss of chloride oxidation products when the reactor is evacuated. It has been found that the treatment of weakly alkaline aqueous solutions of sodium chloride with contact plasma produces, along with hydrogen peroxide and chlorites, chlorates and perchlorates. The 2.3-fold rise in pressure contributes to the increase in the concentrations of hydrogen peroxide 1.6-fold, chlorites 1.1-fold, chlorates 1.5-fold, and perchlorates 4.7-fold.

In the calculation of the rate constants of the likely redox reactions in the approximation of the mathematical model of the plasma chemical process, the model of intermittently stirred reactor was used.

The loss of substance due to evacuation was ignored, because the duration of the plasma chemical process did not exceed 20 min. The stirring of the solution in the experimental plasma chemical reactor was primarily provided by gas bubbles released from the cathode surface and in the bulk of the solution.

Because of its relatively small size and amount of solution contained (50 mL), mass transfer between the liquid within the plasma plume and the rest of its volume was disregarded. Therefore, all the calculations were made in the approximation of the model of intermittentlystirred perfect-mixing reactor.

To solve the system of differential equations (IV)–(XI), we used the Runge–Kutta method with fixed-step integration. Following the experimental data and the mathematical model, rate constants for the reactions involved were calculated (Table 3).

Interestingly, according to data obtained, the rate constant of the water oxidation reaction involving radical cations is 3 to 4 orders lower than the oxidation rate constants of chloride ions and the other chlorine compounds. We believe that this phenomenon may stem from the difference between the electron binding energy in water molecules and in chlorine anions and its derivatives. For instance, the first ionic potential for the water molecule equals 12.61 eV, whereas for the Cl^- ion it is about 9 eV. The fact that the rate constant of water oxidation varies within the range $(0.9 - 2) \times 10^{-5}$ s^{-1} testifies that it depends not only on the chemical nature of the reaction but also on the conditions of the process.

The rate constant of the reaction between hypochlorite ions and hydrogen peroxide we determined approximately as being no less than 1×10^5. Calculations with lower k_4 values suggested accumulation of hypochlorites. However, because the latter were not detected in the experiments, the value of k_4 was chosen to be definitely higher. Calculation with $k_4 \geq 1 \times 10^5$ resulted in a vairtually zero concentration of hypochlorites. It does not seem possible to define k_4 more precisely.

Table 3. Apparent rate constants of chemical reactions in an aqueous solution of NaCl at varied pressure in a plasma chemical reactor (current 140 mA, NaCl concentration 3 g/L, pH 11.7)

Chemical reactions	p = 45.1 kPa	p = 19.6 kPa	
		theory[a]	experiment
$H_2O \xrightarrow{k_1} H_2O_2$	2×10^{-5}	0.87×10^{-5}	0.9×10^{-5}
$H_2O_2 \xrightarrow{k_2} O_2$	0.080	0.035	0.03
$Cl^- \xrightarrow{k_3} ClO^-$	0.014	0.006	0.006
$ClO^- + H_2O_2 \xrightarrow{k_4} ClO_2^-$	1×10^5	–	1×10^5
$ClO^- \xrightarrow{k_5} ClO_2^-$	0.1	0.044	0.044
$ClO^- \xrightarrow{k_6} Cl^-$	0.01	–	0.01
$ClO_2^- \xrightarrow{k_7} ClO_3^-$	0.18	0.078	0.08
$ClO_2^- \xrightarrow{k_8} ClO^-$	0.01	–	0.01
$ClO_3^- \xrightarrow{k_9} ClO_4^-$	0.33	0.14	0.14
$ClO_3^- \xrightarrow{k_{10}} ClO_2^-$	0.01	–	0.01
$ClO_4^- \xrightarrow{k_{11}} ClO_3^-$	0.01	–	0.01

[a] The theoretical rate constants at p = 19.6 kPa were calculated by dividing the rate constants at p = 45.1 kPa by the pressure drop coefficient in the reactor: 45.1 : 19.6 = 2.3.

Comparative analysis of the apparent reaction rate constants in NaCl solutions in the process of their treatment with contact plasma has shown that the oxidation rate constants are subjected to regular changes under varied conditions of plasma chemical activation. For example, according to data from Table 3, the oxidation rate constants of chlorine and its compounds change in the following sequence: $Cl^- < ClO^- < ClO_2^- < ClO_3^-$. We believe that this is due to regular changes in the properties of their transition complexes. Both electrophilic and nucleophilic reagent species can react with oxygen-containing chlorine compounds (+1, +3, +5). For example, the reaction between the OH radical and hypochlorite can be represented by the following scheme:

$$^{\cdot}OH + ClO^- \rightarrow [^{\cdot}HO\cdots Cl\text{–}O^-] \rightarrow H^{\cdot} + ClO_2^-.$$

The nucleophilic reagent reacts with the LUMO of ClO^- from the chlorine side and ends by displacement of the bridging oxygen atom. This results in a rise of the oxidation degree of the chlorine atom. Clearly, as the number of oxygen atoms in oxygen-containing chlorine compounds rises, the effective charges of atoms and, therefore, the energies of their activated complexes change regularly.

Modeling the reduction stages of oxygenous chlorine compounds showed that variation of reduction reaction rate constants does not affect materially the shapes of the $C(t)$ kinetic curves. Accordingly, we conclude that the reduction stages in the plasma chemical process under consideration are of marginal importance: their share in the overall process is relatively small, and free electrons, for the most part, act in the gas phase, rather than in the liquid, forming a plasma medium as a result of ionization of molecules and atoms. The equality of the reduction rate constants of oxygenous chlorine compounds testifies that the mechanisms of these processes are identical. Apparently, the reduction stages are due to direct transfer of elementary particles, namely, electrons. As mentioned earlier, reduction may take place either on the cathode surface or in the bulk of the solution as a result of addition of solvated electrons. In both cases, it is the same process mechanism which does not require any specific orientation of the particles being reduced, because the outcome is destruction of chemical bonds rather than formation of new ones.

Of special interest is the dependence of the productyields of the plasma chemical process on the pressure in the reactor. Rate-constant expressions for all oxidation stages include the concentrations of the radical ions $H_2O^{+\cdot}$, $^{\cdot}OH$, or any other species with unpaired electrons capable of triggering oxidation processes. According to Eq. (III), the concentration of ionized species in the liquid phase is proportional to the pressure in the reactor. Therefore, when the pressure drops from 45.1 to 19.6 kPa, that is 2.3 times, the rate constants of all the oxidation stages should also decrease (see the middle column in Table 3). The experimental data correlate well with the aforesaid prediction. The rate constants of plasma chemical oxidation at 45.1 kPa are, with small deviations, 2.24 times higher than those at 19.6 kPa. These deviations may be attributed not only to measurements uncertainty but also to fluctuations of the cathode spot surface area (which is subjected to experimental conditions, specifically, the pressure in the reactor, the electric field intensity, or both [33, 34]).

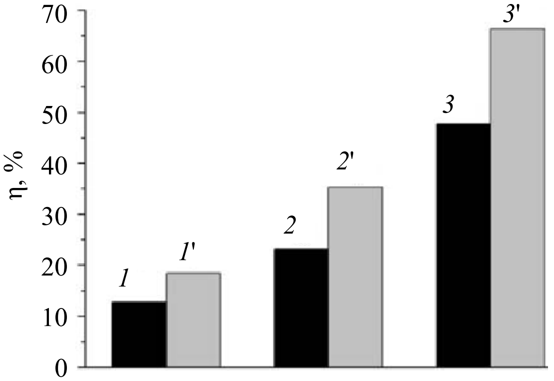

Fig. 4. Comparison of the bleaching powers of activated NaCl solutions to cashmere. Concentration of NaCl 3.0 g/L; pH_{init} 11.0; pressure in the reactor: (*1*–*3*) 19.6 and (*1'*–*3'*) 45.1kPa; current 140 mPa; time of treatment of the solution with plasma: (*1, 1'*) 6, (*2, 2'*) 11, and (*3, 3'*) 20 min; fabric treatment time 180 min.

The practical applicability of plasma chemically “activated” sodium chloride solutions was exemplified by textile bleaching. Figure 4 shows the results of bleaching cashmere with 3 g/L sodium chloride solutions treated with contact plasma in an experimental plasma chemical reactor for 6, 11, and 20 min at pressures of 19.6 and 45.1 kPa.

It has been found that the longer the initial sodium chloride solution is treated with plasma, the stronger is its bleaching power as applied to cashmere. After 20 min of plasma treatment at 45.1 kPa, the bleaching power of activated solutions reaches the level of 66%. The bleaching power of NaCl solutions treated at 45.1 kPa is about 40 to 50% stronger than that of solutions treated at 19.6 kPa. The observed regularities are well accounted for by the differences in the concentrations of oxidizers generated in solutions under nonequilibrium plasma treatment. According to data in Figs. 3 and 4, the concentration of oxidizers in the solution at 45.1 kPa is 1.5 to 1.8 higher than that at 19.6 kPa.

The resulting data point to a high oxidizing power of NaCl solutions activated with plasma. The results of calculations using the developed kinetic model are in close agreement with well-known concepts of the chemistry of chlorine and hydrogen peroxide. Further research should focus on temperature dependences of rate constants, aiming at full collection of data regarding the kinetic parameters of the mail stages of the plasma chemical process and at experimental validation of the possibility of a mixed diffusion/kinetic control mode of that process.

CONCLUSIONS

Contact nonequilibrium plasma affects the structural characteristics and physicochemical properties of aqueous solutions, resulting in a wide range of chemical transformations in the gas and liquid phases, primarily, at the phase boundary of plasma discharge and liquid. The chemically active contact nonequilibrium plasma offers opportunities of developing flexible and selective technologies for treatment of liquid media.

Examples of the treatment of water and aqueous solutions provide strong evidence showing that in each particular case, be it the goal of obtaining antibacterial media or those for precious metals recovery, there is a new leading-edge technological approach. Thus, the production of oxamide (oxalic acid diamide, a low-release nitrogen fertilizer and gas-generating gunpowder and solid rocket propellant) from aqueous formamide solutions is a new step in technologies for liquid-phase organic synthesis. Of practical interest are studies on the oppression of pathogenic and opportunistic microorganisms in water and sewage disposals, extraction of radioactive and toxic elements from industrial wastes, the use of plasma-chemically treated aqueous solutions in food technologies, etc. [35, 36]. When used with conventional filtration and ultrafiltration methods, these processes create a technological complex effectively countering threats to population and livestock [37–40].

Major advances were made by Ukrainian scientists in the development and practical implementation of plasma-based devices. Beginning with laboratory tests and up to pilot and experimental industrial installation, they created sophisticated multipurpose technologies [41]. The Dniprovsky Machine-Building Plant (Dnepropetrovsk, Ukraine) has manufactured portable research devices for industrial laboratories, as well as experimental industrial plasma chemical plants with productivities of treating 0.5 and 2.0 m^3/h liquid media.

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