LOW-PRESSURE DISCHARGE PLASMA TREATMENT OF AQUEOUS SOLUTIONS WITH MN, CR AND FE

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Abstract. The effect of low-pressure glow discharge on the formation of peroxide and the degree of oxidation of Mn, Cr and Fe was studied in the aqueous solutions of different compounds. The plasma treatment causes the reduction of Mn(VII) through Mn(IV) to Mn(II), Cr(VI) to Cr(III) and oxidation of Fe(II) to Fe(III). Among other reactive species, peroxide formed under the action of plasma treatment takes an active part in redox reactions. The concentration of peroxide usually increases with treatment time, but its presence is detected only after completion of activeredox processes.

Keywords: low-pressure glow discharge plasma treatment, redox reactions, peroxide formation, reduction, oxidation.

1. Introduction

The application of plasma discharge to treat liquid solutions is characterised by high diversity. In particular, in mining and metallurgy, plasma technologies are used for material processing [1], intensification of leaching of noble metals from ore concentrates [2], obtaining fullerenes and nanopowders [3], *etc*. In analytical chemistry, plasma discharges are utilised in the course of sample preparation, as microsized sources of emission for analysis of water solutions, as ionisation sources for mass spectrometry, as well as for enhancement of an analytical signal [4-6]. In the chemical industry, there are known examples of modification of polymer surfaces, cellulose bleaching and chemical synthesis. Plasma-aided blood coagulation, tissue ablation, wound healing and sterilisation are among typical medical applications of the plasma discharge [7].

Environmental remediation and wastewater treatment are reckoned among the most critical applications of

plasma technologies [8]. The wastewater releasing from industrial plants or households often contains harmful elements and compounds, in many cases of organic origin. So, it is vital to remove them from the Earth biosphere.

Various methods of water treatment, such as physical, biological and chemical, have been developed during centuries. Physical and biological processes are usually low cost but, in some cases, they do not efficiently remove some kinds of pollutants, especially organic compounds. Also, the biological treatment is typically much slower than other processes. Chemical methods are based on direct oxidation *via* reactants with high oxidation potential such as chlorine, ozone, potassium permanganate, *etc*. However, the use of such reagents is limited due to the formation of potentially hazardous by-products (for example halogenated in case of chlorine treatment). The ozonation is very efficient but the most expensive method of water treatment.

Plasma treatment realised in various forms of plasma discharge is a very effective attractive alternative to the methods of solution treatment mentioned above. Plasma discharge was successfully used to treat wastewaters contaminated with herbicides/pesticides, decompose pharmaceuticals, surfactants, sulfonol, phenol and textile dyes [9-12]. Many of the researches have focused on the decomposition of organic compounds which are key contaminants in source water. Another critical application is to remove ions of heavy metals contained in wastewaters [13].

The discharge releases high energy into a liquid phase and generates highly reactive species. Plasma in liquids can be produced in devices with different electrode configurations (a corona discharge over the surface solution, a contact glow discharge, a pulsed streamer discharge in or above solution, dielectric barrier discharge, gliding arc) and voltage regimes (DC pulsed, DC non-pulsed, AC, HF, *etc*.) [14]. A diversity of configurations promotes a variety of applications.

The plasma discharge causes various physical and chemical effects in the treated medium. Among physical phenomena, diffusion and advection, local heating, surface tension, secondary emission and charge deposition, sputtering and evaporation can be listed as

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typical for plasma discharges in solutions. Processes of surface electrolysis, hydrolysis, charge transfer, electron-ion and ion-ion recombinations, reduction-oxidation (redox) reactions, and collision relaxation take simultaneously place in gas-plasma and liquid regions, as well as the gas-liquid interface, that determines the complexity of chemical effects.

As was classified in [15], three different species of particles take part in the processes of plasma treatment. The gaseous parent species are determined by the ambient gas. For a plasma reactor operated in air, for example, these species are molecules of O_2, N_2, and H_2O. The primary species are being directly formed in the burning discharge. They include various highly reactive particles, such as radicals, high energetic electrons, excited ions, molecules, and photons. Further, the secondary species result from reactions which are not directly formed in the discharge but involve either primary species or primary and parent species. The primary species quickly appear but are not stable. The secondary species result from chemical reactions and, at least, some of them are more stable and thus are of interest for practical applications.

The chemical effects induced by the discharge and concerning the solutes depend on the formed species. Essential reactive species are hydroxyl radicals which are characterised by a high oxidation potential. Other strong oxidation reagents produced by plasma are oxygen radicals, ozone and hydrogen peroxide. A synergic effect of more oxidation reagents is possible as was discussed in [16] where simultaneous reduction of Cr(VI) and oxidation of As(III) were observed in wastewaters under plasma treatment.

The formation of peroxide in water and aqueous solution has been observed in many works [17-19]. There is a consensus that peroxide results from various reactions between chemically reactive particles produced by a plasma discharge and thus is a secondary species of plasma treatment. However, observations of its behaviour are less definite. In some cases, the peroxide concentration is a linear function of plasma treatment time. Sometimes, a clear time-delay is observed in the peroxide emergence. In other cases, the peroxide concentration remains depressive over the observation time.

It is well known that peroxide can participate in redox reactions and affect the oxidation state of metallic elements in various compounds. Therefore, it is of practical interest to study the rates of peroxide formation and consumption in the course of redox reactions in different aqueous solutions. The paper goal is to research the concentrations of peroxide and ions that contain metals (Fe, Cr and Mn) as a function of plasma treatment time in correlations with different pH and to reveal any relationships between peroxide and oxidation level of metallic elements.

2. Experimental

A barrel-type glass reactor with inside diameter of 30 mm and 180 mm in height was used for plasma treatment. Stainless steel electrodes were made of the wire rod of 4 mm in diameter. The plasma discharge used is reckoned in a low-pressure glow discharge type. One of the electrodes (cathode), being immersed in the studied solution, was placed in the lower part of the reactor. Another electrode (anode) was set at an adjustable distance of 5–7 mm above the solution surface. Air pressure in the reactor was held constant by a vacuum pump at a level of 12–15 kPa. The discharge was generated by applying a DC high voltage (~500–700 V) between the metal anode and water solution. The discharge current varied between 10 and 100 mA. Optimal values of the discharge current and air pressure were determined and applied to each treated solution.

The volume of the solution in the reactor was 50 ml. The time of plasma treatment varied from 0.1 to 30 min. Continuous circulation of cold water was maintained in an outer jacket to cool down the reaction mixture. The initial temperature of the solution was 293 K; it elevated to 303–308 K in the course of plasma treatment. Evaporation of the solution was observed during the discharge process. However, the lowering in solution level was negligible at the time of the experiment. The compositions of as-treated solutions, as well as crucial treatment regimes, are shown in Table 1.

The method of flame atomic absorption spectroscopy (FAAS) was used to measure the total content of metals (Cr, Fe or Mn) in filtered solutions. The quantification of FAAS was performed with the use of certified reference materials produced by O.V. Bogatsky Physics and Chemistry Institute (Odessa, Ukraine). The concentration of Mn^{2+} ions in solutions was measured by the Volhard method.

The solute concentrations of Fe(III), Cr(VI) and Mn(VII) were determined by spectrophotometry. Chemical methods controlled the Mn(IV) level. The completeness of Mn(VII)-to-Mn(II), Cr(VI)-to-Cr(III) and (Fe(II)-to-Fe(III) transformations was estimated by a combination of FAAS and spectrophotometry.

The total content of oxidisers, including peroxide, was measured in the plasma-treated solutions by an iodometric titration method. Also, the content of hydrogen peroxide was separately determined by either permanganatometry or spectrophotometry using the reaction of H_2O_2 with ions that contain Ti(IV) by the analysis of the maximum absorbance of the yellow $[TiO \cdot H_2O_2]^{2+}$

complex at the wavelength of 410 nm. The difference between the total oxidiser content and peroxide content studied by different methods was used to consider the influence of particles of different types on the reaction course.

3. Results and Discussion

3.1. Solutions with Mn

The results of plasma treatment of solutions that contain Mn in different oxidation states are shown in Fig. 1. A pronounced decrease of the total Mn concentration is observed in two more concentrated solutions after 2–4 min of treatment (Fig. 1a). This effect is accompanied by intense precipitation. With increasing treatment time, the precipitates interact with active reducers accumulated in the solution and start to dissolve increasing the Mn concentration.

The total Mn concentration in two diluted solutions is less changeable (Fig. 1a). A small amount of precipitates is observed in these two solutions after more prolonged plasma treatment.

All changes of pH with treatment time also depend on the Mn concentration (Fig. 1c). A clear local maximum on the pH curves with simultaneous decolouration of the solutions is observed in diluted solutions with 37 and 58 µmol/l Mn after 1–3 min of treatment. With a further increase of treatment time, the pH values start to decrease from 8.7 to 3.1 with concurrent precipitation.

For more concentrated solutions, such as 173 and 335 µmol/l, initial pH growth and its follow-up reduction are more temperate and peaks on the pH curves are less pronounced.

Peroxide H_2O_2 appears in the solution in the course of plasma treatment (Fig. 1b). For diluted solutions, this process starts very quickly, just after some seconds of plasma treatment. For concentrated solutions, there is a noticeable time delay in H_2O_2 formation. The value of such a delay usually increases with Mn concentration.

The comparison of Mn (Fig. 1a) and H_2O_2 (Fig. 1b) curves allows one to conclude that peroxide starts to accumulate actively in the solution only after completion of the process of Mn(VII) reduction. Evidently, this time depends on the initial Mn concentration. It is tiny in diluted samples and varies between 6 and 10 min in concentrated solutions.

Table 1

Plasma treatment regimes of aqueous solutions that contain Mn, Cr and Fe in different oxidation states

| Soluted compound	Metal	Initial valence	Metal concentration, µmol/l	Discharge current, mA	Air pressure, kPa	Treatment time, min
$KMnO_4$	Mn	VII	37–336	15–25	15	0–15
$K_2Cr_2O_7$	Cr	VI	250	25	12	0–20
K_2CrO_4	Cr	VI	250–700	25	12	0–20
$KCr(SO_4)_2 \cdot 6H_2O$	Cr	III	280	25	12	0–20
$FeSO_4$	Fe	II	2850	25	13	0–12
$Fe_3(SO_4)_2$	Fe	III	2500	25	13	0–12
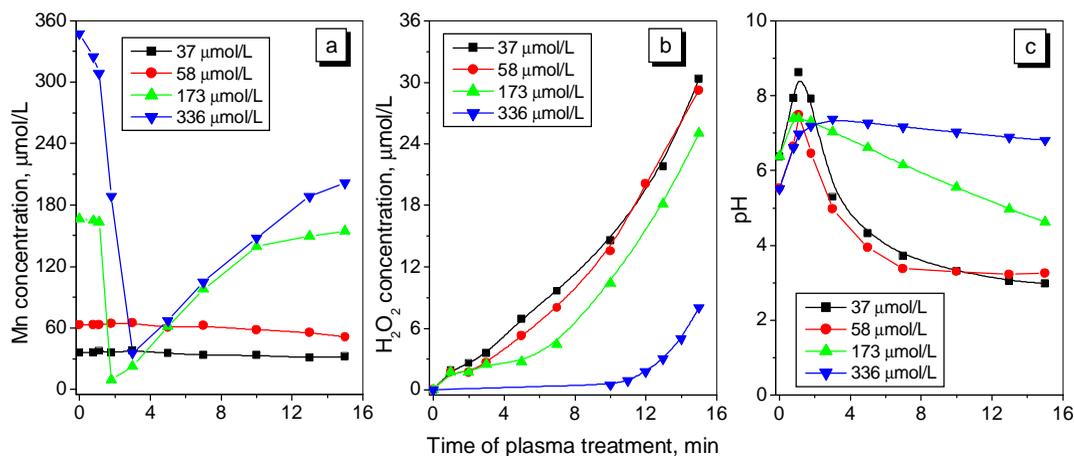
Fig. 1. Concentrations of Mn (a), H_2O_2 (b), and pH (c) in aqueous solutions of $KMnO_4$ with different Mn concentrations as a function of plasma treatment time

3.2. Solutions with Cr

Redox effects under plasma treatment become apparent in changes of the oxidation level of Cr in compounds. Aqueous solutions of potassium dichromate and bichromate were treated with a low-pressure plasma discharge and the results obtained are shown in Fig. 2. Approximately half of the Cr(VI)-containing ions in chromate solutionis reduced to Cr(III) for 2 min while the reduction process is completed for approx. 18 min of the plasma treatment (Fig. 2a). The formation of peroxide in chromate and dichromate solutions accelerates after completing the Cr(VI) reduction process (Fig. 2b). In particular, the delay in H_2O_2 formation for the most concentrated 700 µmol/l K_2CrO_4 is observed for more than 16 min.

When a solution of chromic potassium alum was treated, no visible changes in the solution and the oxidation level of Cr(III) were observed. The formation of H_2O_2 proceeds with a high rate without any delay (Fig. 2b). Therefore, ions with Cr(VI) seem to react actively with peroxide while Cr(III) ions remain inactive in plasma-treated solutions.

The plasma treatment of solutions with fixed started concentrations of Cr(VI) and Cr(III) for 5–10 min lead to decreasing hydrogen index by at least four units to pH = 2.8 (Fig. 2c). The shapes of pH(t) were almost independent of the initial Cr concentrations. Evidently, the observed decrease of pH is mainly caused by an interaction of plasma with water molecules as follows from the shape of the pH(t) curve for distilled water. Plasma discharge, interacting with a liquid phase, generates particles with strong acid properties. As a result

of further recombination processes, peroxide, which is detected in all studied solutions, is formed.

3.3. Solutions with Fe

Taking in mind different behaviour of ions containing Cr(VI) and Cr(III) in plasma treated solutions, both Fe(III) and Fe(II) sulphates were studied in experiments with Fe-containing solutions. The concentration of Fe(III) ions quickly increases in $FeSO_4$ within the first minute of plasma treatment but remains unchanged in $Fe_3(SO_4)_2$ during the whole period of observation (Fig. 3a). Simultaneously the concentration of Fe(II) ions drops to zero in $FeSO_4$ solutions, and this ion is never observed in plasma-treated $Fe_3(SO_4)_2$.

The form into which Fe(II) is transformed under the plasma action depends on the initial pH of a $FeSO_4$ solution. The quantitative transition of Fe(II)↔Fe(III) without the formation of a solid phase is carried out at pH = 1.6. The oxidation rate of Fe(II) slightly increases with increasing pH from 1.6 to 2.9. However, at pH > 2.2, precipitation of $Fe(OH)_3$ occurs. Due to partial deposition, the total concentration of Fe begins to decrease after 1–3 min treatment of solutions with pH > 2.2.

The peroxide concentration generated by the plasma discharge (Fig. 3b) behaves similarly as in solutions of manganese compounds (Fig. 1b) and Cr (Fig. 2b) ions. The H_2O_2 concentration in general increases with treatment time. In $FeSO_4$ solutions, some time-delay is observed in the peroxide formation which correlates well with the time of active oxidation of Fe(II)-to-Fe(III). On the contrary, no delay is detected in $Fe_3(SO_4)_2$ solutions where no plasma-induced redox processes occur.
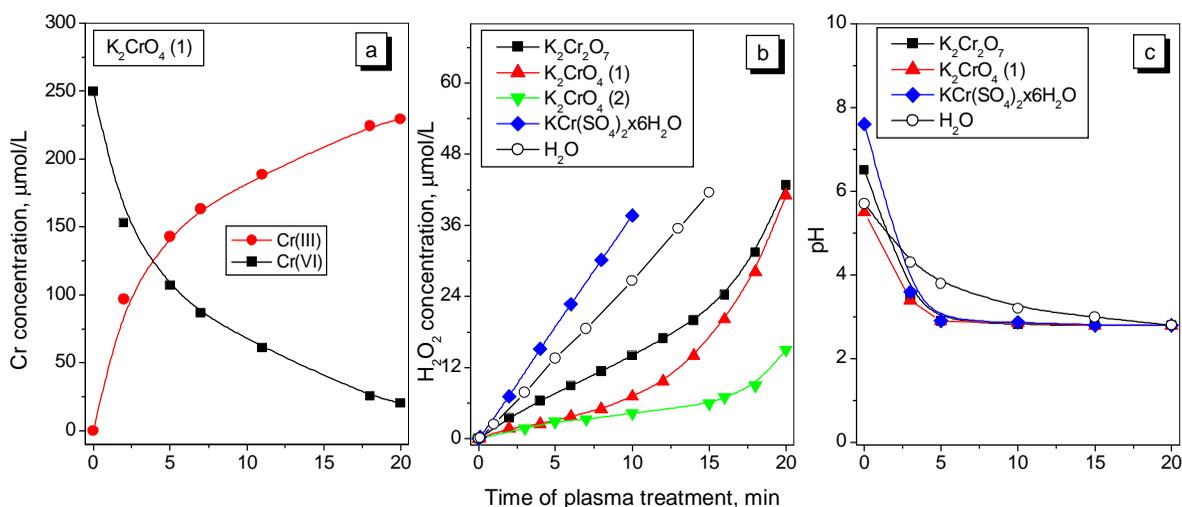

Fig. 2. Concentrations of Cr (a), H_2O_2 (b), and pH (c) in aqueous solutions of $K_2Cr_2O_7$ (250 µmol/l Cr), K_2CrO_4 (1 – 250 µmol/l Cr, 2 – 700 µmol/l Cr) and $KCr(SO_4)_2·6H_2O$ (280 µmol/l Cr) as a function of time of plasma treatment
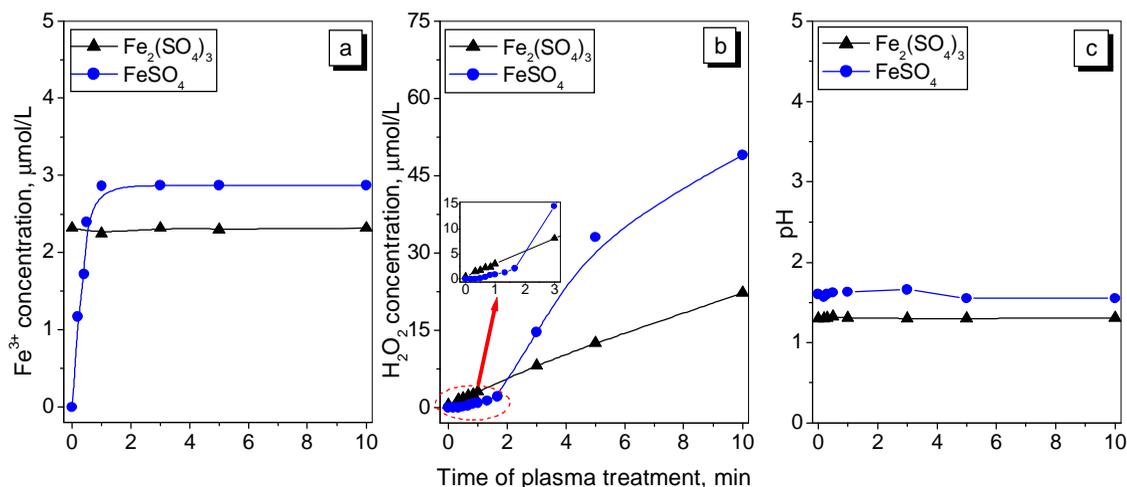
Fig. 3. Concentrations of Fe(III) (a), H_2O_2 (b) and pH (c) in aqueous solutions
of $FeSO_4$ (pH = 1.3) and $Fe_2(SO4)_3$ (pH = 1.6) with 2.85 mmol/l Fe and 2.5 mmol/l Fe, respectively,
as a function of time of plasma treatment

3.4. Peroxide Formation

Peroxide plays an essential role in plasma-induced redox reactions. While OH radicals have higher oxidation potential, however, they are unstable and easily decay in reactions with one another or hydrogen atoms. There is a consensus that peroxide is formed in plasma-treated solutions due to secondary reactions occurring with the participation of plasma-induced primary species. The basic processes of formation of primary active particles begin in the gas phase [20]. After discharge ignition, collisions of charged particles and gas molecules lead to the formation of several radicals and active species like solvated electrons (e_{eq}), OH, H, O, O_3 in the gas phase. These radicals may then react with themselves in a gas phase and with other particles in a thin subsurface layer of a liquid. The charged-particle bombardment of the solution surface causes the transfer of neutral particles to the plasma zone. Therefore, the reaction types and rates are dependent on gas medium and characteristics of a liquid phase, such as pH.

Reactions with the participation of $OH^{\bullet}$ radicals are usually considered as the main source of H_2O_2 formation [18]:

$$OH^{\bullet} + {}^{\bullet}OH \rightarrow H_2O_2 \qquad (1)$$
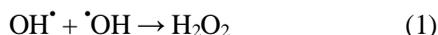
On the other hand, $OH^{\bullet}$-radicals, as well as solvated electrons e_{eq} can simultaneously react with the hydrogen peroxide and thus decrease its concentration in the solution:

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (2)$$
$$OH^{\bullet} + H_2O_2 \rightarrow O_2 + H_2O \qquad (3)$$
$$e_{eq} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} \qquad (4)$$
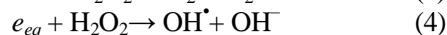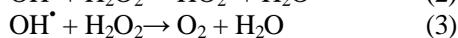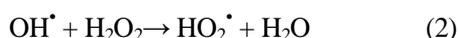
Therefore, the relationship between the rates of reactions (1) and (2-4) can determine the behaviour of

peroxide concentration [12]. Such a course of events seems to describe the simplest situation, but it does not always fit the experimental observations. For examples, sometimes the measured rate of formation of $OH^{\bullet}$ radicals was much lower than the rate of formation of H_2O_2 [18]. As found in [21], $OH^{\bullet}$ radicals play an important role in the H_2O_2 formation under nitrogen and helium atmosphere where the reaction of $OH^{\bullet}$-radicals dimerisation dominates.

In air with water vapour, $OH^{\bullet}$-radicals have a limited direct effect, and the most probable mechanisms include hydrogen atoms reacting with HO_2 and process of HO_2 dimerisation:

$$H^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 \qquad (5)$$
$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (6)$$
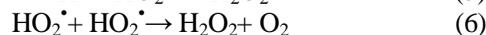
Also, excited oxygen molecules can contribute to the formation of H_2O_2 in the solution in an air discharge by the following reactions [21, 30]:

$$H + O_2 \rightarrow HO_2 \qquad (7)$$
$$O_2 + e \rightarrow O_2^{-} \qquad (8)$$
$$O_2^{-} + H^{+} \leftrightarrow HO_2 \qquad (9)$$
$$HO_2 + e \rightarrow HO_2^{-} \qquad (10)$$
$$HO_2^{-} + H^{+} \rightarrow H_2O_2 \qquad (11)$$
$$HO_2 + H \rightarrow H_2O_2 \qquad (12)$$
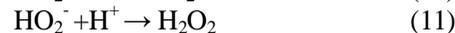
When accumulating in the course of chemical transformations, hydrogen peroxide tends to polymerise forming hydrogen polyoxides [22]. In general, this process can be described as follows:

$$(n-1)H_2O_2 \rightarrow HO_nH + (n-2)H_2O \qquad (13)$$
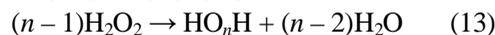
The action of plasma on electrolyte solutions initiates oxidation and reduction processes. Since both H^{+} and OH^{-} ions participate in plasma-initiated redox reactions, their concentration in the solution changes with treatment time [23]. Therefore, the acidity of the as-

treated solution, as well as redox potentials, will also change with treatment time. The plasma treatment of distilled water reduces its pH to a level 2–3 that can be explained by the accumulation of hydrogen polyoxides which have acidic properties [23].

Also, the plasma forms nitric oxides (NO_x) in nitrogen/oxygen-rich environments, such as air. They dissolve in the solution to form nitrous (HNO_2) and nitric (HNO_3) acid which also lowers pH [24].

In the solution with different pH, different ways of peroxide formation are operative [22] and, thus, the rate of H_2O_2 formation is sensitive to the pH index. In alkaline solutions, the H_2O_2 yield is usually much lower than that in neutral or acidic mediums [25]. Being a weak acid, H_2O_2 is intensively consumed by reacting with OH^- to form HO_2^- that causes a rather low H_2O_2 yield:

$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O \qquad (14)$$
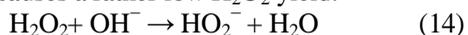
3.5. Effect of the Discharge Current of Peroxide Formation

Depending on discharge type, the yield of $H^\bullet$ and $OH^\bullet$ radicals fluctuates in a rather narrow range 3–8 [20] or 7.6–10 mol/F [18]. The initial yield of peroxide was estimated to be close to ~1.5 mol/F [20]. However, the concentrations of peroxide vary in a rather broad range. That indicated that the rate of peroxide degradation is sensitive to the solution type and may differ by almost two orders of magnitude even for similar types of the discharge.

The analysis of experimental and literature data [13, 18 26, 27] suggests that the rate of formation of peroxide depends on the type of discharge, its polarity, and, as a rule, increases with increasing discharge current. There is also some evidence that the material of cathode influences the chemical reactions in the solution via catalytic effects of emitted ions [28]. Such dependencies are easily observed by treating distilled water when the presence of solute compounds does not affect the rate of peroxide release.

During first minutes of plasma treatment, the peroxide concentration (C_{H2O2}) exhibits a linear dependence of treatment time t. Therefore, the slope angle dC_{H2O2}/dt in coordinates $C_{H2O2} = f(t)$ can be used as a measure of the rate of peroxide formation. The dependences of dC_{H2O2}/dt on the discharge current are shown in Fig. 4 for different plasma types and configurations. As is seen, the experimental curves are divided into three clusters and thus clearly illustrate the effectiveness of one or another type of discharge relative to the formation of peroxide.

The glow discharge exhibits the highest peroxide formation rates and the most pronounced dependence on the current while the frontal discharge is the least effective

in both parameters. Similar results were discussed in [29]. Discharge with water as a cathode is usually much more efficient for H_2O_2 production as is seen from Fig. 4 and reported in many researches [30, 31]. When liquid acts as an anode, the cathode voltage fall is formed on the metallic electrode, and the charged particles are electrons entering the anodic solution [25]. Thus, no sputtering and field-induced ion emission takes place at the liquid surface. Evaporation is the only way to transfer water molecules from the liquid phase into the gaseous plasma resulting in a low H_2O_2 yield. Higher energy of $OH^\bullet$·radicals excited by an intensive electron flux in the configuration with a liquid anode may also cause their quicker decay and thus suppress the rate of peroxide production.
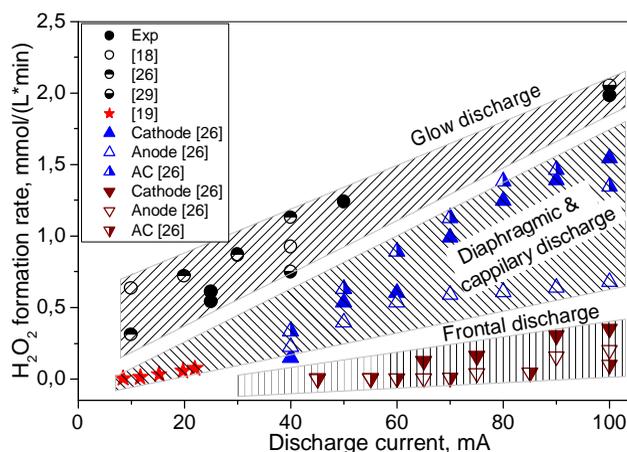
Fig. 4. The rate of H_2O_2 formation (dC_{H2O2}/dt) as a function of discharge current for different plasma configurations: dots – glow discharge by various authors, triangles up – diaphragmic discharge in cathode, anode and AC configurations, triangles down – frontal discharge in cathode, anode and AC configurations, stars – AC capillary discharge

3.6. Plasma-Induced Redox Reactions

The experimental results obtained, in particular, changing the oxidation state of metals, show that the plasma treatment initiates both oxidation and reduction processes with participation of ions that contain Fe, Mn and Cr. Some redox processes observed in the given paper and other reports are listed in Table 2. Both oxidation and reduction reactions are possible in the considered solution under the action of plasma discharge, as follows from Table 2. Their direction, as well as intensity, depend on many factors, including pH, the concentration of components, discharge type and modes. Evidently, an essential stage of technological applications is the optimisation of the modes and type of discharge. Optimal conditions are dependent on application field.

As was stated before, peroxide molecules formed in the course of plasma treatment in the solution play an important role in redox processes. This statement is evidenced by the correlations observed between concentrations of peroxide (Fig. 5) and Mn-containing ions (Fig. 1a). As is seen the peroxide appears in the solution after a certain time-delay which increases from approximately 4 to 10 min with increasing Mn concentration from 150 to 336 µmol/l.

The anticipated sequence of chemical transformations is as follows:

$$Mn(VII) \rightarrow Mn(VI) \rightarrow Mn(IV) \rightarrow Mn^{2+}. \quad (15)$$
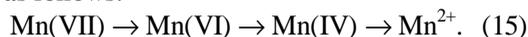
Several methods, namely: titrimetric (permanganatometric and iodometric) and spectrophotometric (formation of complex compounds with titanium) have been used to determine the content of hydrogen peroxide. For solutions containing $KMnO_4$, the use of both titrimetric methods yields different curves for the H_2O_2 concentration as a function of plasma treatment time (Fig. 5). The possible explanation for this fact is that both titrimetric methods may not be selective for H_2O_2 in the presence of other oxidising and reducing particles in the system. Then, the curve obtained from the results of iodometric titration can show the presence of other oxidizing particles that are formed both under the influence of the plasma and in the process of redox reactions with hydrogen peroxide. The H_2O_2 curves obtained by spectrophotometry and permanganatometric titration coincide. Therefore, these two methods more adequately characterise the presence of H_2O_2 in the system.

Reducing particles enter into a reaction with Mn(VII)-containing ions, and they cannot be detected until all Mn(VII) have reacted. The curves in Fig. 5 support this conclusion: an apparent time delay is observed at both parmanganatometric and spectrophotometric curves, and the duration of the delay increases with the Mn concentration.

Table 2

Redox processes in aqueous solutions with Mn, Cr and Fe caused by plasma treatment

| Process	Transformations	Medium	Reference
Oxidation	$Mn^{2+} \rightarrow MnO_2$	Neutral, acid	Experiment, [32]
Reduction	$MnO_4^- \rightarrow MnO_2$	Neutral, acid	[32]
Reduction	$MnO_4^- \rightarrow MnO_2$	Alkaline	[33]
Reduction	$MnO_4^- \rightarrow MnO_2 \rightarrow Mn^{2+}$	Neutral, acid	Experiment
Oxidation	$Fe^{2+} \rightarrow Fe^{3+}$	Acid	Experiment, [32]
Oxidation	$Fe^{2+} \rightarrow Fe(OH)_3$	Neutral	Experiment,
Oxidation of the central ion	$[Fe(CN)_6]^{3-} \rightarrow Fe[Fe(CN)_6]$	Neutral	[32]
Reduction	$Cr_2O_7^{2-} \rightarrow Cr_2O_3$	Neutral	[32]
Oxidation	$Cr^{3+} \rightarrow Cr_2O_6^{2-}$	Neutral, acid	[32]
Reduction	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	Neutral, acid	Experiment
Reduction	$CrO_4^{2-} \rightarrow Cr^{3+}$	Neutral, acid	Experiment
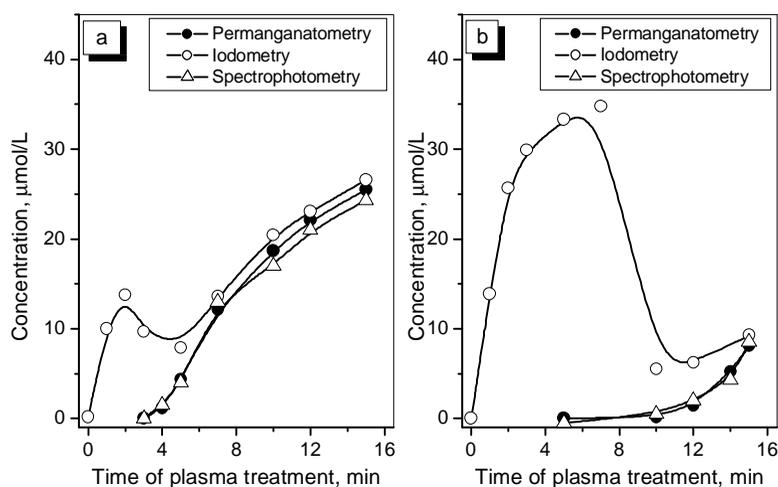
Fig. 5. Concentrations of oxidising compounds and peroxide, determined by permanganatometry (black dots), iodometry (open dots) and spectrophotometry (triangles), in aqueous solutions of $KMnO_4$ with 150 µmol/l Mn (a) and 336 µmol/l Mn (b) as a function of plasma treatment time

After reduction of manganese to Mn^{2+}, an excess of reducing particles reacts with oxidising particles. Such a reaction results in a temporal decrease of the total concentration of oxidising compounds at a particular stage of plasma treatment as is illustrated by the iodometric curves in Fig. 5.

Later, redox processes tend to their completion, and the rate of consumption of both reducing and oxidising particles diminishes. As a result, accumulation of these particles is resumed in the solution. Hydrogen peroxide is then determined both iodometrically and permanganatometrically/spectrophotometrically. At this stage, all the above methods give close values of the peroxide concentration.

4. Conclusions

Aqueous solutions of various compounds containing Mn, Fe and Cr were treated by a low-pressure glow discharge. The discharge conditions, such as polarity, discharge current and air pressure, were preliminary optimised regarding increasing the effectiveness of its influence on the redox processes. The concentration of peroxide, as well as the concentration and oxidation level of metals in the as-treated solutions, were studied as a function of treatment time.

The effect of plasma treatment of manganese permanganate solutions consists in the reduction of Mn(VII) first to Mn(IV) and then to Mn(II). Hydrogen peroxide is generated under the plasma action but is initially expended in reducing the Mn-containing ions. When the redox processes diminish, H_2O_2 molecules accumulate in the solution.

In ferrous solutions, the oxidation of Fe(II) to Fe(III) ions occurs under the action of plasma. If pH of the solution is less than 2 (strong-acidic medium), the transformation of Fe(II) to Fe(III) is almost complete, and the total content of iron ions does not change in the solution. If pH is higher than the value mentioned above, the oxidation process is also completed, but the total concentration of Fe in solution is reduced because of partial precipitation. In solutions with Fe(III), the plasma discharge does not change the oxidation level of Fe.

In solutions of chromium compounds, the reduction of Cr(VI) to Cr(III) is observed in an acidic medium. The value of pH index reduces from 6–8 to 2.8 concurrently with the Cr reduction. The oxidation level of metal does not change under the plasma action in solutions that contain Cr(III).

The action of a plasma discharge results in the acidification of the treated medium. Such a phenomenon was observed in all Cr- and Mn-containing solutions and was less-pronounced in solutions of Fe compounds.

The concentration of hydrogen peroxide formed under the plasma discharge was measured by titrimetric (permanganatometric and iodometric) and spectrophotometric methods. The permanganatometry and spectrophotometry allowed to estimate the amount of hydrogen peroxide molecules which act as reducing agents. The results of iodometric measurements described the total concentration of all oxidisers.

The concentration of hydrogen peroxide usually increases with treatment time, but it is not detected during active redox interaction with metal-containing ions. In general, the curves characterising the change in the ion concentrations with metals of different oxidation level correlate well with the curves describing the hydrogen peroxide formation.

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ОБРОБЛЕННЯ ПЛАЗМОВИМ РОЗРЯДОМ ПОНИЖЕНОГО ТИСКУ ВОДНИХ РОЗЧИНІВ, ЩО МІСТЯТЬ Mn, Cr ТА Fe

Анотація. *Досліджено вплив тліючого розряду пониженого тиску на утворення гідроген пероксиду та зміну ступеню окиснення металів у водних розчинах сполук Mn, Cr та Fe. Показано, що плазмове оброблення спричиняє відновлення Mn(VII) через Mn(IV) до Mn(II), Cr(VI) до Cr(III) та окиснення Fe(II) до Fe(III). Гідроген пероксид, що утворюється під дією плазмового оброблення, активно бере участь в окисно-відновних реакціях. Концентрація гідроген пероксиду зазвичай збільшується з часом оброблення, однак виявити його наявність стає можливим тільки після закінчення перебігу активних окисно-відновних процесів.*

Ключові слова: *оброблення плазмовим розрядом пониженого тиску, окисно-відновні реакції, утворення гідроген пероксиду, відновлення, окиснення.*