ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
https://www.icf.ro/rrch/

Rev. Roum. Chim.,
2026, *71*(7–8), 501–512
DOI: 10.33224/rrch.2026.71.7-8.08

Dedicated to Professor Mihaela Hillebrand
on the occasion of her 85th anniversary

SPECIFIC ASPECTS OF REDOX PROCESSES IN WATER ENVIRONMENT

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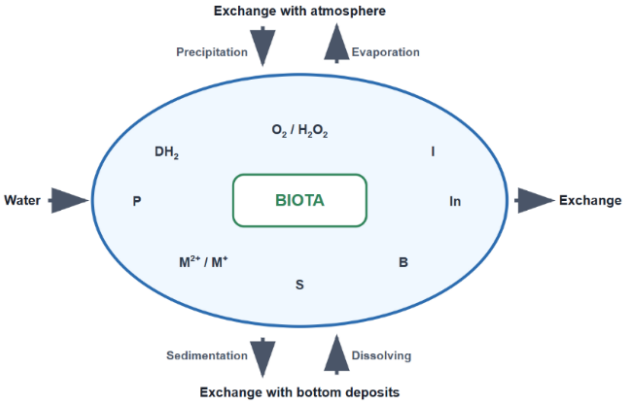
Received June 18, 2025

This paper briefly summarizes the vast experimental and theoretical material resulted from the detailed multi-annual studies of the condition, composition and evolution of the natural water bodies, with special focus on water pollution and self-purification through the chemical reduction-oxidation processes with the involvement of oxygen, hydrogen peroxide and transition metal ions and complexes, performed at the Faculty of Chemistry and Chemical Technology of Moldova State University. The role and different pathways of hydrogen peroxide formation in natural waters and subsequent H_2O_2 decomposition, free radicals' generation and oxygen activation are discussed, along with the detailed mechanisms of pollutants' transformations with the involvement of series of active species and catalysts.



INTRODUCTION

There are certain important technological and environmental challenges connected with the production, storage and reactivity of hydrogen peroxide – a substance which found rather broad application in various fields due to its relatively low cost, availability, high reactivity, environmentally friendly products formed following its decomposition. The unresolved technical issues are related to its on-site production and storage, safe using, etc.; whereas no less important aspects are linked with H_2O_2 involvement in the natural reduction-oxidation reactions in natural water environment, including formation of the natural water quality, self-purification processes, pollutants transformation.

The pollutants' transformation in natural water bodies depends upon the physical, biological and chemical factors, closely linked with each other. The physical factors involve the seasonal dynamics of pressure and temperature values, water aggregate condition, evaporation, sorption, deposition, dissolving, hydrological processes, etc. Biological factors are mainly linked to the biota's vital processes and involve metabolism, bioaccumulation, biodegradation. The most important contribution to the pollutants'

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transformation is provided by the chemical factors, including the redox reactions (photolytic, redox-catalytic, radical oxidation, biochemical transformations, decarboxylation, etc.), as well as hydrolysis, chemical synthesis and decomposition processes in water environment. The most of the redox processes occur with the participation of hydrogen peroxide, active oxygen forms, free radicals and transition metal complex compounds.

There are still a series of contradictions and fragmental approach in explaining the mechanisms of the multi-step redox processes with the involvement of hydrogen peroxide. That is why the problem of hydrogen peroxide specific reactivity in various environmental, as well as vital and technological systems still remains within the focus of scientists' interest, provoking numerous subsequent research to discover reaction mechanisms, identify the transformation products and detect the most optimal pathways to obtain desired products with targeted properties.

As chemical processes mainly determine the water quality formation and depend on a great variety of factors, their study requires a multi-lateral approach, starting from the fundamental bases' development.

MATERIALS AND METHODS

For the elaboration of this paper various approaches have been applied related to the environmentally significant redox processes with the involvement of hydrogen peroxide and other reactive species, which finally determine the natural waters' condition which in its turn, defines the possibility of living organisms' existence and development.

Material presented here comprises the research results obtained by the team of researchers, including the authors of this paper, during the over 30-year studies performed at the Department of Ecological and Industrial Chemistry of Moldova State University. Thus, an interdisciplinary approach was applied to study the mechanisms of the redox processes and the reactivity of intermediates formed, in view to expand and complete the existing theories regarding the elementary act of electron transfer.[1,2] For this scope, a combination of research techniques was used that included experimental kinetic methods and mathematical modeling of redox reactions in the presence of metal complexes.[3] Broad series of the experimental and theoretical studies of the reduction-oxidation processes in water environments, in natural and modelled streams and polluted waters have been conducted and discussed.

A thorough examination of the internationally recognized, peer-reviewed scientific journals has been performed, based on the selected broad range of the keywords directly related to the research topic of this article. The keywords included specifically: hydrogen peroxide, active species, redox state of natural water bodies, reaction mechanisms, etc.; however, the area of our studies was not limited to the abovementioned notions. The important databases have been examined such as Google Scholar, Web of Science, and Scopus.

In addition, the newly published conference abstracts and papers, related to the studied subjects, have been examined, which enabled us to follow the latest trends in the studied area. Therefore, this article represents an attempt, through summarizing the previous research experience based on the novel views and assumptions, the literature investigations, to thoroughly examine the state-of-the art in the vitally important research domain related to the occurring redox processes in natural water environment, and to promote rising a new wave of interest towards this vitally important research area.

RESULTS AND DISCUSSION

Fundamental aspects of the redox processes in the natural aquatic environment

Theoretical and experimental studies of the redox processes with participation of hydrogen peroxide and other reactive species had revealed their key role in the pollutants' transformations in natural aquatic environment.[4] However, in the last thirty years practically no detailed research has been carried out regarding these processes' kinetics and mechanisms. This period is marked with lesser interest towards the fundamental aspects of chemical physics in general and electron transfer reactions in particular. But, since recently, this attitude has been radically changed because of the pragmatic considerations and upgraded research infrastructure.

Tracing back the evolution of the redox processes' theory, the merits of Rudolph Marcus should be noted, who, in order to elucidate the mechanisms of redox reactions, proposed a revolutionary theory of outer-sphere electron

transfer reactions. According to this approach, two chemical species are exchanging with their charges with no major structural modifications.[5] Marcus' theory was later on extended to the inner-sphere electron transfer reactions, where the modification of distances and geometry of solvate or coordination shells in two chemical species is taken into account.[6] Further development of this research field included the research of other types of chemical reactions, based on the interdisciplinary studies including the methods of computational chemistry, quantum-chemistry and chemical physics.

The other approaches have been developed, such as the Franck-Condon principle, to explain the specificity of some experimental results, namely, why the electron transfer reactions with small-sized cations in water solution are running relatively slow, whereas the similar reactions with larger sized ions are relatively fast.[7,8] This principle has been widely used in spectroscopy to interpret the excitation spectra of molecular electronic-vibrational quantum states. Its application in the assessment of chemical reaction's rates proved to be a novelty at the time. The main idea of such an approach was that the systems with redox reactions could be treated as consisting of two subsystems: fast, including the movement of electrons, and slow, encompassing the movement of nuclei and rearrangement of the surrounding dipoles in the polar environment. Obviously, the rate-limiting step of the overall process depends on the slow motion of heavy subsystem.

Based on the theoretical justifications, the experimental investigations in the mid-1950s contributed to the studies of the redox processes. Application of new experimental techniques, such as stop-flow method offered the possibility of direct recording and tracking of high-speed reactions.[9] Following the works of Marcus, the rate constants calculations of the outer sphere redox reactions, provided a large number of quantum-chemical details.[10,11]

At the same time, the rapid development of the RES (Electronic Spin Resonance) method and the large-scale detection of free radicals made it possible to demonstrate the predominance of one-electron transfer in the redox reactions. Normally, for one-electron transfer in water the calculated value of medium reorganization potential is $\lambda \approx 170$ kJ/M, whereas for the two-electron transfer the calculation result gives about 670 kJ/M, much higher than the chemical bond energy. The experiments have shown that no redox couple exceeded the potential difference of 2–3 volts (100–150 kJ/M), that is insufficient to overcome the Franck-Condon prohibition. That's why the synchronous multielectron transfer routes are less possible. However, the recent studies have demonstrated that for the efficient electrochemical production of hydrogen peroxide, based on the 2-electron water oxidation, the complex catalysts may be applied containing the Ti and Ni oxides.[12]

Another progressive idea in the field was proposed by Henry Taube who described the correlation between the rate of chemical reactions and the electronic structure of chemical compounds.[13,14] This research was the first to recognize the relationship between the ligand substitution rate and the d-electron configuration in the metal atom. Taube had introduced the terms "labile" and "inert" instead of "unstable" and "stable" into kinetic practice and explained the main difference between these concepts. His essential assumption was that the ligands form a 'chemical bridge' for the transport of electrons within the redox couple, between the electron donor and the electron acceptor, rather than a simple coordination bond as previously thought. In such a case, the inner-sphere reaction is shielded by the Franck-Condon reorganization energy, so that the multielectron transfers can occur simultaneously. However, the overall reaction rate cannot be higher than the coordination sphere lability. The main stipulations of the Taube's approach have been confirmed later, along with the development of the crystal field theory.

Natural waters as an unbalanced open system

Natural water cannot be regarded as just a passive medium; on the opposite, it is an open chemical reactor within a complex adaptive system.[1,15,16] It operates under the non-equilibrium conditions in a highly reactive manner, driven by continuous exchanges of energy and matter with the environment. Therefore, the natural waters are unbalanced reactors within adaptive systems – where chemistry, biology, and physics coevolve unpredictably. This dual nature – chemical reactor + dynamic system – explains its unpredictability and sensitivity to perturbations (Table 1).

Table 1

Natural waters as an unbalanced open chemical reactor and complex adaptive system

Nr.	Traits of natural water	Specifics	Main processes
1	Chemical Reactor	Multiphase Reactions	Dissolution, precipitation, redox, catalytic, radical and photochemical reactions occur simultaneously (*e.g.*, iron oxidation, carbonate buffering).
		Catalytic Surfaces	Clays, bottom sediments, organic colloids, and biofilms accelerate reactions (*e.g.*, nutrient transformations).
		Kinetic Imbalance	Reactions compete, rarely reaching steady state due to the fluctuating inputs (*e.g.*, stormwater altering solute concentrations).
2	Complex Adaptive System	Feedback Loops	*Positive feedback*: pH buffering stabilizes aquatic life. *Negative feedback*: Algal blooms deplete O_2 causing dead zones; eutrophication of water bodies.
		Emergent Properties	Self-organization (*e.g.*, stratification in lakes,). Threshold behaviors (*e.g.*, sudden acidification from cumulative pollution).
		Nonlinearity	Small changes (*e.g.*, a 1°C temperature rise) can disproportionately shift system state (*e.g.*, methane release from wetlands).
3	Drivers of Instability within an Open System	Inputs/Outputs	Sediment loads, atmospheric deposition, biotic excretion.
		Energy Fluxes	Solar radiation drives photosynthesis; thermal gradients mix layers
		Anthropogenic Forcing	Pollutants discharges, disrupting natural cycles (*e.g.*, pharmaceuticals altering microbial metabolism). Impacts of dams and irrigation systems, affecting the water biota, fauna and water composition.
		Extreme Natural Conditions	Droughts, floods, volcanic eruptions, radioactive irradiation, other natural disasters.

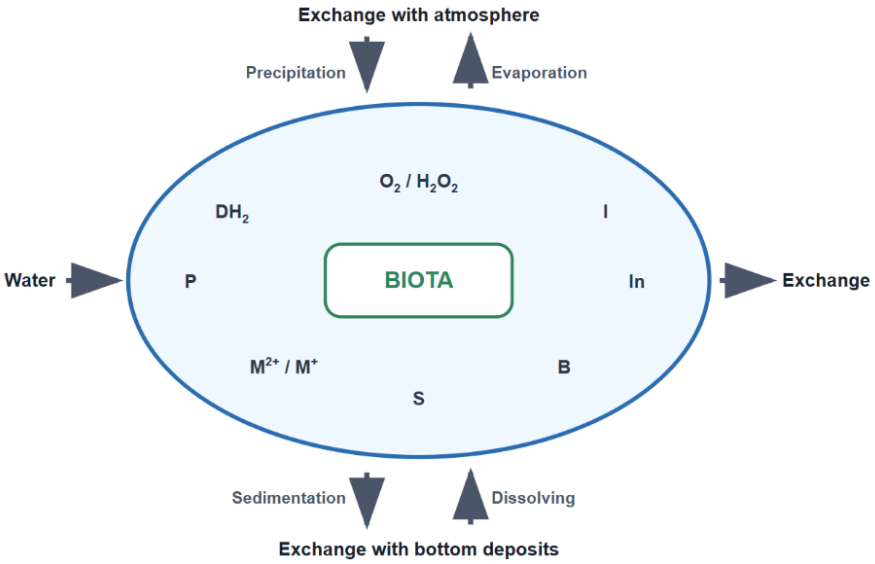

Fig. 1 – Schematic representation of natural water body as a catalytic multi-component open-type system.

M – variable valence metal ions, L – ligands, DH_2 – substrates with ligand and reducing properties, P – pollutants, B – biogenic substances, I – initiators of active intermediates (free radicals, singlet oxygen, etc.), In – free radicals' acceptors/scavengers forming non-reactive secondary radicals, S – suspended solids/sorbents, Biota – all microorganisms' species.

From the chemical viewpoint, various oxidative and reducing species in the natural water bodies are in the continuous entering, production and transformation within the natural aquatic systems, ensuring the redox processes being in a dynamic balance in terms of the biotic and abiotic composition (Fig. 1).[17] To estimate adequately the ecological status of natural waters, the studies of physical, chemical and biological processes are usually carried out. Chemical processes in the aquatic environment proceed via catalytic or irradiation pathways.

Water under the natural conditions is an open, multi-component, multi-phase reduction-oxidation system of M^+ - M^{2+} - O_2 – H_2O_2 – L – DH– S - $h\nu$ - R type in which oxygen activation processes occur, along with the generation of hydrogen peroxide (about 10^{-5} M during the daytime) and pollutants decomposition. It was demonstrated in previous studies[3,18,19] that natural

waters are very vulnerable to minor changes in the concentrations of redox compounds and represent an unbalanced open system that includes numerous processes with the participation of coordination compounds, organic substrates and a variety of intermediaries. Such systems have also been shown to exist in multiple steady states, unstable regimes, and unpredictable random dynamics.[20,21]

Formation of the natural waters' quality as a habitat for aquatic organisms requires the presence of continuous flows of oxidizing and reducing substances, the balance between these flows characterizing the redox state of water and its self-purification capacity.[22–25] The oxidized state of natural waters is determined by the presence of hydrogen peroxide and oxidizing equivalents,[26–27] while the reducing state – by the presence of the substances of reducing nature, such as enodiols and thiols that enter the composition of water following the transformation of hydrobionts.[28] These species determine the formation of the ecological state appropriate to the biological value of the habitat.

Pathways of hydrogen peroxide generation in natural waters

Detected hydrogen peroxide contents in natural waters was relatively low (10^{-4} – 10^{-7} M/L)[29,30]. In its way, hydrogen peroxide enters or is generated in natural water bodies through several pathways, main of them being represented schematically on Fig. 2.

The pathways displayed on Fig. 2 can be described as follows. Solar light plays a predominating role in hydrogen peroxide formation in the natural waters, as soon as under its influence the formation of superoxide anion-radical $\bullet O_2^-$ occurs (path. 1):[31–33]

$$O_2 + h\nu \rightarrow \bullet O_2^- + 2H^+ \rightarrow H_2O_2 \qquad (1)$$

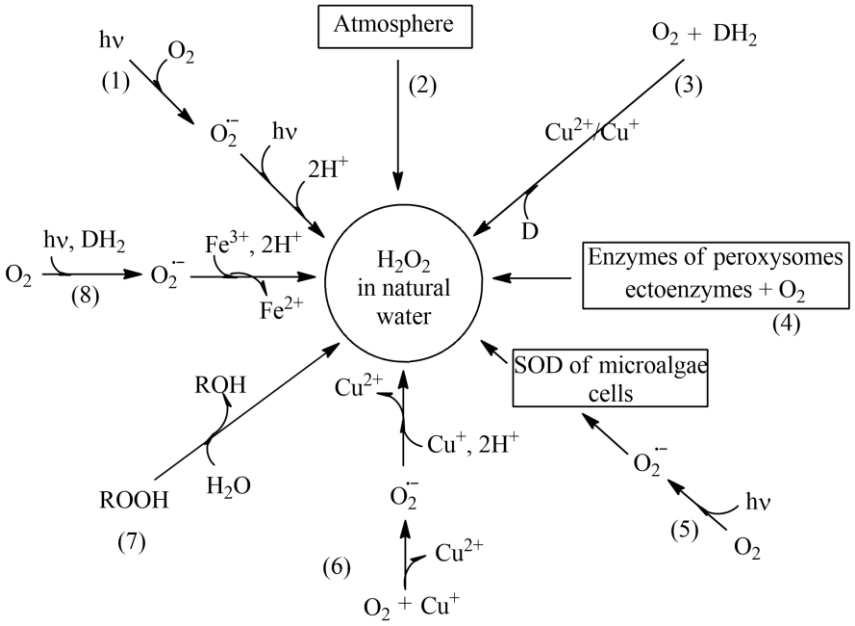

Fig. 2 – Sources and reactions of hydrogen peroxide generation in natural water.

In its turn, superoxide anion radical is a precursor of hydrogen peroxide generated in water. Some part of hydrogen peroxide enters the water bodies from the atmosphere with rains and snow (path. 2). Another portion of H_2O_2 is supplied by the reducing-oxidation catalytic processes (path. 3):

$$O_2 + DH_2\ (+ M^+/M^{2+}) \rightarrow H_2O_2 \qquad (2)$$

where DH_2 – reducing agent; M^+/M^{2+} – transition valence metal ions catalyzing the redox processes.

Besides, some amounts of H_2O_2 are formed with the peroxysomes of water microorganisms, then penetrating into the cytosole, from which, through the cell membrane, hydrogen peroxide enters the natural waters (path. 4).[34–36] On the external surface of phytoplankton microorganisms the so-called ecto-enzymes are placed, such as deaminases, capable to oxidize the nitrogen-containing organic substances, accompanied with the reduction of oxygen to hydrogen peroxide, which is emitted into water.[37]

Microalgae are emitting hydrogen peroxide in water during the photosynthesis process under the UV irradiation.[38,39] Thus, superoxide-radical formed in within the cell, interacts with its

superoxide-dismutase (SOD) turning into H_2O_2, which excess penetrates into water (path. 5):

$$O_2 + h\nu \rightarrow \bullet O_2^- + SOD \rightarrow H_2O_2 \quad (3)$$

Interaction of O_2 with Cu^+ will also lead to the formation of H_2O_2 (path. 6):[40]

$$Cu^+ + O_2 + H_2O \rightarrow Cu^{2+} + \bullet O_2^- + 2H^+ \rightarrow H_2O_2 + Cu^+ \quad (4)$$

Also, hydroperoxides ROOH in the natural waters can partially be transformed into hydrogen peroxide (path. 7). In its turn, ***formation of hydroxoperoxides*** can be represented as a variety of catalytic and non-catalytic processes:[41]

$$RH + h\nu \rightarrow \bullet R + H \quad (5)$$

$$\bullet R + O_2 \rightarrow \bullet RO_2 \quad (6)$$

$$\bullet RO_2 + RH \rightarrow ROOH + \bullet R \quad (7)$$

$$\bullet RO_2 + DH^- \rightarrow ROOH + \bullet D \quad (8)$$

$$\bullet RO_2 + M^+ + H^+ \rightarrow ROOH + M^{2+} \quad (9)$$

$$\bullet RO_2 + NO_2^- + H^+ \rightarrow ROOH + NO_2 \quad (10)$$

$$\bullet RO_2 + HSO_3^- \rightarrow ROOH + SO_3^{2-} \quad (11)$$

$$M^+ + ROOH \rightarrow \bullet RO + MOH^+ \quad (12)$$

The reactivity of $\bullet RO_2$ radicals in these reactions is usually 3–5 orders lower than that of $\bullet RO$ radicals.

Oxygen, in the presence of light quanta or the DH_2 reducers generated by microorganisms, is reduced to form superoxide-radical $\bullet O_2^-$ which in its turn will reduce Fe^{3+} ions with the subsequent generation of hydrogen peroxide (path. 8)[42].

Decomposition of hydrogen peroxide in natural waters

Numerous authors have studied decomposition of hydrogen peroxide, through both the abiotic and biotic ways.[43–46] Experimental and theoretic data regarding the catalytic decomposition of hydrogen peroxide with the transition valence metal ions[47–50] can be used to describe the abiotic decomposition of H_2O_2 in natural waters, where homogeneous forms of copper ions, iron chelate complexes, and traces of Mn and other ions, can be present.[51–53]

The specific trait of hydrogen peroxide is its dual behavior: while occurring in non-dissociated form, it is a strong two-electron oxidizing agent, and while in the ionized form, it demonstrates properties of an electron donor. Thus, it can act as a reducer with regard to the transition metal ions, and it can also generate a series of free radicals including $OH\bullet$, $HO_2\bullet$, as well as intermediates of ferryl or manganyl type or other intermediate compounds and species. This duality may explain instability of hydrogen peroxide in homogeneous media, when it can be readily decomposed in the presence of transition metal ions as catalysts, yielding oxygen and water as final products.[54]

Interaction of metal complex containing the metal oxidized form M^{2+} with hydrogen peroxide leads to the generation of a peroxocomplex, which further is subjected to the acid-alkaline dissociation and final decomposition:

$$M^{2+} + H_2O_2 \rightleftharpoons (MH_2O_2)^{2+} \rightleftharpoons H^+ + MHO_2^+ \rightleftharpoons M^+ + HO_2^{\bullet} \quad (13)$$

Peroxocomplex MHO_2^+ having the reducing properties, either dissipates through the one-electron transfer, or, interacts with another metal ion, generating O_2 or/and free radicals. Interaction of H_2O_2 with the reduced metal form M^+ can run following two different mechanisms. The first was identified by Gaber and Weiss in 1932:[55–57]

$$M^+ + H_2O_2 \longrightarrow M^{2+} + OH^- + OH^{\bullet} \quad (14)$$

$$M^+ + OH^{\bullet} \longrightarrow M^{2+}OH^- \quad (15)$$

The second mechanism was discovered as early as in 1932 by Bray and Gorin, when the intermediate generation of ferryl-ion has been shown:[58–60]

$$Fe^{2+} + H_2O_2 \longrightarrow FeO^{2+} + H_2O \quad (16)$$

$$FeO^{2+} + Fe^{2+} \xrightarrow{H^+} Fe^{3+} + Fe(OH)^{2+} \quad (17)$$

In neutral water environment the catalytic decomposition of H_2O_2 may occur on the microcolloidal Fe hydroxides, following the non-radical mechanism.[61] This process may also take place on the Cu ions through the formation of free radicals.[1,54]

$$CuOH^+ + HO_2^- \rightarrow Cu^+ + \bullet O_2^- + H_2O \quad (18)$$

Further interaction of Cu^+ with H_2O_2 yields in the formation of CuO^+ particle (hydrolised Cu^{3+} ion) which oxidizes water with the formation of $\bullet OH$ radicals which are among the most reactive species.

Radical processes of •OH hydroxide radicals generation

There are numerous pathways of $\bullet OH$ radicals generation in natural water bodies, including abiogenic and biogenic ones.[62–64]

Thus, in the presence of electron donor DH_2 hydrogen peroxide is consumed for the catalytic

oxidation of donor without the formation of free radicals, but in case when DH_2 possess the properties of redox-ligands, they may initiate generation of •OH radicals. Also, •OH radicals can be generated through the UV-irradiation of H_2O_2, or hydroperoxides ROOH, or as a result of peroxides interaction with metal ions, or photochemical transformation of NO_3^- and NO_2^-. In the presence of the reducing agents DH_2 ozone will interact with NO_3^- resulted in subsequent generation of •OH radicals. Dissolved ozone (its concentration in the surface water layers may reach 10^{-8} M/L) can interact with the dissociated form of H_2O_2, decomposing it following the radical-chain mechanism, with the formation of $\bullet O_2^-$ and •OH radicals.

Fe^{2+} ions and their complexes can be oxidized with hydrogen peroxide, following the scheme:

$$Fe^{2+} + H_2O_2 \leftrightarrow FeHO_2^+ \leftrightarrow (FeHO_2^+)(OH^-) - H_2O \rightarrow (OH^-)FeO^{2+} \rightarrow Fe^{3+}(OH^-)_2 + \bullet OH \quad (19)$$

Besides, interaction of hydrogen peroxide with Fe(II) coordination compounds can lead to the formation of highly oxidized form Fe(IV) as intermediate, yielding, as a result of further transformations, to the formation of •OH radicals.[65–66] These radicals can also be generated as a result of UV-irradiation of L_nFeOH^{2+}.

In case of copper ions interaction with hydrogen peroxide, the •OH radical will be generated through the formation of a series of intermediates, such as cupryl-ion (CuO^+):

$$Cu^+ + H_2O_2 \rightarrow CuO^+ \quad (20)$$

$$CuO^+ + H_2O \rightarrow Cu^{2+} + OH^- + \bullet OH \quad (21)$$

An example of the biogenic production of •OH radicals as a result of interaction between Cu^{2+} and H_2O_2 with DH_2 eliminated in water by algae. Although is not easy to assess quantitatively the contribution of different pathways of free radicals' generation, their steady-state concentration can be easily detected though the direct measurements, or by calculation of radicals' generation rate and the effective rate constant of free radicals' destruction.

Generation of $\bullet O_2^-$ ($\bullet HO_2$) superoxide radicals

Along with the formation of hydrogen peroxide and •OH radicals under the solar irradiation and during the catalytic processes in the natural waters, generation of superoxide-radicals by several pathways also occurs.[1,31,67,68] Although being a short-living species, these radicals are involved in many redox transformations in water environment.

From thermodynamic point of view, the one-electron reaction of oxygen molecule activation is unfavorable:

$$O_2 + e^- \rightarrow \bullet O_2^- \ (\Delta Go = +15.4 \text{ Kj/M}) \quad (22)$$

However, in natural water environment the organic matter (aminoacids, primary alcohols, etc.) under the UV-irradiation are transferred into the excited condition, and, giving an electron to the O_2 molecule, generate the superoxide radicals $\bullet O_2^-$, as well as the hydrated electron (e_{aq}^-) and other electron-excited particles. Such photo-electron transfer is frequently occurring in the nature. Radioactive irradiation (α-, β-, γ-rays) in case of radiation pollution leads to the generation of •OH radicals, hydrated ions, H^+ atoms, which interacting with O_2 form the superoxide radicals $\bullet O_2^-$. The reduced metal forms M^+ resulting from the secondary transformation processes, reacting with oxygen, will also promote generation of $\bullet O_2^-$. Radicals-reducers $\bullet D^-$ can be involved into the O_2 transformation into the superoxide-radicals.

Superoxide-radical can also be formed during the reaction between hydrogen peroxide with Cu or Fe ions and complexes. During the photolysis, peroxocomplexes of transition metals are decomposed, generating $\bullet O_2^-$. Catalytic decomposition of H_2O_2 with the formation of $\bullet O_2^-$ may occur in the presence of Cu ions.[40,69] Interaction of hydrogen peroxide with •OH radicals c of $\bullet HO_2$. In addition, ozone dissolved in water can promote generation of both forms – $\bullet O_2^-$ and $\bullet HO_2$. Also, NO_2 dissolved in water can generate $\bullet HO_2$ through the electron detaching from donor HO_2^-. As a result of these and other processes, the mean steady-state concentration of superoxide-radicals in the natural water makes about ~$10^{-8} – 10^{-9}$ M.

Therefore, the most important natural oxidants in the water bodies are O_2, H_2O_2 and their free radicals (superoxide and hydroxyl). It was also suggested that that redox processes with the participation of O_2 and H_2O_2 in the presence of variable valence metal ions can proceed with the formation of not only the reactive species, but the intermediate complex compounds, such as partial charge transfer complexes.[1,31] These complexes are also involved in

various redox transformation processes in natural waters.

Redox reactions of pollutants' transformations in water environment

Involvement of hydrogen peroxide in the numerous reactions of pollutants transformations occurs, as a rule, following the radical, redox-catalytic, photolytic, etc. pathways.[22,31,70,71]

Pollutants oxidation in water environment is running most efficiently, following the radical mechanism. Unlike •OH radicals, superoxide radicals $\bullet O_2^-$ possess the double reduction-oxidation function. Thus, in the neutral and acid environments these radicals can be easily disproportioned to form oxygen and hydrogen peroxide. In the alkaline environment $\bullet O_2^-$ radicals are stable and play an important role in catalytic radical-chain processes of hydrogen peroxide decomposition.

Activation of hydrogen peroxide molecule in the natural waters through UV-irradiation and catalytic processes, leading to the intermediate formation of active radicals, promotes their interaction with numerous organic pollutants RH, oxidizing them to the relevant radicals •R.

A pollutant in the •R form (being already activated) rather readily enters the other reactions, turning into the final low-toxic or harmless compounds. Thus, H_2O_2 is a species, which catalytic and photocatalytic decomposition promotes the removal of pollutants from water. An example can serve rather rapid destructive deep oxidation of pyridine and its derivatives with Fenton reagent with the additional UV irradiation with the 254 nm wavelength. It was shown that more than 90% of pyridine degradation was reached in 10 min, whereas about 70% of the TOC (Total Organic Carbon) was removed in 60 min:[68]

$$Fe^{2+}(L_nFe^{2+}) + H_2O_2 \rightarrow Fe^{3+}(L_nFe^{3+}) + OH^- + \bullet OH \quad (23)$$

$$Fe^{3+}(L_nFe^{3+}) + h\nu \rightarrow Fe^{2+}(L_nFe^{2+}) \quad (24)$$

$$\bullet OH + RH \rightarrow H_2O + \bullet R \quad (25)$$

The generation of substrate-radicals •DH in the peroxidase reactions is also possible, if the natural water contains the substrates – donors of hydrogen atoms:

$$Fe^{3+} + H_2O_2 \rightarrow FeO^{3+} + H_2O \quad (26)$$

$$FeO^{3+} + DH_2 \rightarrow FeOH^{3+} + \bullet DH \quad (27)$$

$$FeOH^{3+} + DH_2 \rightarrow Fe^{3+} + \bullet DH \quad (28)$$

$$\bullet DH + \bullet DH \rightarrow D + DH_2 \quad (29)$$

In these reactions •DH are the products of DH_2 radical transformation.

In the presence of Cu^{2+} ions in the natural water, the following homogeneous reactions with hydrogen peroxide may occur:

$$Cu^{2+} + H_2O_2 - 2H^+ \leftrightarrow CuO_2 \rightarrow Cu^+ + \bullet O_2^- \quad (30)$$

$$Cu^{2+} + \bullet O_2^- \rightarrow Cu^+ + O_2 \quad (31)$$

$$Cu^+ + H_2O_2 \rightarrow Cu(OH)_2 \rightarrow CuO^+ + H_2O \rightarrow \rightarrow CuOH^+ + \bullet OH \quad (32)$$

When the appropriate ligands are present in water, such as bicarbonates, phosphates, *etc*., capable to transform Mn(IV) oxide into the dissolved complexes, the following one-electron transfer reactions are possible:[72]

$$LMn(IV) + e^- \rightarrow LMn(III) \quad (33)$$

$$LMn(III) + H_2O_2 - 2H^+ \rightarrow LMn(II) + \bullet O_2^- \quad (34)$$

$$LMn(III) + H_2O_2 + H^+ \rightarrow LMn(IV) + \bullet OH \quad (35)$$

$$LMn(II) \bullet OH \rightarrow LMn(III) + O_2 \quad (36)$$

Therefore, under the interaction of H_2O_2 with the transition valence metal ions or compounds, both highly reactive Cu(III), Fe(IV), Mn(III), Mn(IV) complexes, and strong oxidants including •OH and other radicals may be generated. Up to 50% of hydrogen peroxide can thus be turned into the free radicals, and the measured steady-state concentration of •OH radicals makes $\sim 10^{-15} - 10^{-17}$ M/L. Given that the constant makes $k_{\bullet OH+RH} \sim 10^9 - 10^{10}$ M^{-1} sec^{-1}, the lifetime of many pollutants (RH) only makes a few days, which determines the necessary optimal conditions for natural water self-purification.

Self-purification processes in natural waters

Water pollution must be compensated by the natural self-purification processes in which oxygen and hydrogen peroxide play a paramount role. Self-purification of natural waters implies: physical-chemical processes of mass transfer (physical self-purification), biological self-purification due to the metabolic and co-metabolic processes and chemical transformation of substances (chemical self-purification), which occur within the water body,

reducing the pollutants concentrations that leads to the safe functioning of ecosystems.[1,26,27,73]

It is highly important to consider the self-purification processes from the viewpoint of chemical kinetics and catalysis, as the pollutants transformations usually occur through the catalytic reactions, oxidation with free radicals, decarboxylation, hydrolysis and other reactions, which are often catalyzed with the transition metal ions or complexes.

•OH-radicals featured with strong oxidizing properties, will interact with the pollutants, favoring the purification of natural water. The metal ions Fe^{3+} or Cu^{2+}, interacting with different reducers in water (in the presence of $O_2^{\bullet -}$ or UV-irradiation) are transformed into Fe^{2+} or Cu^{+} ions, and this cycle is then repeated. In order to estimate the concentration of free radicals, there is a need to know their initiation rate (Wi) and effective constant of their decay (ki), which, in case of OH-radicals, can be determined spectrophotometrically. As a OH-radicals trap p-nitrosodimethylaniline (PNDMA) could be used.

In this way, the "inhibiting capacity of water" parameter – $\sum k_i[S_i]$, s^{-1} – can be calculated. It is an effective constant of the first-order rate of OH• radicals decay in natural water.[29,74] In this formulae k_i is the rate constant of OH• interaction with the "trap" which value normally is within the range 10^8–$10^{10} M^{-1}s^{-1}$. The chemical self-purification processes with the involvement of active radicals and radicals' traps are reflected on Fig. 3.[31]

The share of hydrogen peroxide in natural waters, decomposing into OH• radicals, makes about 10–50%.[75] The rate of H_2O_2 photochemical generation in water (W_f) can be conventionally considered as OH• radicals initiation rate (W_i), and thus, $W_i \approx W_f$. Using the parameter $\sum k_i[S_i]$, the steady-state concentration of OH• radicals in water and the effective rate constant of radical oxidation of any pollutant (k_{RH}) can be assessed, based on the following formulae:

$$[OH^{\bullet}] = \frac{W_i}{\Sigma k_i[S_i]} \text{ and } k_{RH} = k_{OH^{\bullet}+RH}[OH^{\bullet}] = k_{OH+RH} W_i / \Sigma k_i[S_i] \quad (37)$$

where $k_{OH^{\bullet}+RH}$ is the constant of OH• interaction rate with the pollutant RH.

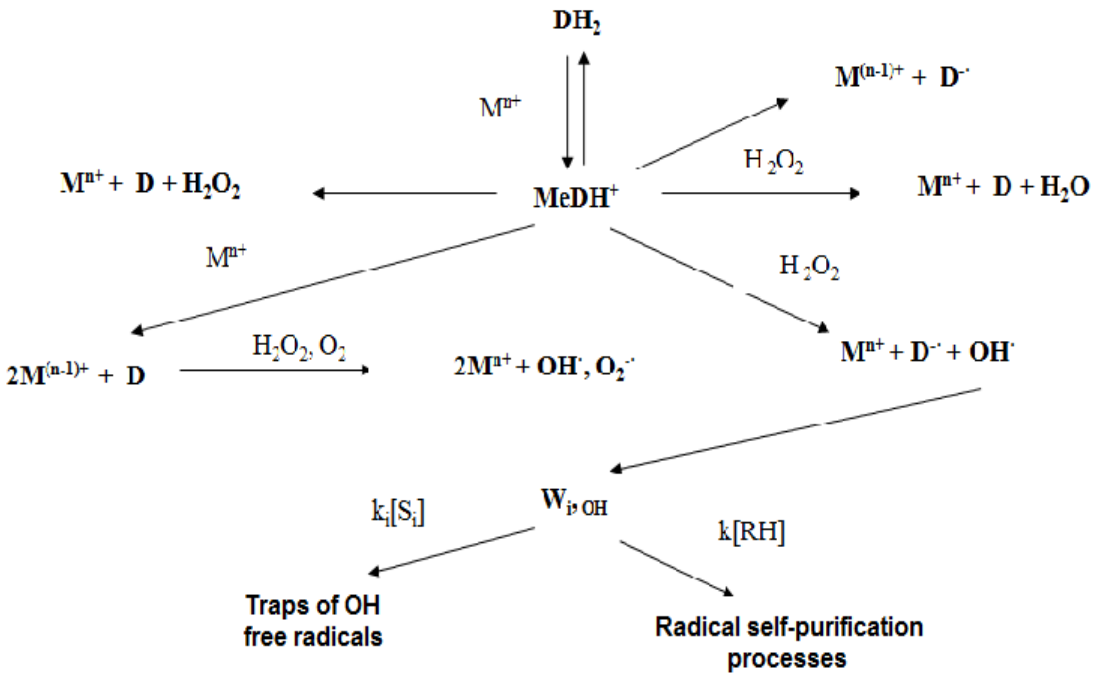

Fig. 3 – Schematic representation of the redox processes during the chemical self-purification.

Based on these considerations, a dynamic model outlining the chemical-biological redox processes in natural water was proposed, including the constantly running biotic and abiotic processes with the involvement of oxidative and reducing equivalents (Fig. 4).[1,31]

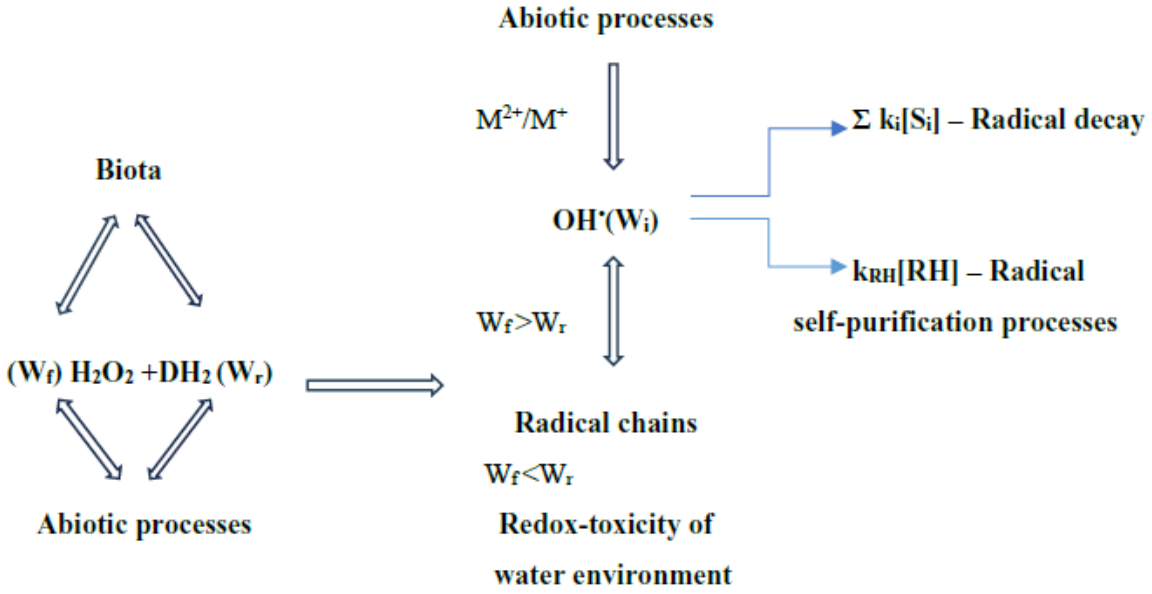

Fig. 4 – Dynamic model of chemical-biologic redox-processes in natural water.

Intensity of the self-purification processes depends on the redox-state of natural water. In the surface water layers' hydrogen peroxide generation occurs mainly through the photochemical pathways, whereas in the deeper layers – through the catalytic oxidation of pollutants and substances generated by water microorganisms with the molecular oxygen.

From the ecological viewpoint oxygen is an ideal oxidant, as the final stable product of its reduction is water:[76]

$$O_2 + 4e^- + 4H^+ \rightarrow 2\,H_2O \qquad (38)$$

Meanwhile, the molecular oxygen is known to be kinetically inert. This fact can be explained with the fact that in the most cases the overall multi-electron redox process is occurring as a series of consecutive elementary stages of one-electron transfer.[17,27] This means that on the first stage, the reaction of one-electron O_2 reduction should be realized:

$$O_2 + e^- \rightarrow \bullet O_2^- \quad (\Delta G^0 = +15.4\ \text{kJ/M}) \qquad (39)$$

The inertness of the molecular oxygen is connected with the thermodynamic disadvantage of this reaction. Still, in case of the biological oxidation, either the synchronous transfer of several electrons will occur, or energetic conjunction of thermodynamically favorable and unfavorable reactions.

Thus, the problem of oxygen using in technological processes is a purely kinetic issue and requires revealing of elementary activation mechanisms of oxygen redox transformations. The mechanisms of O_2 activation can be subdivided into the thermal, photolytic and chemical ones, and the transition metal ions and complexes often act as catalysts in these processes[46]. In other cases, and external initiation of free radicals triggers the oxidation of multiple substrates in natural waters.

CONCLUSION

Natural water bodies can be regarded as open-type unbalanced multi-component, multi-phase, photochemical, catalytic reduction-oxidation systems, with permanent influx, generation, decomposition of these species, along with the multiple redox-reactions of pollutants transformations and destruction. Ecological balance in the natural water bodies is directly linked with the formation of water condition suitable for the biological value of habitation. The long-term studies had revealed that the paramount role in the formation of water quality is played by such species as hydrogen peroxide, oxygen, transition metal ions and complexes, active radicals, specifically, hydroxyl radical •OH and superoxide-radical $\bullet O_2^-$ ($\bullet HO_2$). This article shows the general mechanisms of pollutants' transformations as water self-purification phenomena, revealing the catalytic role of metal ions and complexes, such as Fe (II) and Fe (III), Cu (I) and Cu (II) and Mn (IV) in these processes.

Acknowledgement. This article was elaborated under the National Research Project Nr.010603 implemented at the Moldova State University, Institute of Chemistry.

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