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HYDROGEN PEROXIDE IN ECOLOGICAL AND ENVIRONMENTAL CHEMISTRY

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Abstract. This review paper is focused on the detailed consideration of the structure, properties and reactions of hydrogen peroxide. Basic principles of chemical processes with the involvement of H_2O_2 are discussed, considering its dual donor-acceptor properties and broad applications in the numerous environmental and technological redox processes. The paper highlights the importance of revealing these processes mechanisms, since they have been insufficiently studied so far, or the related data have a fragmentary and incomplete character. A special attention is given to catalytic oxidation reactions, formation and properties of intermediates, their role in the natural environment. The H_2O_2 plays a specific role in biochemical transformations in living organisms. Its presence in natural fresh water bodies is considered to be a necessary condition for waters self-purification, a process opposite to water pollution, especially given that the share of H_2O_2 decomposition leading to the formation of active OH• radicals is 10–50%.

Keywords: hydrogen peroxide, redox process, catalysis, transition valence metal ion, intermediate specie.

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List of abbreviations and notations:

DH_2	Electron donors
EDTA	Ethylenediaminetetraacetic acid
FAD	Flavin adenine dinucleotide
NADPH	Nicotinamide adenine dinucleotide phosphate
PNDMA	*p*-Nitrosodimethylaniline
PCT	Partial charge transfer
RH	Polluting organic compounds
S	Organic substances
SOD	Superoxidedismutase
UV	Ultraviolet
W	Water

Introduction

Hydrogen peroxide and the reduction-oxidation reactions with its involvement have been studied for over 200 years. However, many important aspects of these processes in the environment and technology and their mechanisms are still insufficiently investigated, rising the great interest of scientists worldwide. This fact is caused by the theoretical and practical complexity in revealing and explaining the redox reactions mechanisms in which hydrogen peroxide plays a significant role [1].

Although the structure of hydrogen peroxide molecule is rather simple, and it can be readily decomposed into oxygen and water, following the reaction (Figure 1), this process in the environment passes through a series of intermediate stages which may differ, dependending on the process conditions (temperature, pH, catalysts, UV-irradiation, water chemical composition and biota, *etc.*).

Environmental importance of hydrogen peroxide consists in its direct participation in numerous oxidation and reduction processes which had laid the pathway for the appearance of life on Earth. According to the Early Evolution theory [2], in the beginning there was no oxygen in the protoatmosphere.

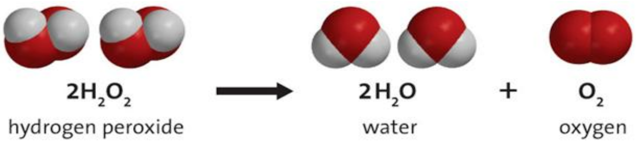


Figure 1. Representation of hydrogen peroxide molecule decomposition [1].

According to some assumptions, around 2.3-2.5 bilion years ago, following the 'Great Oxygenation Event', the atmosphere of our planet has passed through the reducing and oxidizing states [3]. Initially, due to the intensive volcanic activity accompanied by huge amounts of emitted gases with reducing properties (H_2, CH_4, H_2S, *etc.*) and high metal concentrations in the reduced state (Fe^{2+}), oxygen accumulation in the atmosphere was impossible [4].

The Earth's atmosphere and planetary ocean may be viewed as a gigantic imaginary gas-liquid reactor, and through the UV-irradiation penetrated through its walls quite easily. This promoted the abiotic synthesis of organic matter from simple gases, such as hydrocarbons, aldehydes, ketones, aminoacids and carboxylic acids. As a result of chemical evolution of matter and circulation of organic compounds, structures of increased complexity have formed in the absence of destructive processes. Under the solar irradiation, in the presence of the dissolved substances in the Ocean, the evolution of life started, and heterophobous non-photosynthetic organisms of bacteria type occurred. Perhaps it looks strange, but the very first organisms lived due to the anoxygenic photosynthesis, a possibility that was proved taken as an example the purple bacteria [5]. At that time, the oxygen content in the atmosphere was approximately 1/100 million as compared to the current content [6]. Over this period, the dissolved hydrogen peroxide was the main biogenic oxidant.

Then, at the later stage, the autotrophic photosynthetic bacteria appeared as well, which used solar energy to oxidize the soluble gases in water and evolve molecular oxygen into the environment. As a result, free oxygen appeared in the atmosphere. Oxygen contents began to grow gradually, and the organisms were adapted to exist under the aerobic conditions. The oxygen producing blue-green algae had won the Evolution competition, because they had higher conversion coefficient of solar energy to biologic matter, as compared to the anoxygenic purple bacteria.

During the life evolution, the chemical-biologic auto-regulatory system appeared, capable to maintain the favorable conditions for biota [7]. It is important, that counteraction between the opposite flows of oxygen and reducers always produce hydrogen peroxide, a key intermediary in the transformation of oxygen into water. The oxygen cycle has become fundamental for the biosphere [8,9]. Within the global biologic circuit, the molecular oxygen is formed as a result of photosynthesis by water oxidation and is reduced back to water during the oxidative destruction, with the elimination of accumulated energy.

Based on the chemical reactions mechanisms with participation of oxygen, hydrogen peroxide, free radicals and other reactive species, it would be possible to select the best necessary reactions' pathways to adopt them in manageable technological systems or to apply in environmental compartments. However, given that the data on the reactions mechanisms with hydrogen peroxide involvement are in many cases incomplete and vague, it became necessary to systematize the accumulated knowledge on the relevant redox processes' mechanisms on formation, decomposition, transformations of H_2O_2 in the presence of various reductants, transition valence metal ions and other species. Thus, the goal of this paper is to fulfil this existing gap, to assist the researchers outlining the perspective research approaches in this area.

Background

Formation of hydrogen peroxide in natural environment

Hydrogen peroxide is not generally a long-living substance, but due to its permanent formation in numerous natural processes, both in water and in atmosphere, it makes part of the systems and the reactions establishing and maintaining the fluxes' equilibrium responsible for substances circulation and vital processes [10]. In natural fresh and salty water bodies H_2O_2 can be formed both under the UV-irradiation and in dark conditions, in case of the ground waters [11-14]. It is decomposed through the various mechanisms [15]. Due to its implication in chemical and biological processes, including self-purification, metabolic transformations, pollutants decomposition, *etc.*, it affects the ecogeochemistry of natural ecosystems [16]. In the living organisms, including plants, hydrogen peroxide can be formed with the help of superoxide and superoxide dismutase, in the electron transport reactions within the chloroplasts and mitochondria, as well as plasma membrane NADPH oxidases, peroxisomal oxidases, and some other apoplastic oxidases [17]. Its intracellular transport is promoted by aquaporins, whereas H_2O_2 removal is ensured by such enzymes as catalase, peroxiredoxin, glutathione peroxidase-like enzymes and ascorbate peroxidase [18-20].

Hydrogen peroxide appears as an intermediate in the transformation of more stable species, namely oxygen, being subsequently involved in the related reactions. Among the other oxidants, oxygen is considered to be of top importance in the nature. However, molecular oxygen under the normal conditions is inert. Its activation is a multi-step process with intermediate formation and catalytic transformation of hydrogen peroxide (Figure 2). Unlike O_2, H_2O_2 molecule has a vacant σ-orbital, capable to receive one or two electrons thus acting as an oxidant. Hydrogen peroxide has at the same time donor properties and can interact with metals as a reducer.

Among other simple compounds, hydrogen peroxide is specific due to its dual nature, as it shows both the properties of an oxidant and a reducer. Hence, it can be readily involved into the big variety of environmental and technological processes, including the redox, catalytic, radical, photocatalytical, biochemical, *etc.* reactions. It is widely applied in environmental, clinical, pharmaceutical, agricultural, food, textile and paper production, wastewater treatment, *etc.* [21,22]. Being an environmentally-friendly oxidant, it is used for the oxidative removal and detoxication of the water solutions containing harmful microbial and chemical pollutants [23,24]. An important feature of these processes is that the reactions are running under room temperature, very soft conditions and yield simple non-toxic products.

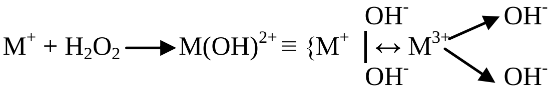
The main types of mechanisms of catalytic oxidation processes with H_2O_2 participation

Reactions of H_2O_2 with metal ions in the reduced form can occur both in the outer- and inner-sphere way. In the case of H_2O_2 inner-sphere interaction with metal ions, having the potential unoccupied sites, two types of hydrogen peroxide molecule coordination are possible: monodentate, if only one vacant site is available, and bidentate, in presence of two sites. In both cases one or two electron transfer is possible, depending on the redox characteristics of the metal [25].

During the inner-sphere one-electron charge transfer, the intermediate formation of metal-peroxide complex occurs, with its subsequent decomposition, yielding OH-radical according to Eq.(1).

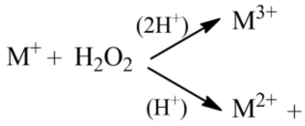
$$M^+ + H_2O_2 \leftrightarrow (MH_2O_2)^+ \equiv (M^+ \ldots OH\text{-}OH^- \leftrightarrow \leftrightarrow M^{2+}\text{-}OH^- \ldots OH) \rightarrow M^{2+}\,OH^- + OH^\bullet \quad (1)$$

In case of two-electron inner-sphere transfer, an intermediate complex formation also occurs, manifesting the properties of metal ion superoxidized state, or atomic oxygen according to Eq.(2).



$$M^+ + H_2O_2 \longrightarrow M(OH)^{2+} \equiv \{M^+ \begin{matrix} OH^- \\ | \\ OH^- \end{matrix} \leftrightarrow M^{3+} \begin{matrix} \nearrow OH^- \\ \searrow OH^- \end{matrix} \quad (2)$$

In acidic environment, MO^+ and $M(OH)^+_2$ particles are hydrolysed forming the hydroxo-derivatives. The hydrolysis of these particles may be accompanied by water oxidation by OH•-radical. In the absence of intermediate particles such as MO^+, $M(OH)^+_2$, MOH^{2+}, $(MH_2O_2)^+$ in proton environment, the interaction of M^+ with hydrogen peroxide is accompanied with the formation of either M^{3+} or OH^- according to Eq.(3).



$$M^+ + H_2O_2 \begin{matrix} \xrightarrow{(2H^+)} M^{3+} \\ \xrightarrow{(H^+)} M^{2+} + OH^- \end{matrix} \quad (3)$$

Therefore, H_2O_2 activation is connected with the formation of free or complex-bound OH•-radical or metal ion in superoxidized state. The reactivity of M^{3+} derivatives are of great interest for the mechanisms understanding of both chemical and biochemical processes.

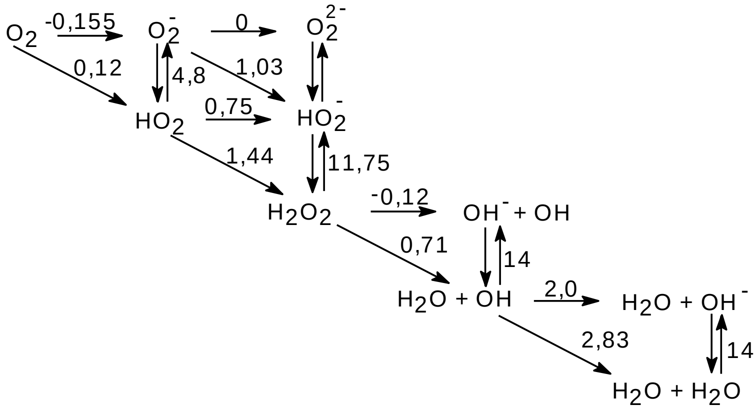
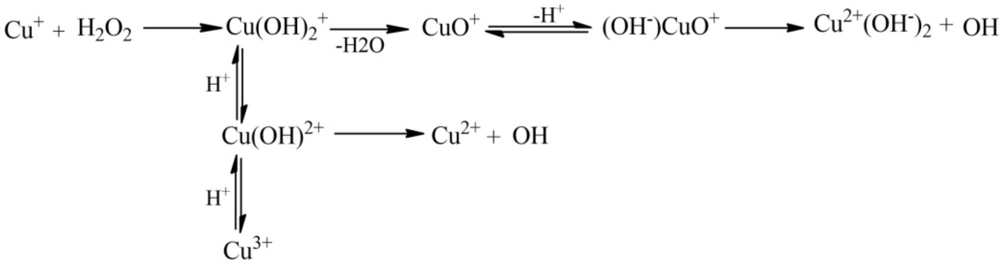


Figure 2. Activation of oxygen molecule with the intermediate formation of H_2O_2 [10].

The most significant catalysts in oxidation processes in natural waters with H_2O_2 involvement were shown to be copper and iron ions and complexes. Despite the seeming simplicity of M^+ with H_2O_2 reaction, the real mechanism of Cu^+ and Fe^{2+} interaction with H_2O_2 is rather complex [16,26]. In case of copper, it can be represented by the reaction according to Eq.(4). For iron ions, depending on the pH, the formation of both OH-radical and ferryl-ion is possible according to Eq.(5). Under natural conditions, the catalytic activation of O_2 and H_2O_2 can be efficiently realized only in the case of metal reduced forms regeneration, *i.e.* in the presence of reducing equivalents in the system [27].

The principal stage in catalytic oxidation of various substances with hydrogen peroxide is the complete or partial reducing of the transition valence metal ion with its subsequent interaction with H_2O_2. Such reducing is possible either due to the external M^+ initiation, or due to the M^{2+} interaction with electron donors (DH^-). If DH^- donors have ligand properties, their interaction with metal ion in the oxidized form is accompanied with the intermediate formation of partial charge transfer (PCT) complex. This complex can then be decomposed yielding the electron transfer products, such as M^+ reduced form and D^- redox ligand radical, or interact with another oxidative particle [28,29]. Apart from this, hydrogen peroxide can serve as an oxidant making part of the metal-complex coordination sphere, with the formation of triple PCT complex in such reactions. The general scheme of M^{2+} interaction with DH^- can be presented as in Eq.(6). Generally, the redox-catalytic processes with the transition valence metal ions and H_2O_2 involvement can be cyclic, activated and radical-chain (or induced) [16,27].

In *cyclic mechanism* the metal ion in oxidized or the super-oxidized state plays the role of oxidation particle, directly involved in the substrate oxidation. The role of H_2O_2 is thus reduced to the regeneration of the metal ion initial form. The separate stages of such process can be the following stoichiometric reactions (Eqs.(7-10)).



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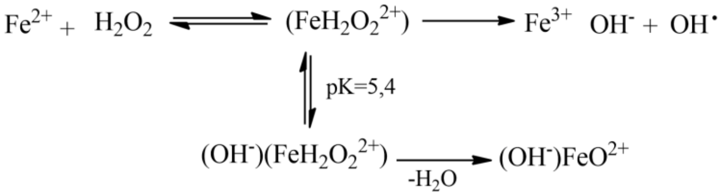

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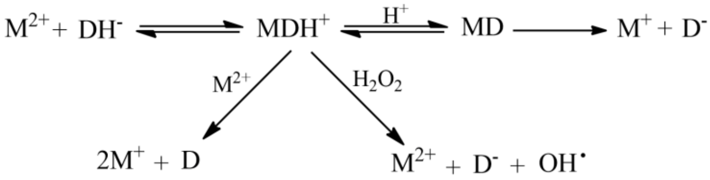


(6)

$$2M^{2+} + DH_2 \xrightarrow[-2H^+]{} 2M^{+} + D \qquad (7)$$

$$2M^{2+} + O_2(H_2O_2) \xrightarrow{2H^+} 2M^{2+} + 2H_2O_2(2H_2O) \qquad (8)$$

$$M^{3+} + DH_2 \xrightarrow[-2H^+]{} M^{+} + D \qquad (9)$$

$$M^{+} + O_2(H_2O_2) \xrightarrow{2H^+} M^{3+} + H_2O_2(2H_2O) \qquad (10)$$

These overall reactions can proceed both with and without the intermediate involvement of free radicals. The chain processes will not be realized in this case.

In a cyclic mechanism, for each oxidized substrate there exists a catalyst with the optimal redox potential value of the pair M^{2+}/M^{+} (M^{3+}/M^{+}). The higher is E_o (M^{2+}/M^{+}), or E_o (M^{3+}/M^{+}), the more rapid is the interaction with H_2O_2. Depending on E_o value and the reagents concentration, two cases may be distinguished: a) the reaction rate is limited by the substrate oxidation with metal ion in oxidized form; b) the rate is limited by M^{+} oxidation, the metal ion being in the reduced form.

In the first case, the rate of reaction is independent on H_2O_2 concentration, in the second case – on substrate concentration. If the reagents concentration is varied within the broad range, the variable (partial) reaction orders are observed. With the increase in substrate concentration, the reaction rate is increased as well, reaching its limiting value. The cyclic mechanisms are widely spread in biological systems and technological processes [16].

In the *activation mechanism*, the oxidizing particles are metal-oxygen and metal-peroxide complexes. Depending on the metal ion formation in the reduced form, the activation mechanism can be molecular-chain or non-chain. As a rule, activation mechanisms are realized without the intermediate formation of reactive radicals. The non-chain activation mechanisms are spread in vital activity processes.

The ascorbate (DH^{-}) oxidation with hydrogen peroxide is an example of molecular-chain mechanism according to Eqs.(11-14).

$$\text{initiation} \longrightarrow Cu^{+} \tag{11}$$

chain development

$$Cu^{+} + H_2O_2 \longrightarrow CuO^{+} \tag{12}$$

$$CuO^{+} + DH_2 \longrightarrow Cu^{+} + D \tag{13}$$

chain breakage

$$Cu^{+} + CuO^{+} \xrightarrow{2H^{+}} 2Cu^{2+}\ H_2O_2 \tag{14}$$

In this reaction, CuO^{+} particles take part in the chain development stages of two-electron oxidation of substrate – H^{+} donor. The similar mechanism is also realized during the oxidation of other natural reducers with ligand properties, such as dihydroxyfumaric acid, hydroquinone.

The redox-catalytic *radical-chain processes* can occur with free radicals' initiation with metal ions participation, or due to the external influences. Catalytic initiation of radicals in acidic environment is mostly typical for iron ions during their interaction with H_2O_2. The classical example of a radical-chain process is the catalytic decomposition of hydrogen peroxide according to Eqs.(15-20).

initiation

$$Fe^{3+} + H_2O_2 \xrightarrow[-H^{+}]{} Fe^{2+} + HO_2 \tag{15}$$

or

$$2Fe^{3+} + H_2O_2 \xrightarrow[-2H^{+}]{} 2Fe^{2+} + O_2 \tag{16}$$

chain development

$$Fe^{2+} + H_2O_2 \xrightarrow{H^{+}} Fe^{3+} + H \tag{17}$$

$$OH^{\bullet} + H_2O_2 \xrightarrow[-H^{+}]{} HO_2 \tag{18}$$

$$HO_2 + Fe^{3+} \longrightarrow Fe^{2+} + O_2 \tag{19}$$

chain breaking

$$Fe^{2+} + HO_2 \xrightarrow{H^{+}} Fe^{3+} + H_2O_2 \tag{20}$$

Here, hydrogen peroxide is acting as an oxidant, the source of OH-radicals and as a substrate – electron donor (H^{+}).

In case of copper ions, the redox-potential of pair Cu^{2+}/Cu^{+} is too low (0.153 V) to ensure H_2O_2 oxidation with Cu^{2+} ion in acidic environment. At the same time, in the presence of other initiation sources (iron ions, UV-irradiation), the efficient radical-chain process will occur according to Eqs.(21-25).

initiation

$$H_2O_2 \xrightarrow{h\nu} 2OH^{\bullet} \tag{21}$$

development

$$OH^{\bullet} + H_2O_2 \longrightarrow HO_2 \tag{22}$$

$$HO_2 + Cu^{2+} \xrightarrow[-H^{+}]{} Cu^{+} + O_2 \tag{23}$$

breakage

$$Cu^{+} + H_2O_2 \xrightarrow{H^{+}} Cu^{2+} + OH^{\bullet} \tag{24}$$

$$Cu^{+} + HO_2 \xrightarrow{H^{+}} Cu^{2+} + H_2O_2 \tag{25}$$

Under neutral pH values, copper ions can be involved into the free radicals' initiation process, since the electron-donor properties of hydrogen peroxide are increased, and intermediate copper-oxygen partial charge transfer complex is formed.

Inner-cellular redox-processes with H_2O_2 participation

The reactions with H_2O_2 involvement play an exceptionally important role in living organisms [16,30]. Thus, the peroxide oxidation of lipids (aliphatic acids) is of great importance for the vital activity of cells. Physiologic significance of lipids consists in the regulation of membrane permeability and monooxygenase reactivity. Lipid peroxidation under the external influence can result in the membrane deformation or destruction, or preventing the activity of poly-enzymatic system providing the electron transport on large distances [31,32]. Peroxidation of lipids is connected with inner-cellular formation of OH-radicals, which are formed in the cells during the catalytic reaction between the superoxide-radical and H_2O_2. This process is regulated by the metal enzymes, the main of them being glutathione-peroxidase.

In general, the catalytic reaction between O_2^- and H_2O_2 provokes the formation of OH-radicals within the living cells by Eq.(27).

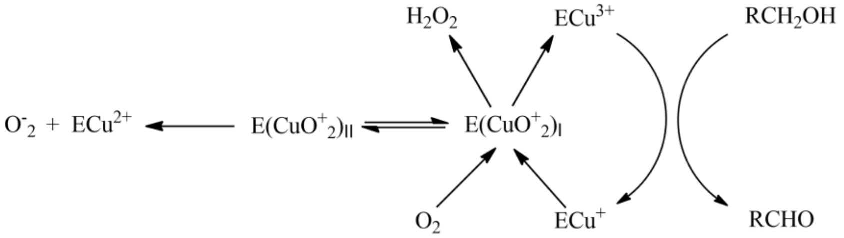
$$O^-_2 + H_2O_2 \longrightarrow OH + O_2 + OH^- \qquad (26)$$

Another widespread group of oxidases catalyse the reduction of O_2 to H_2O_2 [27,33]. As a rule, one copper ion is contained in the active center of these oxidases [34]. To this enzyme group belong: uricase catalysing the uric acid oxidation, polyphenoloxygase oxidizing the catechin oxidation into the appropriate quinine, aminoacids oxidases oxidizing aminoacids into keto- or aldehydoacids with simultaneous deamination (NH_3 formation), aminooxidases catalysing the complex amines oxidation to the appropriate ketone or aldehyde and HN_3, glycocoloxidase oxidizing the glycolic acid to glyoxalic one, xanthinogenase catalysing xanthine oxidation into the uric acid, *etc*. The cyclic or activation mechanisms of these processes can take place.

For example, in the case of galactooxidase, the cyclic mechanism of two-electron oxidation of substrate and Cu^+ is realized. In this process the oxidizing particle is copper ion in the super-oxidized state ECu^{3+}. On the secondary stage, H_2O_2 as well as O_2^- radical is formed as a result of the intermediate oxygen complex decomposition [35]. The oxidizing effect of uricase and some other oxidases is caused by the direct activation of oxygen with intermediate formation of hydrogen peroxide (Eq.(28)) [36].

In the mechanism of xanthinoxidase action, the one-electron reduction of oxygen molecule is efficiently realized, equally with two-electron reduction. The substrate in this enzyme is oxidized under the influence of MO^{5+}, which is part of the active center. Further, the electron, *via* the intermediation of Fe_2S_2 clusters, is transformed into flavin (FAD) involved in the O_2 reducing in O_2^- (Eq.(29)).

Catalases and peroxidases, being heme-containing enzymes, serve as natural catalysts of processes with H_2O_2 involvement. Catalase provokes the decomposition of excessive hydrogen peroxide, contained in the cells, yielding O_2 and H_2O_2. Peroxidase reduces H_2O_2 to water using the oxidizing equivalents liberated from the metabolic processes. These leads, at the simultaneous cells auto-purification from the harmful substances with electron-donor function. The low-molecular complex compounds containing Fe^{3+}, CN^-, F^-, N^{3-}, *etc*. are inhibitors for catalase and peroxidase activity [37].



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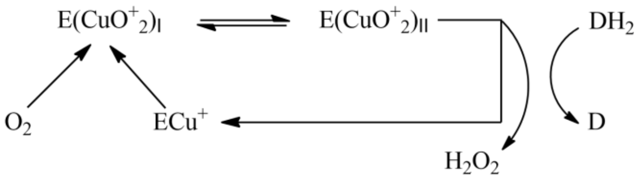

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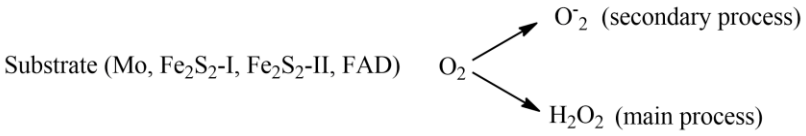

(29)

The liberation of the reducing equivalents form the organic substrates during the inner-cellular processes proceeds as a result of dehydrogenases activity – enzymes transporting the reducing equivalents to nicotinamide adenine dinucleotide (NAD, one of the most abundant and crucial molecules in cellular metabolism), forming the bi-electron oxidizing substrate and NADH - ubiquinone oxidoreductase, the largest of the respiratory complexes. The redox-state of inner-cellular environment is determined by the ratio of fluxes of oxidizing equivalents (H_2O_2) and the reducing equivalents (NADH, *etc.*) [38]. When the cell is in the normal condition, the dehydrogenase reactions accompanied with the reducing equivalents formation, are balanced with the oxidation reactions, giving H_2O_2. The regulation of inner-cellular fluxes of oxidizing and reducing equivalents usually proceeds with the help of glutathione and ascorbic acid [39]. However, in the case of blue-green algae cells, the regulation of redox-state proceeds without the involvement of ascorbic acid.

In the case of the intensive water-exchange with the external environment, its redox-state can influence the inner-cellular ratio of redox equivalents. The disbalance of the inner-cellular redox processes may affect other functional systems of living cells.

Mechanisms of H_2O_2 decomposition in the peroxide catalytic systems

The redox systems including a metal ion and hydrogen peroxide have been in the focus of scientists’ attention for over a hundred years [40]. However, this interest has not faded as hydrogen peroxide is an ideal model for studying redox reactions. The interest of researchers is constantly arousing due to the new theoretical concepts and approaches. To gain a better insight into the detailed mechanism of the reactions between H_2O_2 and metal ions, a more in-depth knowledge is required regarding the elementary redox reactions in catalytic systems. The kinetic studies are applied to establish, among the other objectives, the number of electrons transferred in elementary reaction [27,29,41].

The specific feature of hydrogen peroxide is its duality: in non-dissociated form, it is a strong two-electron oxidizing agent, while in the ionized form, it acts as an electron donor. Thus, on the one hand it reduces systems containing ions of transition metals, on the other hand, it generates a number of free radicals such as OH•, HO_2•, intermediate particles of ferryl or manganyl type, and intermediate compounds of various composition. This duality is a reason why hydrogen peroxide is not stable in solution and is decomposed in presence of catalysts (transition metal ions) into oxygen and water [42].

On metal compound interaction in oxidized form M_2^+ (metal ion or metal complex in the oxidized form, whereas M^+ - in the reduced form) with hydrogen peroxide the peroxocomplex will be formed, undergoing acid-alkaline dissociation and then decomposition by Eq.(30).

$$M^{2+} + H_2O_2 \rightleftharpoons (MH_2O_2)^{2+} \rightleftharpoons$$

$$\rightleftharpoons H^+ + MHO_2^+ \rightleftharpoons M^+ + HO_2^{\bullet} \qquad (30)$$

The peroxocomplex MHO_2^+ possessing reducing properties, either dissipates on the products of one-electron transfer, or, interacting with the second metal ion, is oxidized to O_2 or free radicals. In the case of H_2O_2 interaction with the reduced metal form M^+ two different mechanisms have been distinguished. The first was identified by Gaber and Vilsteter in 1931 (Eqs.(31,32)) [27,43]. The second was identified by Bray, W.C. and Gorin, M.H. in 1932 with intermediate formation of ferryl-ion Fe^{IV} D O_2C by Eqs.(33,34) [27,44,45].

$$M^+ + H_2O_2 \longrightarrow M^{2+} + OH^- + OH^{\bullet} \qquad (31)$$

$$M^+ + OH^{\bullet} \longrightarrow M^{2+}OH^- \qquad (32)$$

$$Fe^{2+} + H_2O_2 \longrightarrow FeO^{2+} + H_2O \qquad (33)$$

$$FeO^{2+} + Fe^{2+} \xrightarrow{H^+} Fe^{3+} + Fe(OH)^{2+} \qquad (34)$$

Hydrogen peroxide involvement in catalytic redox processes in natural water and its self-purification

Among the most significant problems in the natural water studies nowadays is revealing the mechanisms of the redox processes’ mechanisms, including the self-purification capacity [27,46,47]. The ions and complex compounds of the transition valence metals play an important role in catalytical reactions involving hydrogen peroxide transformations. Hydrogen peroxide content in natural water is relatively low (10^{-4} – 10^{-7} M) [29,48]. The main sources and appropriate reactions of hydrogen peroxide formation in natural water are shown in Figure 3 [27].

Solar light plays a dominant role in H_2O_2 formation in natural water (1), because under its influence the superoxide anion radical formation occurs, being the main predecessor of hydrogen peroxide generated in water. Some H_2O_2 comes from the atmosphere (2) in the form of rain and other precipitates. A certain share of H_2O_2 is supplied by the redox catalytic processes (DH_2 is a reducer) (3). The large amounts of H_2O_2 are formed in peroxisomes of aquatic microorganisms' cells capable to penetrate into the cytosole, and to come out of it, through the cell membrane [49]. The ectoenzymes or surface enzymes, such as deaminases, present on the outer surface of the microorganisms from phytoplankton, are capable to oxidize the nitrogen-containing organic substances with O_2, reducing it to H_2O_2 which is emitted into water (4) [50]. In the presence of microalgae, they convert H_2O_2 into water during the photosynthesis under the influence of UV part of solar irradiation.

Superoxide-radicals formed in the cell, interacting with its superoxidedismutase (SOD), are transformed into H_2O_2, and the excess is excreted by the microorganism into water (5). Oxygen interaction with Cu^+ also yields H_2O_2 (6) [51]. At last, hydroperoxides, with contents in natural water of ten times lower than that of H_2O_2, can be partly transformed into hydrogen peroxide (7) (Figure 3). In its turn, hydroperoxide ROOH formation in natural water can be represented as a series of catalytic and noncatalytic reactions according to Eqs.(35-42) [52,53].

The reactivity of RO_2• radicals in these reactions is usually three to five orders less than that of RO• radicals. Hydrogen peroxide decomposition in natural waters has been addressed repeatedly [54-56] and it was shown that this process may proceed in both abiotic and biotic ways.

Experimental and theoretical data on H_2O_2 decomposition catalysis with transition metal ions [57-61] have been used to describe the abiotic decomposition of H_2O_2 in natural water. In water medium, copper ions, iron chelate complexes [62], and partly manganese ions [63] can be found in homogeneous form.

Meanwhile, the catalytic decomposition of H_2O_2 (at pH 7) mainly proceeds on the microcolloidal iron hydroxide (by nonradical mechanism) and on copper ions (through free radicals' formation) [64,65], yielding Cu^+ and superoxide-radicals. Further, Cu^+ interaction with H_2O_2 yields CuO^+ particles (hydrolyzed cooper ion), which oxidizes water with OH•-radical formation [66].

$$RH \xrightarrow{h\nu} \dot{R} + H \qquad (35)$$

$$\dot{R} + O_2 \longrightarrow R\dot{O}_2 \qquad (36)$$

$$R\dot{O}_2 + RH \longrightarrow ROOH + \dot{R} \qquad (37)$$

$$R\dot{O}_2 + DH^- \longrightarrow ROOH + \dot{D} \qquad (38)$$

$$R\dot{O}_2 + M^+ \xrightarrow{H^+} ROOH + M^{2+} \qquad (39)$$

$$R\dot{O}_2 + NO_2^- \xrightarrow{H^+} ROOH + NO_2 \qquad (40)$$

$$R\dot{O}_2 + HSO_3^- \longrightarrow ROOH + SO_3^{2-} \qquad (41)$$

$$M^+ + ROOH \longrightarrow RO + MOH^+ \qquad (42)$$

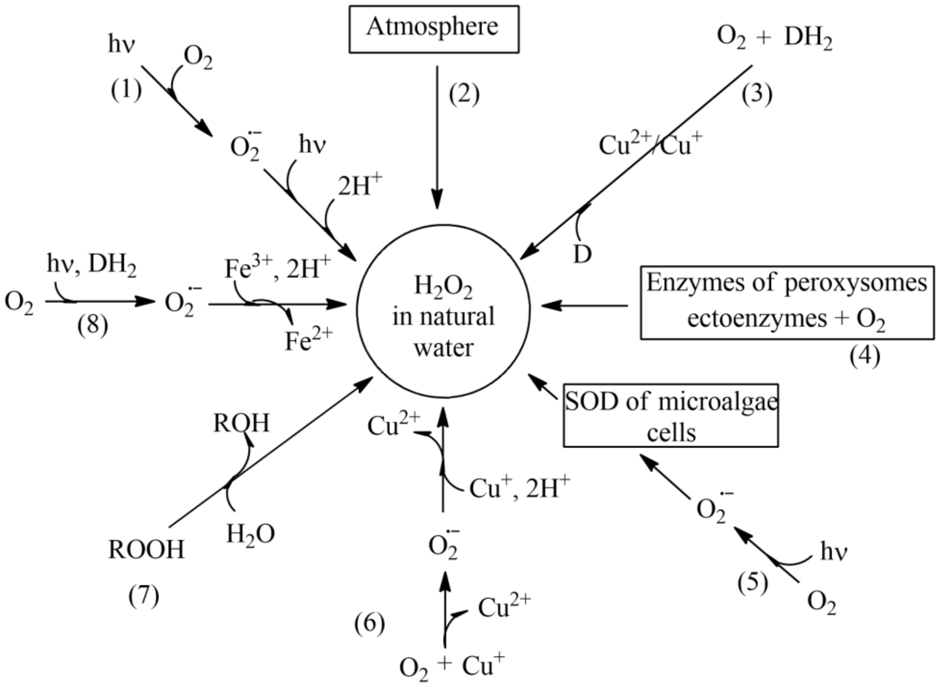

Figure 3. The main sources and reactions of hydrogen peroxide formation in natural water [27].

Possible ways of OH•-radical formation in natural water are as follows (Figure 4) [27]. In the presence of the electron donor DH_2, hydrogen peroxide is consumed for its catalytic oxidation without the formation of free OH•-radical (1). If DH_2 possesses the properties of redox ligands, it can initiate OH•-radical formation (2). This radical can also be formed under the hydrogen peroxide irradiation with light (especially 686 nm UV) (3). The same process takes place during the hydroperoxide (ROOH) irradiation with light (4). A similar picture is observed on their interaction with the reduced forms of metal M^+ (5). If ozone ($O_{3,aq}$) dissolved in water interacts with the dissociated form of peroxide, its decomposition will proceed according to the radical-chain mechanism with the formation of superoxide-radical and the OH•-radical. The last radical can also be formed in the NO_3^- photochemical transformation (7). In the presence of reducers DH_2, ozone (its concentration in water surface layers reaches 10^{-8} M) will interact with them and will also generate OH•-radicals (8). Hydrogen peroxide interaction with iron(II) coordination compounds can result in the formation of superoxidized form of Fe(IV) (provided the ligand is capable to stabilize such a form), and, *via* this intermediate, it can lead to the generation of OH•-radicals (9). These radicals can also be formed by irradiation with light of the L_nFeOH^{2+}-type complexes (10). Superoxide anion-radical $O_2•^-$ interaction with hydrogen peroxide in water is catalysed by metal compounds, in particular, copper compounds, which results in the production of OH· (11). The photochemical reactions of charge transfer with the same effect are also possible (12). There are nitrogen oxides in natural water, in particular NO, which make possible the formation of OH-radicals during the reaction with superoxide (13). These can be also formed during the photochemical transformation of NO_2^- (14).

In natural water, free radicals can also be formed by abiotic and biotic ways. Thus, for example, algae will induce DH_2 into water reducers, which in the presence of H_2O_2 and Cu^{2+} ions are capable to form OH•-radicals in accordance with (2) in Figure 4. Although the qualitative assessment of contribution for different ways of free radical initiation is not very simple [67,68], their stationary concentrations can be estimated both by the direct measurement and by calculation, proceeding from the rate of radical initiation and efficient rate constant of their disintegration [69,70].

Equally with H_2O_2 and OH radicals formation in natural water under the solar light, superoxide radicals $O_2•^-$ are also formed as primary ones, the main ways of their generation being presented in Figure 5 [71-73].

Organic substances (S) such as amino acids, primary alcohols, *etc*. in natural water under the sunlight will be transformed into the excited state (S*) and then, giving an electron to the molecule O_2, will generate $O_2•^-$ (1). These radicals may be preceded by hydrated electron (e^-_{aq} and other electron-excited particles. Such photoelectron transfer is widely distributed in natural water.

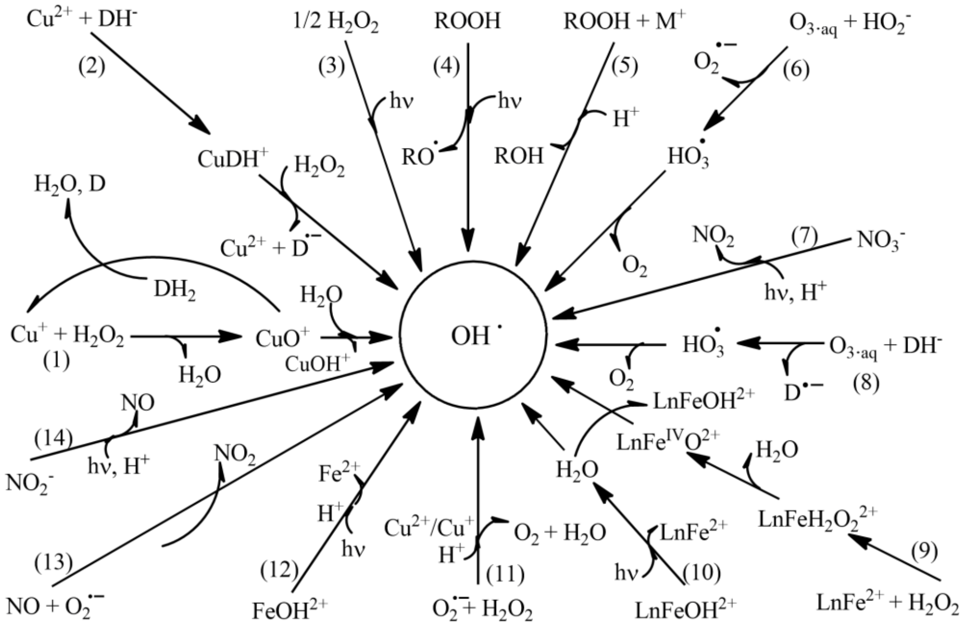

Figure 4. **Ways of hydroxyl-radical generation in natural water [27].**

Radioactive irradiation (α-, β- and γ-rays) in the case of radiation pollution will provoke the formation of OH•-radicals, hydrated electrons and H atom, which, interacting with O_2, will form O_2•$^-$ (HO_2•) superoxide radicals (2). As a result of secondary processes, the reduced forms of metal M^+, reacting with O_2, will promote the generation of result in O_2•$^-$ radicals (3). The transformation of O_2 into O_2•$^-$ in natural water can result in the formation of radical-reducers D•$^-$ (4). Super-oxide anion radicals can also be formed on hydrogen peroxide reaction with copper ions and complexes (5). During the photolysis, the transition metal peroxocomplexes can be decomposed in a reducing way with O_2•$^-$ radical generation (6). Catalytic decomposition of hydrogen peroxide with O_2•$^-$ radical formation occurs in the presence of copper ions in a natural (close to neutral) water medium (7). Ozone dissolved in water $O_{3,aq}$ as well can be a generator of both superoxide forms (O_2•$^-$ and HO_2•) (8) or only one of its forms (O_2•$^-$) (9). Nitrogen dioxide NO_2^- dissolved in water, capable of detaching an electron from donor HO_2^- (10), can take part in HO_2• generation. The photochemical charge transfer reactions are also important (especially for Fe complexes) in HO_2• producing (11). The reactions of hydrogen peroxide with OH•-radicals in natural water can also produce HO_2• (12). The stationary concentration of O_2•$^-$ radical in natural water reaches approx. 10^{-8} to 10^{-9} M. These are the main ways of the most important intermediates of the O_2 molecule reduction (hydrogen peroxide, OH•-radical and O_2•$^-$ radical) (Figure 5).

H_2O_2 molecule activation in natural water

H_2O_2 activation can occur in the presence of metal (such as Fe) complexes with simultaneous UV irradiation according to Eq.(43).

OH•$^-$ -radicals interact with numerous water polluting organic compounds (RH), oxidizing them to appropriate radicals R by Eq.(44).

A pollutant in the activated form R• readily enters other reactions, finally being turned into less toxic or nontoxic compounds. Thus, the catalytic decomposition of hydrogen peroxide can ensure water purification from pollutants.

An example of rapid deep destruction is oxidation of pyridine carbonic acids (pyridine-2,3,6-dichloropyridine-2-carbonic acids - RH) by Fenton reagent with additional irradiation with light at the wavelength 320 nm according to Eqs.(45-47) [74].

$$H_2O_2 \xrightarrow{FeL_n,\ h\nu} 2OH^\bullet \tag{43}$$

$$OH^\bullet + RN \longrightarrow H_2O + R^\bullet \tag{44}$$

$$Fe^{2+}(L_nFe^{2+}) + H_2O_2 \longrightarrow Fe^{3+}(L_nFe^{3+}) + OH^- + OH^\bullet \tag{45}$$

$$Fe^{2+}(L_nFe^{3+}) + h\nu \longrightarrow Fe^{2+}(L_nFe^{2+}) \tag{46}$$

$$OHg + RH \longrightarrow Rg + H_2O \tag{47}$$

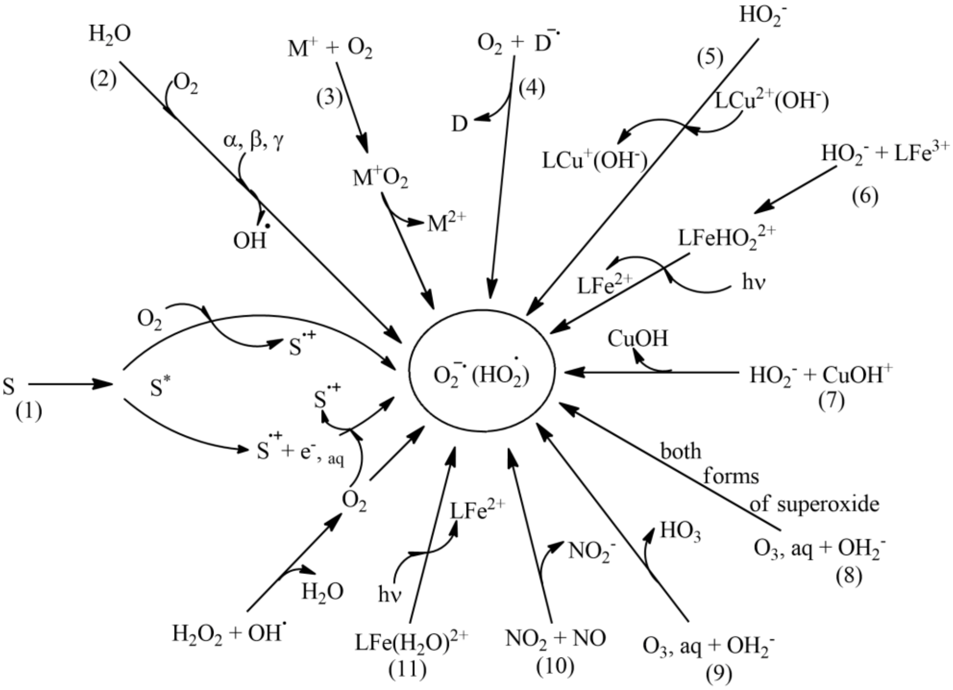

Figure 5. Ways of supperoxide-radical O_2•$^-$ generation in natural water [71-73].

In the presence of Cu^{2+} ions in natural water, the following reactions with hydrogen peroxide can proceed in a homogeneous way according to Eqs.(48-50). If there are suitable ligands (bicarbonates, phosphates, *etc*. in water medium, capable of transforming manganese(IV) oxide into manganese(IV) soluble complex compounds, the following one-electron reactions are possible by Eqs.(51-54).

Thus, during H_2O_2 interaction with the transition metal compounds, both highly-reactive compounds of Cu(III), Fe(IV), Mn(III), and Mn(IV) and strong oxidant OH-radicals are formed. Up to 50% of hydrogen peroxide can be transformed into free radicals, and the stationary concentration of OH-radicals in natural water reaches about 10^{-15} to 10^{-17} M [29,46]. Taking into account that $k_{OH^\bullet + RH} \approx -10^9\text{-}10^{10}$ M/s, the lifetime of many pollutants (RH) is only several days, which demonstrates the need for optimal self-purification conditions in natural water.

Catalytic redox processes in natural water have been discussed in detail in research papers [27,75-77]. The further development and amplification of these ideas are given in [27,29,78,79]. In accordance with the concepts discussed, the natural water, from chemical point of view, under the natural conditions may be represented as an open-type multicomponent, multiphase, photochemical, catalytic redox system of $M^+–M^{2+}–O_2–H_2O_2–L–DH_2–S–In–h\nu$ type, in which the processes of oxygen activation, hydrogen peroxide and pollutants decomposition proceed [10]. Thus, both the stoichiometric reduction and oxidation of metal ions occur with the appropriate activation of oxygen and hydrogen peroxide Eqs.(55-57) and catalytic processes of pollutant SH_2 oxidation by Eqs.(58,59).

The concentration of Fe ions in natural water reaches 10^{-5} M, and for Cu and Mn ions ≈ 10^{-6} to 10^{-8} M. The ions and compounds of these transition metals are the most important in the redox transformation of O_2 into H_2O_2. To be mentioned that Cu ions are in natural water in homogeneous form in both oxidized and reduced states [80], whereas the Fe ions are found predominantly in oxidized form (as microcolloidal hydroxide) and Mn ions, in the form of either free ions Mn^{2+} or as microcolloidal oxide of Mn(IV) [81]. For copper ions the reactions with one- or two-electron transfer with O_2 and H_2O_2 involvement are typical, while in case of Fe and Mn ions, two-electron transfer reactions of H_2O_2 catalytic decomposition occur [27,82].

$$Cu^{2+} + H_2O_2 \longrightarrow CuO_2 \longrightarrow Cu^+ + O_2^{\bullet -} \tag{48}$$

$$Cu^{2+} + O_2^{\bullet -} \longrightarrow Cu^+ + O_2 \tag{49}$$

$$Cu^{2+} + H_2O_2 \longrightarrow Cu(OH)_2 \longrightarrow CuO^+ + OH^\bullet \tag{50}$$

$$LMn(IV) \xrightarrow{e^-} LMn(III) \tag{51}$$

$$LMn(III) + H_2O_2 \xrightarrow{2H^+} LMn(II) + O_2^{\bullet -} \tag{52}$$

$$LMn(III) + H_2O_2 \xrightarrow{H^+} LMn(IV) + OH^\bullet \tag{53}$$

$$LMn(II) + OH^\bullet \longrightarrow LMn(III) + O_2 \tag{54}$$

$$2M^{2+} + SH_2 \xrightarrow{-2H^+} 2M^+ + S \tag{55}$$

$$2M^+ + O_2 \xrightarrow{+2H^+} 2M^{2+} + H_2O_2 \tag{56}$$

$$2M^+ + H_2O_2 \xrightarrow{2H^+} 2M^{2+} + 2H_2O \tag{57}$$

$$SH_2 + O_2 \xrightarrow{M^{2+},\, M^+} S + H_2O \tag{58}$$

$$SH_2 + H_2O_2 \xrightarrow{M^{2+},\, M^+} S + 2H_2O \tag{59}$$

In natural water, the metal ions of transition valence play the role of process catalysts during the redox reactions. The natural water pollution must be compensated with self-purification processes, in which a major role is played by O_2 and H_2O_2. It is important that the self-purification processes to be studied and considered, based on the stipulations of chemical kinetics and catalysis, as the pollutants' transformations usually proceed through the catalytic reactions, free radical oxidation, decarboxylation, hydrolysis and other reactions.

Under neutral conditions (pH 5–8), the iron ions in natural water can be found as either insoluble hydroxides or soluble complexes. Insoluble iron forms, settling in bottom deposits, can be reduced to Fe(II) compounds, possessing much higher solubility than Fe(III). Diffusing from bottom deposits into the water bulk, Fe^{2+} ions can be once again be oxidized with oxygen and hydrogen peroxide dissolved in the water. In case of their binding into complexes, they can take part in active intermediates generation, which will later oxidize the pollutants. Thus, iron complexes play an important role in the self-purification of natural water.

The molecule O_2 is activated within this process. The mechanism of O_2 activation with iron coordination compounds involves the formation of intermediate oxide complex, and then – the peroxide complex (Figure 6) [10,83].

The most efficient reactions of pollutant oxidation in water medium proceed through the radical mechanism, hydroxyl radical being the most reactionary among all the other radicals

($OH\bullet$, $O_2\bullet^-$ ($HO_2\bullet$), $RO_2\bullet$, *etc.*). It is initiated mostly in photochemical reactions with H_2O_2 participation according to Eqs.(60-63).

Unlike $OH\bullet$, superoxide radicals possess a dual redox function. For this reason, these radicals in neutral and acid media are easily disproportioned to O_2 and H_2O_2. In the alkaline medium they are stable. They play an important role in catalytic radical-chain processes of H_2O_2 decomposition according to Eqs.(64-67). The possible mechanism of oxygen activation with iron ions in natural water may be presented as two-electron transfer by Eqs.(68-71) [10,27,84].

Hydrogen peroxide thus formed can be transformed into OH-radicals through the intermediate compounds of ferryl-ion type FeO^{2+} or $LFeO^{2+}$ (Eqs.(72,73)).

Unlike the oxygen molecule activation with iron ions, its activation with copper ions proceeds by one-electron mechanism with the formation of $HO_2\bullet$ superoxide radical and hydrogen peroxide [85].

Hydrogen peroxide, in its turn, is transformed into OH-radical according to Eqs. through the formation of a number of intermediate compounds of “cupryl-ion” type (CuO^+) (77,78).

OH-radicals, being strong oxidants, interact with pollutants thus purifying natural water. Fe^{3+} or Cu^{2+} ions, interacting with various reducers of water (such as $O_2\bullet^-$ or quantum of light) will be transformed into Fe^{2+} or Cu^+, and the cycle will be repeated. To assess the free radicals’ concentration, one has to know the rate of their initiation (*Wi*) and efficient constant of their decay (k_i), which, in case of OH-radicals, can be determined spectrophotometrically (using the competitive reactions reactions) according to *p*-nitrosodimethylaniline coloration fading (PNDMA-trap for OH-radicals).

$$H_2O_2 \xrightarrow{h\nu} 2OH^{\bullet} \tag{60}$$

$$FeOR^{2+} \longrightarrow Fe^{2+} + RO^{\bullet} \tag{61}$$

$$Fe^{2+} + H_2O_2 \longrightarrow FeOH^{2+} + OH^{\bullet} \tag{62}$$

$$LFeDH^- + H_2O_2 \longrightarrow LFeOH^{2+} + D^{\bullet -} + OH^{\bullet} \tag{63}$$

$$2O_2^{\bullet -} + 2H^+ \longrightarrow H_2O_2 \;\; (pH \le 7) \tag{64}$$

$$HO_2^{\bullet} + Fe^{2+} \longrightarrow HO_2^- + Fe^{3+} \tag{65}$$

$$O_2^{\bullet -}\, Fe^{3+} \longrightarrow O_2 + Fe^{2+} \tag{66}$$

$$HO_2^{\bullet}{}^{+}\, H_2O_2 \longrightarrow O_2 + 2OH^{\bullet}{}^{+}H^+ \tag{67}$$

$$\begin{aligned} Fe^{2+} + O_2 \rightleftharpoons FeO_2^{2+} &\xrightarrow{2H_2O} \\ &Fe^{4+}(OH^-)_2 + H_2O_2 \end{aligned} \tag{68}$$

$$Fe^{4+}(OH^-)_2 \longrightarrow Fe^{3+}(OH^-) + OH^{\bullet} \tag{69}$$

$$Fe^{2+} + FeO_2^{2+} \xrightarrow{2H_2O} 2Fe^{3+}(OH^-) + H_2O_2 \tag{70}$$

$$Fe^{2+} + Fe^{4+}(OH^-)_2 \longrightarrow 2Fe^{3+}(OH^-) \tag{71}$$

$$Fe^{2+} + H_2O_2 \rightleftharpoons Fe^{2+}(HO_2^-) + H^+ \tag{72}$$

$$\begin{aligned} Fe^{2+}(HO_2^-) + OH^- &\rightleftharpoons (OH^-)Fe^{2+}(H_2O^-) \\ (OH^-)Fe^{2+}(H_2O^-) &\longrightarrow (OH^-)FeO^{2+} \\ (OH^-)FeO^{2+} &\longrightarrow Fe^{3+}(OH^-) + OH^{\bullet} \end{aligned} \tag{73}$$

$$Cu^+ + O_2 \rightleftharpoons CuO_2^+ \rightleftharpoons Cu^{2+} + O_2^{\bullet -} \tag{74}$$

$$Cu^+ + O_2^{\bullet -} \overset{2H^+}{\rightleftharpoons} Cu^{2+} + H_2O_2 \tag{75}$$

$$CuO_2^+ + Cu^+ \xrightarrow{2H^+} 2Cu^{2+} + H_2O_2 \tag{76}$$

$$Cu^+ + H_2O_2 \rightleftharpoons CuO^+ \tag{77}$$

$$CuO^+ + H_2O \rightleftharpoons Cu^{2+} + OH^- + OH^{\bullet} \tag{78}$$

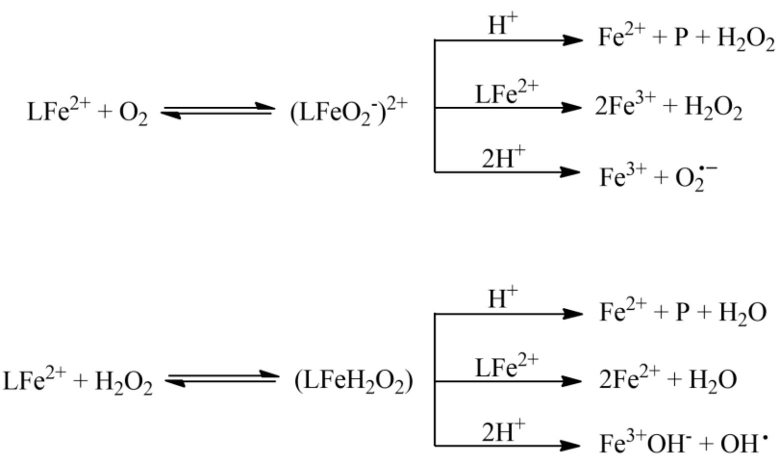

Figure 6. The mechanism of O_2 activation with iron coordination compounds [10].

Based on this approach, the so-called "inhibiting capacity" parameter of water environment can be calculated - $\sum k_i[S_i]$, s^{-1} which is an effective rate first-order constant of OH• radicals decay in natural water [46,86]. In this case k_i is the rate constant of OH• interaction with "trap", with a value usually within the limits 10^8-10^{10} M/s.

In natural water, the content of H_2O_2, decomposing into OH• radicals, is 10–50% [87]. Tentatively, the rate of OH• initiation (W_i) and the rate of photochemical formation of H_2O_2 in water environment (W_f) can be considered as $W_i \approx W_f$. Proceeding from the value of parameter $\sum k_i[S_i]$, the stationary concentration of OH• and efficient rate constant of radical oxidation of any pollutant (k_{RH}) can be estimated by Eq.(79).

$$[OH^\bullet] = \frac{W_i}{\Sigma k_i[S_i]} \text{ and } k_{RH} = $$
$$= k_{OH^\bullet+RH}[OH^\bullet] = k_{OH+RH}W_i/\Sigma k_i[S_i] \quad (79)$$

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

Based on these considerations, a dynamic chemical-biological redox model of natural water medium was proposed, considering that both the biotic and abiotic processes of oxidative and reductive equivalents constantly proceed within it (Figure 7) [10,25,27]. Thus, the biotic and abiotic processes with the involvement of oxidative and reductive elements constantly proceed in natural water. The general result of their interaction is determined by the ratio and interaction efficiency of the inner oxidative flows in water reservoirs (hydrogen peroxide), and substances-reducers (DH_2). The blue-green algae in natural water are used by the substances-reducers to neutralize the toxic action of H_2O_2 (the latter even in concentration of 10^{-5} to 10^{-6} M suppresses these algae photosynthesis) [16,29].

In case the oxidative element predominates ($W_f > W_r$), the oxidative condition of the environment will be realized. The reducers (DH_2) in water will be easily oxidized with hydrogen peroxide (more exactly, with radicals which will further decay), or will initiate the conjugate radical self-purification processes of water basins containing the pollutants (RH).

In the inverse case (the flow of reducers will exceed the flow of H_2O_2, *i.e.*, $W_f < W_r$) the quasi-reducing redox state of water environment is observed. Thus, the various toxic effects appear in water, mainly connected with the rapid growth of blue-green algae in the reducing conditions and increased pH of medium sometimes up to ten and even higher. In these conditions, the pathogenic flora and intestinal pathogenic organisms (such as *Vibrio cholerae*) appear.

In all these processes, taking place in natural water, an important role is played by the hydrated metal ions, especially iron and copper, metal hydroxides, and also their complex compounds with numerous ligands that catalyse a variety of redox reactions. Iron(III) compounds are most often found in water medium. The solubility product (SP) for Fe(III) reaches the value $3.8 \cdot 10^{-38}$, at pH> 4 equilibrium concentration of iron aquatic form $[Fe^{3+}_{aq}]$ is low compared to hydroxide, at pH≈ 5 it is present in water solution in the form $Fe(OH)_2^+$, and at pH> 6 it exists in the form $Fe(OH)_3$. The maximal concentration of $Fe(OH)_3$ in soluble form is $2 \cdot 10^{-7}$ M [88].

The content of Cu^{2+} ions in surface water is approximately $3 \cdot 10^{-7}$ M. Within the limits pH 7-9 mostly monohydroxocomplex $Cu(OH)^+$ will be in homogeneous form. However, there are numerous ligands in natural water which form various kinds of metal complex compounds.

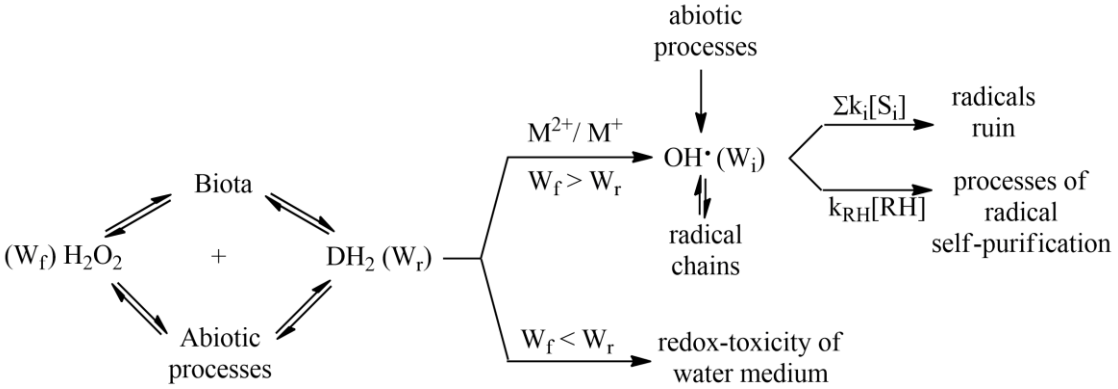

Figure 7. The dynamic chemical-biological model of natural water [10].

Iron hydroxide dissolving will take place only in the presence of ligands capable to bind iron very strongly into the complex compound, for example, the chelate-forming ligands of EDTA type. Copper hydroxide dissolving will occur with a much lower complex-forming capacity of ligand. Various ligands of organic nature are also present in natural water: carbonic acids, amino acids, sulphur-containing compounds, ethylenediamine, and pyridine. However, the main environmental ligands are fulvic and humic acids which form stable compounds with the metal ion. Therefore, the presence of numerous ligands in natural water, as well as of various pollutants (which can also be ligands), render the influence on pH value and the share of different metal complex compounds.

In its turn, the change in the redox potential of the metal ion during the complex compound formation, modification in metal coordination sphere lability, its hydrolytic stability, its composition and the presence of numerous substrates and oxidants (O_2, H_2O_2, *etc.*) promote the catalytic processes running through the various mechanisms, resulting in the self-purification of natural water. Of course, the dominating “motor force” of this overall process is solar light.

Therefore, the redox processes play an important role in the natural water self-purification. Hydrogen peroxide formation within the surface water layers mainly occurs due to the photochemical processes, whereas in the bottom water layers – mostly due to the catalytic oxidation with molecular oxygen of substances generated by water microorganisms. The rate of reducers DH_2 formation depends on the amount and specific diversity of water microorganisms. The most efficient catalysts of pollutant oxidation in natural water in homogeneous form are copper ions and complexes, and in heterogeneous form - Fe(III) and Mn(III) hydroxides. The radicals OH•, HO_2•, and others, involved in the dissolved pollutants oxidation, are, as a rule, the products of hydrogen peroxide decomposition.

The multi-annual research of fresh natural water bodies, which allowed to reveal different ways of their self-purification, promoters and inhibitors of chemical and biological processes, and, finally, the involvement and behaviour of various reducers and oxidants have been performed by Moldovan scientists [25,27,46,47,74,78,85]. This paper is not only a review of the available literature on this subject, moreover, it also summarizes the proper experience of the author and his team based on the original long-term studies since the late 1970s. The studies have been based on principles of chemical kinetics and catalysis, and include the catalytic reactions, free radical oxidation, decarboxylation, hydrolysis and other reactions.

Conclusions

The data on hydrogen peroxide presented in this paper suggest its unique properties and applications, in spite of the seeming simplicity of its molecule and relatively short-term lifespan. The natural counteraction between the two opposite flows - oxygen and reducers, practically in all cases yields hydrogen peroxide as an intermediate, which, in its turn, is involved in chemical and biological processes, such as living cells and organs metabolism, self-purification of natural waters, substances (including pollutants) synthesis and decomposition.

It was shown that the occurrence of the redox reactions with H_2O_2 participation is possible due to the catalytic activity of transition valence metal ions, specifically, Fe(II) and Fe(III), Cu(I) and Cu(II) and Mn(IV) – in case of the environmental processes in water, soil and atmosphere. In case of living organisms, catalytic activity is manifested by enzymes such as catalases, peroxidases, reductases, *etc.*

It was demonstrated that such reactions, accompanied with one- or two electron transfer, can occur both in the outer- and inner-sphere way, considering the two possible types of hydrogen peroxide molecule coordination – monodentate and bidentate. The three main types of the reaction mechanisms of catalytic oxidation with H_2O_2 participation have been distinguished: cyclic, radical-chain, activation mechanism. The stages of these complex processes have been identified, along with the main intermediate products, the most significant of them being active radicals including OH•-radical and superoxide-radical which are the most active species. Formation of partial charge transfer metal complexes in these processes has been suggested.

The broad implication of hydrogen peroxide in numerous processes significant for environment, ecology, living organisms and overall anthropogenic activity makes it a subject of permanent research interest. Hydrogen peroxide formation and decomposition in catalytic system may serve an ideal redox model, therefore, its comprehensive studies can afford determining the mechanisms of other, more complicated, processes.

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