for the technical calculations for the installations in which salts of perchloric acid could be rendered harmless (converted to harmless chlorides) and nitrites and nitrates could be converted to free nitrogen. The nutrient substrate consisted of readily oxidisable organic substrates present in domestic effluents, surplus activated sludge, processed biofilm from normal biological sewage works, effluents from meat-packing plants, and others.

The biological method for the purification of effluents by removal of Cr(VI) devised in the scientific-industrial combine Soyuz in Lyubertsy is now being used in various branches of the national economy, since waste waters containing this harmful toxicant occur extensively not only in the chemical industry but also in a wide range of other industries (especially in the electroplating industry).

With the aid of the method recommended for the purification of chromium-containing effluents it is possible to achieve a three-five-fold reduction in expenditure on the construction of installations and engineering equipment and a five-seven-fold reduction in operating costs depends on the flow-rate of the effluents, the chromium concentration, and the required degree of purification (for each cubic metre of chromium-containing water which may be decontaminated) in comparison with the less expensive installations for the chemical removal of Cr(VI) from effluents. The cost of purifying one cubic metre of chromium-containing industrial effluent in a mixture with domestic waste water is no greater than 5–10 kopeks.

It has been confirmed by reliable medical sources that the microorganisms, which reduce Cr(VI) to Cr(III), are harmless and are not causative agents of diseases. An installation for the biological purification of water to remove Cr(VI) by a batch process has been operating trouble-free since 1974 in the scientific-industrial combine Soyuz in Lyubertsy. A facility for the continuous purification of effluents to remove Cr(VI) has been in operation for ten years in the metal-coating workshop at the "Kommunar" automobile factory in Zaporozhe providing a cost savings of 65,000 roubles. An installation for the continuous purification of ground water in order to remove Cr(VI) operating at an efficiency of 8000 cubic metres per day is now in the second year of operation in the Aktyubinsk Chromium Compound Plant (ACCP). The purified water and the chromium hydroxide obtained are used in industrial processes. A cost savings of 4.4 million roubles has been achieved. A batch process facility is being installed in the Moscow factory "Frezer". It is intended to introduce additional facilities for the removal of Cr(VI) from effluents in the automobile factory "Kommunar" and ACCP. Work will be carried out within the guide-lines of the All-Union programme "Biotekhnika" (Biotechnology) in collaboration with the Institute of Biology of Water Reservoirs, Academy of Sciences of the USSR, on the development of techniques for the removal of Cr(VI) from effluents in different branches of industry and for the reprocessing of chromium-containing dumps in ACCP which amount to five million tonnes.

An economical justification study for constructing installations in the Lyubertsy aeration station for decontaminating treated chromium-containing solutions by a biological method for 900 factories in Moscow and the Moscow district and utilising the extracted chromium is currently being carried out. The anticipated cost savings is 30 million roubles per annum. In 1988 an agreement was reached with the Italian firm Olivetti to introduce the method for biological removal of Cr(VI) in Italy. Three Italian firms are currently expressing an interest in acquiring a license.

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The determining role of the redox process in the formation of the quality of the aqueous environment

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One of the factors determining the adverse effect of man on the environment is the imbalance of redox processes in water reservoirs involving oxygen and hydrogen peroxide, agents which play a key role in the determination of water quality in the natural environment.

In recent years numerous articles have appeared in the literature on the determination of the content of hydrogen peroxide in different water systems, seas, and oceans[2,3] rivers and lakes,[4–7] and in rain and snow[8,9] and even in mineral ice samples in Greenland and in Antarctica.[10] All authors arrive at the same conclusion. Hydrogen peroxide is an inherent component of the natural aqueous environment. It can even be demonstrated that before the intervention of man the evolution of aerobic life on Earth occurred not only in the presence of oxygen and water but also in the presence of hydrogen peroxide.

Hydrogen peroxide in an aqueous environment may arise from four main sources: 1) entry from the atmosphere; 2) formation as a result of catalytic processes for oxidation involving oxygen; 3) formation as a result of photochemical reactions in the presence of sunlight, and 4) formation as a result of biological emission.

When the atmosphere becomes polluted there is an abrupt curtailment of the influx of hydrogen peroxide "from the sky" to the Earth's surface. In environmentally clean regions snow and rain contain $10^{-5}-10^{-4}$ M hydrogen peroxide, whereas according to the data obtained by the present author and co-workers hydrogen peroxide may be totally absent from regions subjected to atmospheric pollution. In turn this leads to a deterioration in the condition of soil ecosystems.

The present author has shown that the presence of hydrogen peroxide in moisture in the soil (in irrigation water) significantly enhances seed germination and plant growth, shortens the duration of the vegetative period, and increases the yield of agricultural crops.

An ecologically safe method for stimulating plant growth devised by the present author is being introduced in Moldova for glasshouse and field cultivation. Results obtained from trials with soya-bean and tomato plants indicate that an increase in yield equivalent to 500–700 roubles/hectare is being achieved.

Catalytic and photochemical processes involving oxygen are of great importance in the formation of hydrogen peroxide within reservoirs.

In the catalytic processes hydrogen peroxide accumulates during the oxidation of reducing substrates which are more reactive with oxygen than with hydrogen peroxide. An increase in the hydrogen peroxide content is usually found in areas in which untreated municipal sewage is discharged.

Sunlight is a determining factor in processes in which hydrogen peroxide is formed in surface waters and in summertime photochemical processes involving microscopic algae resulting in the formation of hydrogen peroxide are most important.[11] Examples in which hydrogen peroxide is formed as a secondary product of photosynthesis have been described in the literature.[12] With the aid of various microscopic algae the author has observed and characterised another effective channel through which the ultraviolet component of sunlight exerts an effect on algae.

The manner in which the hydrogen peroxide content in the natural aqueous environment changes over a 24-hour period is shown in Fig. 1. With the aid of a technique devised by the present author and co-workers[12] for the determination of hydrogen peroxide it is possible to make measurements with an accuracy of 10^{-7} M.

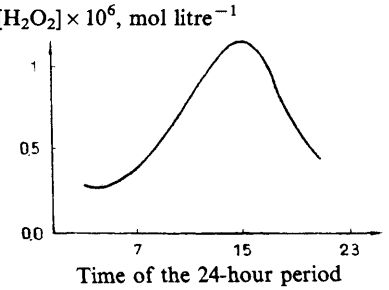


Figure 1. Diurnal course of the hydrogen peroxide content in a natural water.

The fact that the hydrogen peroxide content of natural waters is dependent on solar activity indicates that this molecule is present at a quasi-stationary level in the aqueous environment, i.e. in addition to hydrogen peroxide formation processes exist for the decomposition of hydrogen peroxide.

It has been found that both of these processes, the formation and decomposition of hydrogen peroxide, are accompanied by the efficient generation of reactive particles in the natural water and that these particles are involved in self-purification of the aqueous environment (O_2 and OH radicals and metal complexes in anomalously high oxidation states). Studies carried out by the present author and co-workers have shown that algae involved in the formation and decomposition of hydrogen peroxide promote radical and peroxidase oxidation of contaminating substances. In the summer period of the year an effective channel exists in the natural aqueous environment for the biogenic initiation of self-purification processes (Fig. 2).

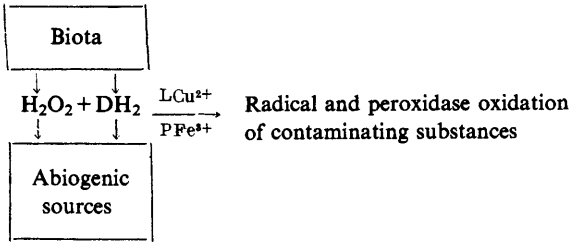


Figure 2. A chemico-biological model for the self-purification of a natural aqueous environment.

The efficiency of radical and peroxidase oxidation of contaminating substances is determined by the rate of photochemical formation of hydrogen peroxide. The present author has calculated that 10–50% of the hydrogen peroxide is decomposed in natural waters with the formation of free OH-radicals and other reactive particles.

A feature of the kinetics of hydrogen peroxide decomposition by microscopic algae is that the process is of zero or first order with respect to the hydrogen peroxide concentration, and in both cases the rate of the reaction is proportional to the algal biomass.[14]

The first-order reactions include the decomposition of hydrogen peroxide by catalase, whereas the zero-order reactions include the peroxidation of reducing substances formed in dehydrogenase reactions. The rate of the zero-order reactions is determined by the rate of formation of these substances acting as reducing agents. Under quasi-stationary conditions the rates of formation and decomposition of hydrogen peroxide are equal to:

$$W_f = k_{f,1} + k_{f,2}\,[\mathrm{B}],$$
$$W_d = (k_{d,1} + k_{d,2}\,[\mathrm{H_2O_2}])\,[\mathrm{B}],$$

so that the quasi-stationary concentration of hydrogen peroxide in the natural aqueous environment is determined by the relationship:

$$[\mathrm{H_2O_2}] = \frac{k_{f,1} + (k_{f,2} - k_{d,1})\,[\mathrm{B}]}{k_{d,2}\,[\mathrm{B}]} \approx \frac{k_{f,2} - k_{d,1}}{k_{d,2}},$$

where $k_{f,1}$ and $k_{f,2}$ are the effective rate constants for hydrogen peroxide formation, and $k_{d,1}$ and $k_{d,2}$ are the rate constants for hydrogen peroxide decomposition.

The main conclusion from this simplified picture is that two situations may arise in the aqueous environment depending on whether the flow of hydrogen peroxide or reducing substances is predominant.

The redox state exhibits a diurnal or seasonal course in accordance with the change in solar activity and water temperature. It has been found that the transition of the environment from a state in which hydrogen peroxide is present in the water to a state in which reducing substances (which readily interact with hydrogen peroxide) are present is of great significance for aqueous ecosystems. When quasi-reducing conditions are formed in the water, the water

becomes toxic for organisms which undergo intensive water exchange with the environment.

Fish larvae in the early stages of development obtained from artificially breeding sturgeons (Chondrostei) and phytophagous fish serve as a bio-assay of the change in redox state of the aqueous environment (Fig. 3).

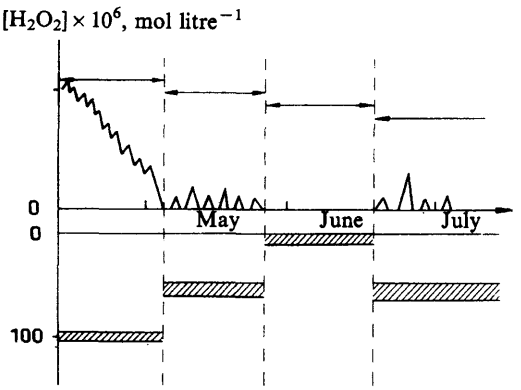


Figure 3. Seasonal time-course of the redox-state and toxicity of the aqueous environment in reservoirs in which blooms of blue-green algae have developed.

Under conditions in which toxic reducing conditions have been formed in the water, addition of hydrogen peroxide to the water leads to the normalisation of larval development. The present author and co-workers have developed and introduced into VORZe Fish Breeding Stations a method for breeding larvae of sturgeons which is based on the addition of further quantities of hydrogen peroxide to the water in which toxic reducing conditions have arisen.

By comparing the results obtained from the determination of the content of hydrogen peroxide in the Volga water with data on the death rate of larvae in Fish Breeding Stations it was possible to conclude that the seasonal changes in the redox state in the Volga began in 1976. Prior to this data the factory produced more than twelve million sturgeon fry per annum, whereas after this data this figure was less than eight million. By addition of hydrogen peroxide to the water it has been possible to breed more than five million additional physiologically sound Caspian sturgeon fry (an increase of more than one million fish above the previous maximum value).

Evidently a change in the redox state of the aqueous environment is a decisive factor in the reduction of the breeding potential for fish which spawn in the summer period of the year.

Two years ago a new problem arose with sturgeons. Stratification of muscle tissue in sexually mature fish and egg resorption was observed. Apparently this phenomenon was also associated with the disruption of the redox state in the Volga which occurred in 1976, since the commercial returns on the fish (catches) begin precisely within 10–12 years. In fact now the results of those impairments in the physiological development of the fish larvae which occurred in the larval stage can be seen.

The blue-green algae act as generators of reducing substances which leads to a change in the redox state of the natural environment.[15] Under conditions of interspecies competition they release into the environment certain substances which readily interact with hydrogen peroxide (Fig. 4).

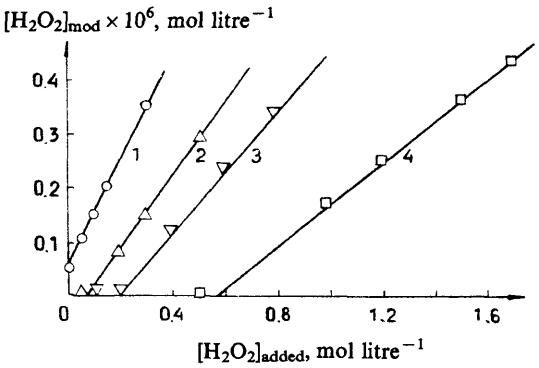


Figure 4. Interaction between hydrogen peroxide and substances acting as reducing agents which were released by blue-green algae (dark conditions).

Note. The key to the numbered plots are not given in the original manuscript (Ed of Translation).

The rate of generation of the reducing substances is determined by the ecological factors, temperature and illumination.

Although the formation of reducing conditions in the water is not accompanied by any significant changes in hydrochemical parameters, several adverse consequences immediately arise.

1. The hydrogen peroxide disappears, the hydrogen peroxide which is essential for the normal operation of physiological processes in organisms with an intensive water-exchange mechanism (the same fish larvae in the early stages of development).

2. There is a transition of copper into the biologically unavailable non-reactive reduced form, apparently in the form of a complex with sulphydryl compounds. Consequently respiratory apoenzymes may be synthesised and these apoenzymes contain no copper in the active centre in the early stages of development of the aquatic organisms. Such cases have been described in the literature in regard to plant cells.[16] It is of great interest that when the biosynthesis is terminated the appearance of copper in the medium does not lead to the activation of the apo-enzyme.

3. It is possible that the reducing agents themselves, which are involved in the formation of the reducing state of the aqueous environment, have a toxic action. One cannot rule out the possibility that substances released by blue-green algae into the environment constitute one variety of the so-called algotoxins.[17] Research workers in many countries throughout the world have studied the algal toxins, which appear in reservoirs in which blooms of blue-green algae have arisen. Cases in which large numbers of birds and animals have perished are known and there have been instances of human food poisoning when water from "blooming" reservoirs has been consumed.

4. There is a sharp decline in the self-purifying capacity of the aqueous environment. Under these conditions toxic compounds of natural or anthropogenic origin may accumulate in the water.

5. The development of a pathogenic microflora is found, and the reducing environment favours the development of these organisms. Cases of large-scale outbreaks of human diseases such as heptatitis, cholera, amoeboid meningitis, etc. have been reported. It has been suggested that the death of large numbers of Baltic seals from distemper was associated with the blue-green algal blooms in the Baltic Sea. One should note that even in small quantities hydrogen peroxide inhibits photosynthesis in blue-green algae and suppresses the mass development of the algae. Thus the control of processes which determine the content of hydrogen peroxide in the natural environment is an urgent problem.

The present author considers that one of the factors which promote an imbalance of reservoir redox processes, in addition to the regulation of river discharge and contamination of waters with nitrogen- and phosphorus-containing mineral compounds, is the fact that the possible effect of the redox state of the municipal effluents purified by biological methods has not been taken into account.

The studies carried out by the present author on the municipal sewage works in Belgorod showed that under oxygen deficient conditions before transfer to the aeration taken reducing substances appear in the effluents which are toxic to aerobic organisms and which can be titrated with hydrogen peroxide. Furthermore these toxic substances partially pass through the biochemical sewage purification plant. At the same time the readily oxidisable compounds are retained in the aeration tank and on entry into a reservoir these compounds would promote the formation of hydrogen peroxide and detoxify the reducing toxins. This implies that the sewage plant for the biological purification of municipal effluents may act as a kind of filter which inhibits the entry of hydrogen peroxide into the water thereby exerting a pronounced effect on the redox processes within the reservoir.

This suggestion is not without foundation. One may recall that sturgeons began to perish in the Volga in 1976. In the same year sewage plants for the biochemical purification of effluents of large cities in the Volga basin came into operation.

A new consequence of the imbalance of redox processes within the reservoirs and the associated radical-mediated processes in natural waters was the appearance of the super-oxidising state of the aqueous environment in a number of reservoirs. This was most pronounced in the Pripyat and Dnepr rivers after the Chernobyl disaster. The super-oxidising state apparently arises during extreme intensification of radical-associated oxidation processes. The carriers of superoxidised equivalents are sorbed on to suspended particles. The nature of these components has not been precisely determined but EPR data indicate that they could be microcolloidal particles of manganese in mixed oxidation states (+3, +4).

During the formation of the superoxidised state of the environment in the water adult breeding fish {phytophagous and fish caught in a fine-mesh [sic. A type of fish? (Ed. of Translation)] net} begin to perish in fish farms and in natural reservoirs. The addition of reducing agents, for example ascorbic acid, to fish farming ponds in which the superoxidised state has been formed, leads to the normalisation of the situation.

Thus redox processes and the associated radical processes play an exceptionally important role in the formation of the quality of the natural aqueous environment and in the resolution of problems of nature conservancy. The latter is associated with the intensification of purification of effluents, the regulation of water quality in fish farms, the improvement of water quality in irrigation farming, the development of water-monitoring systems, and prevention of blooming in reservoirs used as sources of drinking water, etc. The increasing ecological pressures in many regions of the USSR dictates the need for a further extension of studies in the field of hydrochemical processes. Hopefully a real key for the control of the quality of natural waters will be found.

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