Chapter 11
New Kinetic Parameters for Natural Water Quality Assessment

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ABSTRACT

The work describes the processes occurring in the natural waters from a kinetic perspective, highlighting the role of various components of the oxygen cycle and putting into evidence two water quality parameters that evaluate the contents in two intermediate products of oxygen reduction up to water, namely hydrogen peroxide and OH radicals. The flows of oxidative equivalents, hydrogen peroxide, and reducers that interact with it are evaluated by the redox state indicator. The pollution by OH "traps" is evaluated by measuring the inhibition capacity ($\Sigma k_i,OH[S_i,OH]$) parameter. In this work, the authors present the pollution assessment and water self-purification process supported by hydrogen peroxide and OH radicals during the years 2015-2019. The monitored objects were Nistru River in the Dubasari-Vadul-lui-Voda dam segment; its tributaries, Raut and Ichel, at the mouths of confluence with the river; and the Ghidighici and Danceni lakes, the surface water bodies in the Republic of Moldova.

INTRODUCTION

Assessment of the water quality serving as a living environment for hydrobionts, by comparison, chemical quality indicators with the values of maximum allowable concentrations (MAC), proved to be less efficient in certain situations when some toxicity factors affected the hydrobionts. In this case, the hydro-

chemical parameters did not indicate the establishment of such critical states. The situations occurring in aquatic ecosystems, when typical parameters did not signal the critical states, imposed the revision of evaluation of the biological value of habituation in natural waters. Taking into consideration that for natural aquatic systems the biogeochemical cycle of oxygen is indispensable, the different indicators of natural water quality, assessing the pollution and self-purification processes, based on the content and dynamics of intermediate products of the biogeochemical cycle of oxygen, were elaborated and approved. The advantage of these parameters consists in envisaging, beyond the pollution, the development of unfavorable conditions for the aquatic community, such as hydrogen peroxide deficiency, development of blue-green algae, lack in biologically available copper forms, intensification of radical processes, disruption of the biogeochemical cycle of manganese.

BACKGROUND

Due to the sunlight, abiotic redox processes, and metabolic activity of hydrobionts in natural waters, the formation of oxygen and its intermediate reduced forms occur. These derivatives form the flow of main oxidative equivalents in aquatic systems. During photosynthesis, the simultaneous yielding or reception of four electrons takes place only in certain specific biological systems, more common being the processes of transfer of one or two electrons. As a result, intermediate products of oxygen reduction are generated, namely singlet oxygen ($^1O_2$), superoxide radicals ($HO_2^\bullet/O_2^{\bullet-}$), hydroxyl radicals ($^\bullet OH$), hydrogen peroxide ($H_2O_2$) (Sychev et al., 1983).

In natural waters, the action of sunlight causes the effective generation of singlet oxygen ($^1O_2$) (Hoigne et al., 1988; Sandvik et al., 2000; Marchisio et al., 2015). The stationary concentration of these particles constitutes 10^{-14}-10^{-12} M. This value becomes even higher, the higher is the content of organic substances dissolved in water.

The first stage of oxygen activation is concluded by the formation of superoxide radicals ($HO_2^\bullet$), which in natural waters can also be found in the dissociated form of superoxide radical anion ($O_2^{\bullet-}$) (Petasne and Zika, 1988; Ernestova and Skurlatov, 1995; Fujii and Otani, 2017). Out of these two forms, the proton form has higher oxidizing properties. Following the various processes in natural waters, the stationary concentration of this particle varies between 10^{-8}-10^{-9} mol/L. According to the redox and acid-base characteristics, the most stable intermediate product of O_2 reduction is hydrogen peroxide (Sychev et al., 1983). In natural aquatic systems, the oxidant is formed predominantly in photochemical processes (Cooper, 1988; Shtamm, 1991; Ernestova and Skurlatov, 1995; Mostofa et al., 2013). A certain amount of H_2O_2 is formed as a result of the redox-catalytic processes with the participation of organic substances and oxygen (Duca, 1997, 2012; Duca et al., 1997, 2002), and another part is provided by biological processes (Batovskay et al., 1988; Shtamm, 1988). Like for the other biogenic substances, the concentration of H_2O_2 in natural waters is influenced by the ratio between the rate of its formation and decomposition. The multiple measurements on different aquatic bodies have shown that the stationary concentration of H_2O_2 in natural waters is of the order of 10^{-6}-10^{-5} mol/L (Sinelnikov, 1971; Shtamm et al., 1991; Duca and Gladchi, 2000). Also, H_2O_2 is a form of preservation of hydroxyl radicals, as a dimer $(OH)_2$. About 30% of hydrogen peroxide breaks down with the formation of OH radicals (Shtamm et al., 1991).

Hydroxyl radicals are the products of monoelectronic reduction of hydrogen peroxide (Sychev et al., 1983). The main mechanism of OH radicals initiation in natural waters is considered the photochemical one (Zhou and Mopper, 1990; Vaughan and Blough,1998; Landrino et al., 2006), namely, the photolysis

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