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Chapter 3

Redox Self–Purification Mechanism of Natural Waters With the Involvement of Thioglycolic Acid and Thiourea


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ABSTRACT

This chapter studied the influence of TGA and TU on the self-purification processes of aquatic systems on model systems, whose composition was modeled to be as close as possible to the natural waters. As a source of irradiation was used the DRT-400 lamp and the Solar Simulator, Oriel model 9119X, the emission spectra of which overlap with the emission spectrum of the Sun. The results of the research show that on irradiation, TGA can regenerate an additional amount of OH radicals, thus contributing to the intensification of water self-purification processes. But in the presence of transition metals, such as Cu (II) and Fe (III), it has been established that the intensity of self-purification processes decreases due to the formation of the mercaptides, whose catalytic activity is low. Unlike TGA, TU leads to decreasing the intensity of the self-purification processes of aquatic systems, through the intense consumption of OH radicals, and at the same time on the interaction with transition metals, such as Cu (II) and Fe (III), form stable complexes with low catalytic activity.

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INTRODUCTION

Decades of research have demonstrated that natural waters represent an unbalanced open kinetic system, with various redox processes involving pollutants, oxidizing agents, metal ions and their complexes, etc. Research in the field has shown that thiol substances, especially those of allochthonous origin, are hardly oxidized by dissolved oxygen, but easily by hydrogen peroxide. Thiol substances reduce or remove the content of hydrogen peroxide, which plays an important role in regulating the redox state of natural waters, thus contributing to the formation of the quasi-reducing state of waters, which is toxic to hydrobionts. At the same time, thiols, upon interaction with transition metal ions, form stable compounds, whose catalytic activity is low. Some thiols, such as thiourea, inhibit the activity of microorganisms in the biological treatment of wastewater. In this context, the main goal of this research was to evaluate the participation of thioglycolic acid (TGA) and thiourea (TU) in redox processes on model systems, to predict their influence on the self-purification capacity of natural aquatic systems.

BACKGROUND

Water is an essential component of the natural environment and the basis of many productive activities, consequently, all human societies have been developed around it. During recent decades, there has been constantly increasing concern about natural water quality and different problems related to the presence, utilization, and management of water resources (Vaseashta et al, 2021). Aquatic systems may be represented as redox catalytic and photochemical open-type multi-component. This fact is largely due to the redox components, the most important of which are: oxygen, hydrogen peroxide, solar radiation, transition metal ions, and complexes, as well as autochthonous and allochthonous reducers (Gladchi et al., 2008; Duca et al., 2008; Bunduchi et al., 2006; Patel et al., 2019).

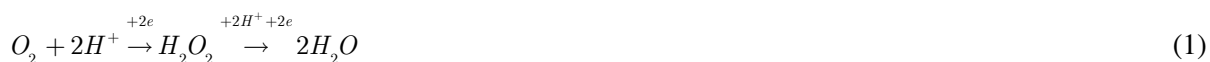
Dissolved oxygen is the most prevalent oxidative component in natural waters, between 0 and 14 mg/L, and is controlled by two main processes: photosynthesis and biotic and abiotic consumption (Gladchi et al., 2022a; Duca & Travin, 2020; Song et al., 2019; Schmidtko et al., 2017; Liu et al., 2018). Oxygen was the chemical substance that determined the change in the redox state of natural waters from reducing to oxidizing, with the appearance on Earth of autotrophic organisms that produce and eliminate molecular oxygen in the aquatic environment (Foyer et al., 2003). In addition to its vital function, oxygen is also a strong oxidizer, but O_2 is normally inert due to its triplet structure (Duca & Vaseashta, 2020, Vaseashta & Duca, 2022). Therefore, for the involvement of oxygen in oxidation processes, it must be activated, either with sunlight or substances with reducing properties (Larson & Mccord, 1977; Wang et al., 2020). Some of the special components of the chemical composition of natural waters are transition metal ions (Subramanian & Madras, 2017; Lo Conte & Carroll, 2013; Chu et al., 2017; Sun et al., 2011). In the presence of dissolved oxygen, metal ions are in an oxidized state. They help to activate oxygen and hydrogen peroxide, which subsequently engage with different substrates and help to convert them. The following active species are generated in natural waters as a result of the activation of molecular oxygen: 1O_2 , $O_2^{\bullet-}$, $\cdot OH$, and H_2O_2 (Morris et al., 2022; Mill et al., 1980). The ranges of these species concentrations in natural waters have been determined by the authors of various papers: $[^1O_2] = 10^{-14}$ - 10^{-12} M; $[HO_2^{\bullet}] = 10^{-9}$ - 10^{-8} M; $[\cdot OH] = 10^{-18}$ - 10^{-15} M; $[H_2O_2] = 10^{-6}$ - 10^{-5} M (Morris et al., 2022; Patterson & Myers, 1973; Wong et al., 2003; Yuan et al., 2018).

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The most stable intermediate product of oxygen reduction in natural waters is hydrogen peroxide (Gladchi et al., 2022b; Duca et al., 2002). According to numerous academic articles, the formation of H_2O_2 inside the body of water during photochemical processes is the primary source of H_2O_2 in natural waters (Garcia et al., 2020; Fujii & Otani, 2017; Yoon et al., 2021). Studies on how radiation affects the photochemical generation of H_2O_2 in natural waters have shown that UVB radiation (wavelength range 280-315 nm), although it reaches the Earth's surface in the smallest amount, has a large contribution - 48%, to the formation of hydrogen peroxide. The contribution of UVA radiation (315-400 nm) is 24%, and the rest of the 28% is accounted for visible radiation (400-700 nm) (Häkkinen et al., 2004; Gerringa et al., 2004; García et al., 2018).

The abiotic decomposition of H_2O_2 includes catalytic decomposition mechanisms. Under neutral pH settings, hydrogen peroxide from the natural aquatic environment undergoes decomposition processes, but only when copper ions or iron complexes are present, which act as catalysts in this process (Duca & Vaseashta, 2020; Shtamm et al., 1991).

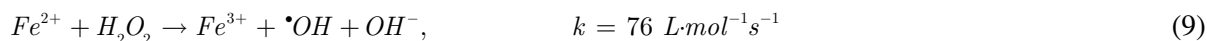
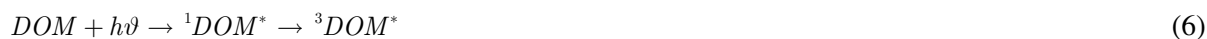
Redox processes, with the participation of oxygen, form a system in which the equilibrium is established very slowly, so the oxidation rates of reducing substances with molecular oxygen are lower than with hydrogen peroxide, which is characterized by a system in which the equilibrium is established quickly. But the slow system has some advantages, namely that the concentration of oxygen in the aquatic environment is much higher than that of hydrogen peroxide, and when the waters are highly polluted with organic substances, which are eventual reducing agents of hydrogen peroxide, it is completely consumed, and then the main oxidant is oxygen. In addition to this, in the oxidation process with the participation of oxygen, additional amounts of H_2O_2 are obtained, because it is an intermediate product in the process of reducing molecular oxygen to water (Duca et al., 2002; Duca & Vaseashta, 2020; Gladchi et al., 2020).



Based on the molecular configuration and oxidative potential (E_0), the most reactive particles in the biochemical cycle of oxygen are OH radicals. The OH radical concentration in surface waters range from 10^{-17} M to 10^{-15} M. The most important sources of OH radicals in surface waters are their formation during the photolysis of many compounds such as DOM (dissolved organic matter), nitrates, nitrites, hydrogen peroxide, other peroxides, Fe(III) monohydroxocomplex, etc. (Vione et al., 2006; Brezonik & Fulkerson-Brekken, 1998; Gong et al., 2021; Bu et al., 2020; Song et al., 2020; Southworth & Voelker, 2003):



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The presence of transition metals in natural waters is of special interest. The most widespread transition metal in natural waters is iron. The iron concentration in surface waters is $\approx 10^{-5}$ M, copper ($\approx 10^{-7}$ M), cobalt, manganese, nickel, and chromium ($\approx 10^{-7}$ - 10^{-6} M) (Munteanu et al., 2011). The chemical speciation of iron (Fe) in natural waters is influenced by pH value and the presence of ligands. It was determined that the trivalent iron ion (Fe(III)), which forms complexes with ligands, predominates in the composition of natural waters. It is known that the photolysis of hydroxo-complexes of Fe(III) is accompanied by the formation of OH radicals in water, but as the pH increases, the effectiveness of this process decreases (Yuan et al., 2018; Duca et al., 2002; Garcia et al., 2020). The Fe(II) ion exists within pH values 6-10, predominantly in the form of $FeHPO_4$. Thus, the balance $Fe^{2+} \rightleftharpoons Fe^{3+}$ is widespread in nature and is of great importance in redox processes (Sun et al., 2011; Seraghni et al., 2021; Ouyang et al., 2020). Besides iron ions, copper ions are of particular interest, possessing important catalytic properties in redox aquatic environment transformations. Depending on the pH value, the copper ions are in states Cu^{2+} (pH=6.5) and respectively Cu^+ (pH=6.5-7.5). Unlike Fe(III) ions, Cu(II) ions participate in free radical, $\bullet OH$ and $O_2^{\bullet -}$, formation reactions within the pH value of natural waters (Sychev et al., 1983).

In the redox processes that take place in natural waters, in addition to oxidants and catalysts, various reducing substances also participate. These substances can be autochthonous (products of the metabolism and decomposition of hydrobionts, such as organic acids, enzymes, amino acids, thiols, etc.) or allochthonous (pesticides, heavy metals, petroleum products, heavy metals, etc.), and they reach natural waters through wastewaters, runoff, atmospheric precipitation, etc. A group of substances with pronounced reducing properties that affect aquatic systems' ecological balance is represented by thiol substances (Patai, 1974). According to their place of origin, thiol substances found in natural waters can typically be classified into two main groups. The first group consists of thiol compounds of autochthonous origin that are produced inside of the aquatic basin, such as cysteine (Cys) and glutathione (GSH). Allochthonous substances, such as thiourea (TU) and thioglycolic acid (TGA), are part of the second group and enter natural waters as a consequence of anthropogenic environmental influence.

Thiourea (TU) is a thiol substance of anthropogenic origin that is used in the synthesis of various substances, in the fertilizer and insecticide industries, and in the production of pharmaceuticals, dyes, plastics, etc. Because the range of applications of TU is very wide and the annual production is quite high (over 10000 t/year), its content in the environment is estimated to be quite high. Based on

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the physicochemical properties of TU and its use pattern, the hydrosphere is expected to be the main target compartment for this compound. Because TU is not biodegradable and is hydrolytically stable, the transformation of TU into aquatic systems will take place through chemical and photochemical processes (Lis, 2016). TU is a dangerous compound for the aquatic environment because it influences the hydrobionts' activity, but its oxidation products (such as urea) are non-toxic and even beneficial for natural habitats (Sahu et al., 2011).

The main goal of water protection is to maintain and improve the physicochemical and biological characteristics of natural waters. Pollution and self-purification processes can change or maintain these physicochemical and biological characteristics. There is a reciprocal cause-and-effect relationship between the processes of pollution and self-purification. If the effect of pollution exceeds the self-purification capacity, then the water quality is getting worse. Therefore, to avoid disturbing the pollution-self-purification balance, special attention must be paid to the wastewater treatment before its discharge into natural waters (Gladchi et al., 2008; Bunduchi et al., 2019, 2006).

The aquatic environment's self-purification represents the totality of the physical, biological, and chemical processes that take place inside the aquatic basins, and lead to reducing the number of polluting substances in the water to a level that does not pose a danger to the ecosystem's functioning (Gladchi et al., 2008; Duca et al., 2008; Bunduchi et al., 2006).

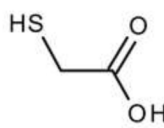
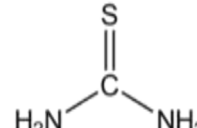
Monitoring of the self-purification capacity of natural aquatic systems is based on different parameters such as the chemical oxygen demand, biochemical oxygen demand, dissolved oxygen concentration, speed of water decontamination by some pollutants, etc. (Nugraha et al., 2020).

MATERIALS AND METHODS

Chemicals and Standards

Thioglycolic acid, thiourea, *p*-nitrosodimethylaniline (PNDMA), oxygen peroxide, potassium oxalate monohydrate, and iron(III) chloride monohydrate were purchased from Sigma-Aldrich (Germany); iron(III) chloride hexahydrate and copper(II) sulfate pentahydrate from Stanchem (Poland), phosphate buffer solution (KH_2PO_4 , $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) from Chem-Lab (Belgium). All solutions were prepared with double-distilled water. The absorption was determined using a double-beam UV-Vis spectrophotometer (T80+ PG Instruments). The structural formulas of the analyzed thiols are presented in Table 1.

Table 1. Structural formulas of the analyzed thiol compounds

| Thiol compounds | Thioglycolic acid (TGA) | Thiourea (TU) |
|--------------------|---|---|
| Structural formula |  |  |

Irradiation Sources

In this study, a DRT-400 lamp (400W, Lisma, Russia) and a Solar Simulator (SS) Oriel Model 9119X (Newport, USA), were used as irradiation sources, some technical parameters are presented in Table 2.

Table 2. The used irradiation sources and their general characteristics

| Irradiation source | Filters | Emitted wavelengths, nm | Comments |
|------------------------------------|-------------------------------------|-------------------------|--|
| DRT-400 lamp | | 220-600 | characterized by three intense lines at 312 nm, 365 nm, and 436 nm. |
| Solar Simulator, Oriel Model 9119X | Air Mass 0 filter (AM0) | 250-2800 | This filter corrects the illuminator output to better match the solar spectrum in extraterrestrial space. This filter is coated to remove excess IR radiation from the beam. |
| | Air Mass 1.5 Direct filter (AM1.5D) | 250-2800 | This filter set simulates the direct solar spectrum with the sun at a zenith angle of 48.2°. |
| | UVC blocking filter (UVC-bl.) | 290-2800 | This filter blocks the passage of UV rays with wavelengths less than 290 nm. |

Determination of the Hydrogen Peroxide Initial Concentration

The spectrophotometric method was used for the determination of the hydrogen peroxide initial concentration. The mixture consisting of 0.5 mL of concentrated hydrogen peroxide and 9.5 mL of double-distilled water was prepared, and the absorbance of the solution was measured at 300 nm wavelength in a high-performance quartz glass cuvette, spectral range 200-2500 nm, pathlength 10x10 mm, chamber volume 3500 μ L (Sigma-Aldrich, Germany). As a blank solution, double-distilled water was used. The hydrogen peroxide initial concentration ($C_{H_2O_2, \text{init.}}$, mol·L⁻¹) is determined according to Eq. (12) (Duca et al., 2002):

$$C_{H_2O_2, \text{init.}} = 20 \cdot A^{300} \quad (12)$$

where: A^{300} - the absorbance of the H₂O₂ solution at the wavelength $\lambda = 300$ nm.

Determination of the Initial Concentration of P-Nitroso-N,N-Dimethylaniline Solution (PNDMA)

The initial concentration of the dye solution $[PNDMA]_0$ (M) is determined spectrophotometrically, at the wavelength of 440 nm in a cuvette with a thickness of 1 cm and is calculated according to Eq. (13) (Duca et al., 2002; Travin et al., 2019):

$$[PNDMA]_0 = \frac{n \cdot A^{440}}{l \cdot 3.4 \cdot 10^4} \quad (13)$$

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where: n - the dilution coefficient of the initial solution; A^{440} - the absorbance of the colored solution at the wavelength $\lambda = 440$ nm; l - the optical path length (thickness of cuvette), cm; $3.4 \cdot 10^4$ - PNDMA molar extinction coefficient.

Determination of the Inhibition Capacity

The determination of the inhibition capacity concerning redox agents is based on the comparison of the rate of 4-nitroso-N,N-dimethylaniline (PNDMA) discoloration, and the interaction with OH radicals in distilled water in the absence and presence of the sample additions, according to Eq. (14) (Duca et al., 2002; Travin et al., 2019):



OH radicals are formed as a result of hydrogen peroxide photolysis upon irradiation by the sources described in Table 2. Schematically, this reaction can be shown according to Eq. (15):



where: $[PNDMA]$ is the concentration of PNDMA, $\text{mol}\cdot\text{L}^{-1}$; $[H_2O_2]$ is the concentration of the hydrogen peroxide, $\text{mol}\cdot\text{L}^{-1}$; $[S_i]$ is the concentration of radical scavengers, $\text{mol}\cdot\text{L}^{-1}$; k_{PNDMA} is the bimolecular constant of the reaction rate of the dye with OH radicals, $\text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$; $k_{H_2O_2}$ is the rate constant of the hydrogen peroxide decomposition; k_i is the reaction rate constant of various substances with OH radicals.

In distilled water, OH radicals interact with the dye and hydrogen peroxide. As a result, the dye discolors and the hydrogen peroxide decomposes into water and oxygen. When $k_{PNDMA}[PNDMA] > k_{H_2O_2}[H_2O_2]$ the rate of dye discoloration in distilled water (W_{PNDMA}) coincides with the rate of hydroxyl radical formation.

When the sample irradiation takes place, except for H_2O_2 , the source of redox agents can be photosensitive compounds such as iron compounds, dissolved organic substances, etc. To estimate the influence of these sources, the sample is simultaneously irradiated in the absence and presence of hydrogen peroxide.

The value of the inhibition capacity ($\sum k_{iOH}[S_{iOH}]$, s^{-1}), is calculated according to Eq. (16):

$$\sum k_{iOH}[S_{iOH}] = \frac{V_{tot}}{V_s} \cdot k_{PNDMA} \cdot [PNDMA]_0 \cdot \left[\frac{W_{d.w.}}{W_s} - 1 \right] \quad (16)$$

where: $W_{d.w.}$ (W_s) – initial rate of PNDMA discoloration upon photolysis of hydrogen peroxide in distilled water (sample); $k_{PNDMA} = 1.25 \cdot 10^{10}$ - the bimolecular constant of the reaction rate of the dye with OH radicals, $\text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$; $[PNDMA]_0$ – PNDMA initial concentration, $\text{mol}\cdot\text{L}^{-1}$; V_{tot} – the total volume of the mixture, mL; V_s – the volume of the analyzed sample, mL.

If $(\sum k_{iOH}[S_{iOH}] < 10^4 \text{ s}^{-1}$ – the water should be classified as very clean;
If $(\sum k_{iOH}[S_{iOH}] < 10^6 \text{ s}^{-1}$ – the water should be classified as highly polluted;
If $(\sum k_{iOH}[S_{iOH}] < 10^5 \text{ s}^{-1}$ – the water is in its normal state with respect to the flow of free radical self-purification processes.

Method for Determination of $\cdot\text{OH}$ Radical Steady State Concentration

The method is based on the interaction of $\cdot\text{OH}$ with PNDMA, resulting in solution discoloration, thus allowing indirect determination of the free radicals using UV-VIS spectroscopy, according to the method previously described (Travin et al., 2019). PNDMA was chosen as an indicator since it acts as a trap for $\cdot\text{OH}$ formed during the photolysis of hydrogen peroxide. The model system consisted of phosphate buffer–PNDMA– H_2O_2 , artificially exposed to UV radiation using the sources mentioned above. After a certain amount of time, the absorbance of the system was measured periodically at 440 nm on a T80+ UV/VIS spectrometer. Oxidation of PNDMA occurs as a result of its interaction with $\cdot\text{OH}$ generated by H_2O_2 under the action of light. When the rate of radical initiation W_i and the rate constant of destruction are known, the stationary concentration of $\cdot\text{OH}$ may be determined (Eq.(17)) (Duca et al., 2002; Travin et al., 2019):

$$[\dot{O}H] = \frac{W_{iOH}}{\sum K_{iOH}[S_{iOH}]} \quad (17)$$

where, W_{iOH} - rate of radical initiation, $\text{M}\cdot\text{s}^{-1}$; $\sum k_{iOH}[S_{iOH}]$ - inhibitory capacity, s^{-1} .

Experimental Procedure

The solutions were prepared using double-distilled water, and the reaction was carried out at pH 7, which was set by the 0.0013 M phosphate buffer (it was used to keep the pH constant and bringing the modeling conditions closer to the natural ones, since the rates of thiols transformation were found to be highly pH-dependent). Additionally, the pH was periodically monitored (before and after the photolytic session) using the WTW Ionlab 720 pH meter (WTW, Germany). All measurements were carried out under thermostatic conditions at a temperature of 25 °C. The solutions were contained in aerobic conditions, bringing the modeling conditions closer to the natural ones. Hydrogen peroxide was used as a source of $\text{HO}\cdot$ radicals. Such important parameters as the rate of photochemical discoloration of the PNDMA in the absence and presence of thiols, the rate of initiation of free radicals, the “inhibitory capacity” of the medium, as well as the steady-state concentration of $\text{HO}\cdot$ radicals, were calculated during this research. The photolytic reactions were induced by irradiating the solution samples using the sources mentioned in Table 2, for 30 minutes, with a time step of 5 minutes, and the absorbance was measured at 440 nm. The constancy of the light flux and its intensity were checked with a standard ferrioxalate actinometer. The samples (50 mL) were placed in a thin-walled quartz glass with a volume of 100 mL and exposed to irradiation. Given the absorption spectrum of hydrogen peroxide and the low concentration of this reagent, the illumination throughout the volume could be considered uniform. However, solutions were mixed with a magnetic stirrer during irradiation, for additional averaging. The initial concentration of hydrogen peroxide in the model systems was determined using the iodometric method ($1\cdot 10^{-2}$ M). The

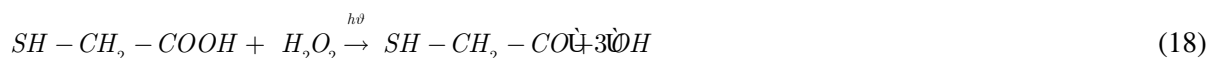
goal of the work was to study the influence of TGA and TU on the processes of radical self-purification in water systems. PNDMA was selected as an indicator because it is a trap for HO radicals produced during the photolysis of hydrogen peroxide.

FOCUS OF THE STUDY

This study examines the role of thioglycolic acid (TGA) and thiourea (TU) in redox processes by predicting their impact on the ability of natural water systems to self-purification using model systems. In this work, the kinetic method was used by applying the parameters: inhibition capacity and steady-state concentrations of OH radicals. In the present study, the principle of “from simple to complex” was used, which implies a step-by-step complication of the investigated model systems. In all model systems, step-by-step, the concentration of one component varied while the concentrations of the other components were kept constant. To determine the influence of TGA and TU on the self-purification process of aquatic systems, several systems were modeled using the PNDMA trap, which allows the determination of the inhibition capacity and the concentration of OH radicals in the modeled systems. The following systems have been modeled for this purpose: phosphate *buffer-TGA(TU)-H₂O₂-PNDMA-hv*; phosphate *buffer-TGA(TU)-H₂O₂-PNDMA-Cu(II)-hv*; phosphate *buffer-TGA(TU)-H₂O₂-PNDMA-Fe(III)-hv*. All model systems were subjected to irradiation with artificial light sources, as described in Table 2, according to the methodology described above.

Influence of TGA on the Radical Self-Purification Processes of Aquatic Systems

Figure 1 shows the practical results for the inhibition capacity and the concentrations of OH radicals, obtained for the simplest system (phosphate *buffer-TGA-H₂O₂-PNDMA-hv*), at the variation of the TGA concentration. The findings showed that an increase in TGA concentration resulted in a decrease in inhibition capacity and an increase in the steady-state concentration of OH radicals, upon irradiation with all sources. The decrease in inhibition capacity of the studied system is related to the formation of OH radicals, which interact with the PNDMA dye, inducing its oxidation. This fact demonstrates that TGA upon irradiation leads to the regeneration of an additional amount of OH radicals in the system, according to Eq. (18), which is supported by the literature data (Duca et al., 2002).

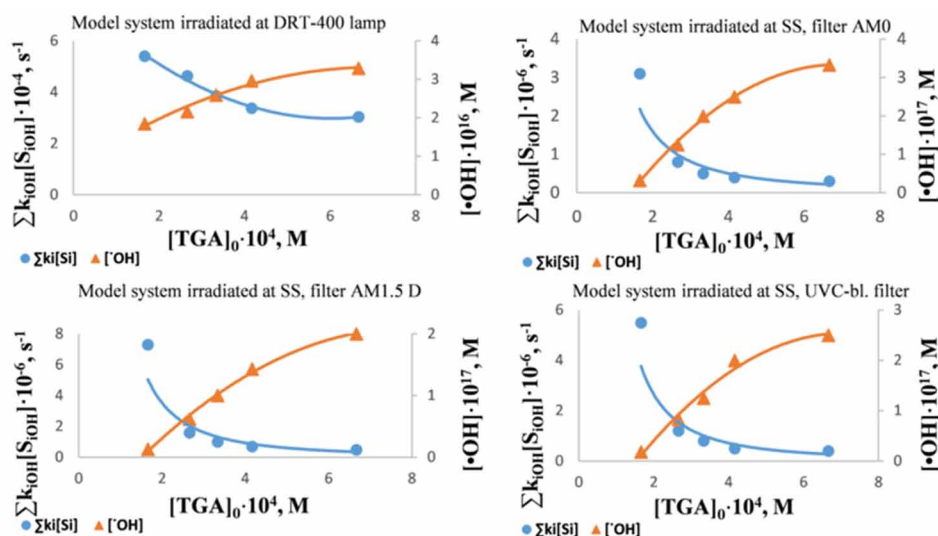


This is due to the fact that TGA contains a -OH group in its structure, which breaks upon irradiation in the presence of hydrogen peroxide and subsequently regenerates an additional amount of OH radicals. Figure 1 shows that, in the presence of TGA, the inhibition capacity values are 10⁴ s⁻¹ for the system exposed to radiation with the DRT-400 lamp (values typical for very pure water) and 10⁵-10⁶ s⁻¹ for the systems exposed to SS, in the presence of all three filters (values characteristic for polluted waters). Also, Figure 1 has shown that inhibition capacity values are dependent on the irradiation source, which is because OH radicals are forcibly generated during the photolytic degradation of hydrogen peroxide (Eq. (1.10)) and their generation rate depends on the emission spectrum of the used lamp (Gladchi et al.,

2014, 2013). The lowest values of inhibition capacity, for TGA concentrations in the range $(1.7-6.7) \cdot 10^{-4}$ M, were found for the system irradiated with the DRT-400 lamp $(5.4-3.0) \cdot 10^4 \text{ s}^{-1}$. This is explained by the fact that the lamp's emission spectrum and hydrogen peroxide's absorption spectrum best overlap. The highest values of the inhibition capacity were determined for the systems irradiated upon the Solar Simulator, and they are between $((7.3-0.3) \cdot 10^6 \text{ s}^{-1})$ and are two orders of magnitude higher than the values of the system irradiated by the DRT-400 lamp. This is explained by the fact that the Solar Simulator emits spectral radiation approximating that of natural sunlight. The used filters block or allow the passage of a very small amount of radiation with wavelengths shorter than 290 nm. So, the emission spectrum of Solar Simulator, in the presence of the three filters least overlaps with the absorption spectrum of hydrogen peroxide.

The steady-state concentrations of OH radicals are also shown in Figure 1. It was found that with the increase of TGA concentrations in the system, the concentrations of OH radicals increase and are of the 10^{-16} M order for the system irradiated with the DRT-400 lamp and of the 10^{-17} - 10^{-18} M order for the system irradiated at SS, in the presence of all three filters. The OH radicals concentration was also discovered to be dependent on the source of irradiation, as shown by their values. Figure 1 shows that the steady-state concentration of OH radicals decreases depending on the irradiation source, in the following order: DRT-400 lamp $((1.8-3.3) \cdot 10^{-16} \text{ M}) > \text{SS, AM0 filter } ((0.3-3.3) \cdot 10^{-17} \text{ M}) > \text{SS, UVC-bl. filter } ((0.2-2.5) \cdot 10^{-17} \text{ M}) > \text{SS, AM1.5D filter } ((0.1-2.0) \cdot 10^{-17} \text{ M})$.

Figure 1. The variation of the inhibition capacity and the steady-state concentrations of OH radicals depending on the TGA concentration at different irradiation sources; $[\text{PNDMA}]_0 = 1.1 \cdot 10^{-5} \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 1 \cdot 10^{-2} \text{ M}$, $\text{pH} = 7$, $t = 25 \text{ }^\circ\text{C}$

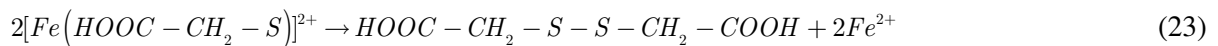
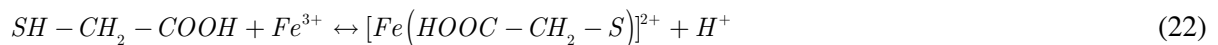
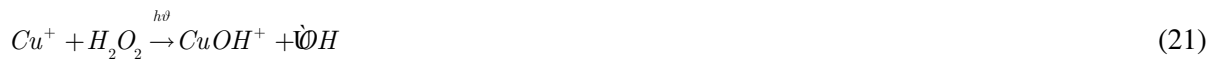
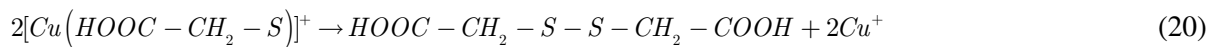
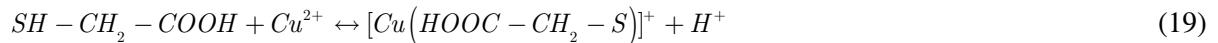


According to the inhibition capacity parameter and steady-state concentrations of OH radicals, it was determined that aquatic systems fell under the categories of very pure and polluted waters at TGA concentrations of the order of 10^{-4} M. It was established that in the presence of TGA in aquatic systems,

the intensity of self-purification processes increases because TGA regenerates an additional amount of OH radicals. It has been proven that the inhibition capacity and steady-state concentration of OH radicals depend on the TGA concentration as well as the emission spectrum and radiation intensity of the irradiation source.

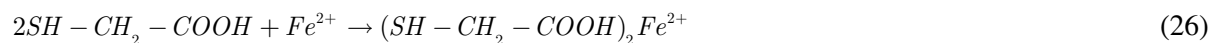
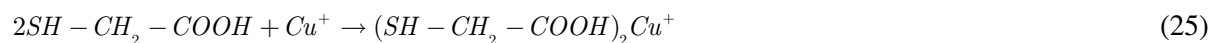
The Influence of TGA on the Radical Self-Purification Processes of Aquatic Systems in the Presence of Cu(II) and Fe(III) Ions

The inhibition capacity values ($\sum k_{iOH}[S_{iOH}]$), on the variation of the TGA concentration in the presence of Cu(II) and Fe(III) ions, are presented in Figure 2, and steady-state concentrations of OH radicals are presented in Tables 3-4. Figure 2 show that in the presence of Cu(II) and Fe(III) ions, for all used irradiation sources, the inhibition capacity values decrease. The decrease in the inhibitory capacity of the studied system is related to the formation of OH radicals, which interact with the PNDMA dye, inducing its oxidation. Thus, an increase in the TGA content in the system contributes to the self-purification processes of aquatic systems. This is explained by the fact that TGA in the presence of H_2O_2 can reduce Cu(II) ions to Cu(I) and Fe(III) ions to Fe(II), even at a neutral pH values (pH=6.5-7.0), which is characteristic for natural waters. Respective to irradiation, active particles are generated, such as OH radicals, according to Eqs. (19-24) (Joo et al., 1990):

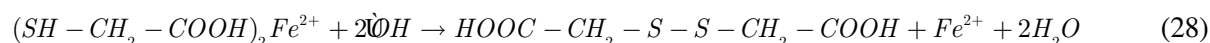
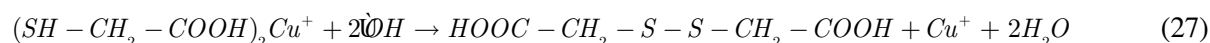


However, it is also clear from Figure 1 that when Cu(II) and, more obviously, Fe(III) ions are added to the system, the situation becomes worse than it would be in their absence. The values of the inhibition capacity in the presence of Cu(II) ions increase by 1.5-3.6 times and depend on the TGA concentration added to the system as well as on the used irradiation source. In the presence of Fe(III) ions, the inhibition capacity values increase by 2.7-6.5 times and also depend on the TGA concentration and used irradiation source. So it can be confirmed that TGA complexes with Cu(II) and Fe(III) ions possess a much higher reactivity towards OH radicals compared to essential TGA, according to the mechanisms described in the literature (Eqs. (25, 26)) (Duca et al., 2002; Joo et al., 1990; Lis et al., 2021):

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The increase in the inhibition capacity values in the presence of Cu(II) and Fe(III) ions demonstrates that the interaction reactions of TGA with Cu(I) and Fe(II) ions take place mainly, and the formed compounds $(TGA)_2Cu^+$ and $(TGA)_2Fe^{2+}$ possess a much higher reactivity towards OH radicals according to the Eqs. (27, 28):



According to the inhibition capacity values for different irradiation sources (Figure 2), the same legality is attested for all sources, but the inhibition capacity values greatly differ from one source to another. The inhibition capacity values decrease with increasing TGA concentration in the system and are of the 10^5 - 10^6 s^{-1} order, values characteristic of polluted and highly polluted waters. The lowest values of the inhibition capacity ($\sum k_{iOH}[S_{iOH}]$) were determined for the systems irradiated with the DRT-400 lamp, and are between $(1.9-1.1) \cdot 10^5$ s^{-1} – for the system in which Cu(II) ions were present and $(3.5-1.9) \cdot 10^5$ s^{-1} – for the system in which Fe(III) ions were present. This is because the DRT-400 lamp has an emission spectrum closest to the absorption spectrum of H_2O_2 . Respectively, the DRT-400 lamp has the largest spectrum of action, and upon irradiation with this lamp, the largest amount of OH radicals are generated. The highest values of the inhibition capacity ($\sum k_{iOH}[S_{iOH}]$) were attested for the systems irradiated with SS, in the presence of the AM1.5 D filter and are between $1.1 \cdot 10^7$ - $7.0 \cdot 10^5$ s^{-1} – for the system in which Cu(II) ions were present, and $2.7 \cdot 10^7$ - $2.4 \cdot 10^6$ s^{-1} – for the system in which Fe(III) ions were present. The same explanation applies here: that the emission spectrum of this filter at least overlaps with the absorption spectrum of H_2O_2 , respectively, upon the system's irradiation with it, a smaller amount of OH radicals is formed, which is consumed to oxidize the substrate.

The OH radicals' steady-state concentration increases with increasing TGA concentration in the system (Tables 3-4). In the presence of Cu(II) ions, it was found that the concentrations of OH radicals are of the 10^{-18} M order, for all systems, except for the system irradiated with the DRT-400 lamp. For DRT-400 lamp the values are of the 10^{-18} - 10^{-17} M order. But also when comparing the systems with and without the addition of Cu(II) ions, it was established that the OH radical concentrations in the presence of Cu(II) ions decreased and were 1.5-3.6 times lower in their presence. This fact once again confirms that thiols form complexes with transition metal ions and that their complexes have a higher reactivity towards OH radicals. At the same time, it was discovered that the source of irradiation also affects the concentration of OH radicals. The highest OH radical concentrations are generated upon irradiation with the DRT-400 lamp, and the lowest in the systems irradiated with SS, in the presence of AM1.5D filter. Thus, the OH radicals concentration in the presence of Cu(II) ions decreases depending on the irradiation source in the following order: DRT-400 lamp $((5.2-9.1) \cdot 10^{-17}$ M) > SS, AM0 filter $((0.1-1.7) \cdot 10^{-17}$ M) > SS, UVC-bl. filter $((0.1-1.4) \cdot 10^{-17}$ M) > SS, AM1.5D filter $((0.1-1.2) \cdot 10^{-17}$ M).

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Figure 2. The variation of the inhibition capacity and the steady-state concentrations of OH radicals depending on the TGA concentration, at different irradiation sources; $[PNDMA]_0 = 1.1 \cdot 10^{-5} M$, $[H_2O_2]_0 = 1 \cdot 10^{-2} M$, $[Cu(II)]_0 = 5 \cdot 10^{-6} M$, $[Fe(III)]_0 = 5 \cdot 10^{-6} M$, $pH = 7$, $t = 25^\circ C$

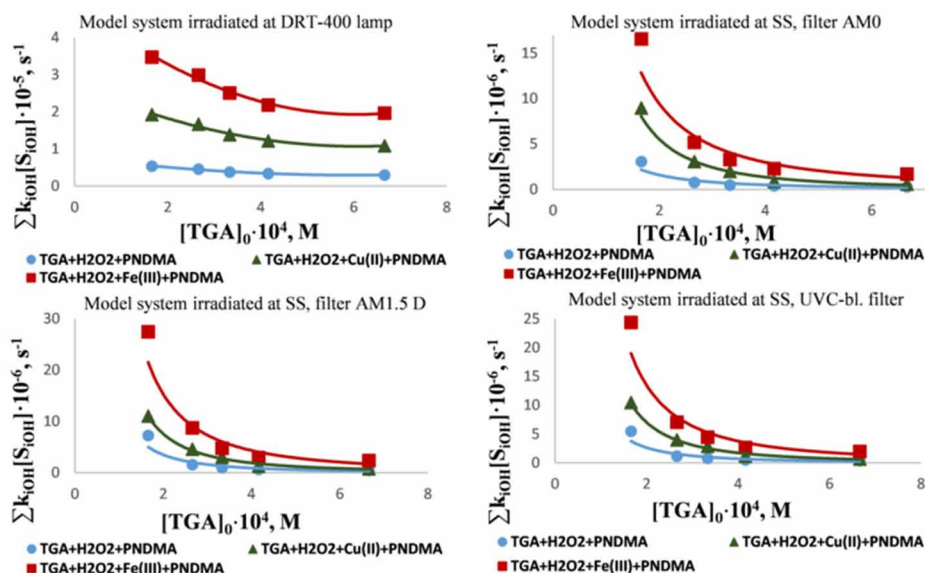


Table 3. Concentrations of OH radicals, generated in the system at different TGA concentrations in the presence of Cu(II) ions; $[PNDMA]_0 = 1.1 \cdot 10^{-5} M$, $[H_2O_2]_0 = 1 \cdot 10^{-2} M$, $[Cu(II)]_0 = 5 \cdot 10^{-6} M$, $pH = 7$, $t = 25^\circ C$.

| $[^{\bullet}OH]_0 \cdot 10^{17}, M$ | | | | |
|--|----------------|------------|----------------|------------------|
| Irradiation source [TGA] ₀ ·10 ⁴ , M | <i>DRT-400</i> | <i>AM0</i> | <i>AM1.5 D</i> | <i>UVC-bloc.</i> |
| | 1.66 | 5.17 | 0.11 | 0.09 |
| 2.66 | 6.00 | 0.32 | 0.21 | 0.25 |
| 3.33 | 7.19 | 0.50 | 0.32 | 0.34 |
| 4.16 | 8.22 | 1.10 | 0.77 | 0.83 |
| 6.66 | 9.14 | 1.67 | 1.25 | 1.43 |

The findings in Table 4 demonstrate that when Fe(III) ions were added to the systems, laws corresponding to those in the presence of Cu(II) ions were discovered. However, compared to the presence of Cu(II) ions, the concentrations of OH radicals are 1.7–2.2 times smaller in the presence of Fe(III) ions. This further shows that, in comparison to Fe(III) ions, which were added to the model systems in similar concentrations, Cu(II) ions manifest higher catalytic activity under natural water conditions.

Table 4. Concentrations of OH radicals, generated in the system, at different TGA concentrations, in the presence of Fe(III) ions; $[PNDMA]_0 = 1.1 \cdot 10^{-5} \text{ M}$, $[H_2O_2]_0 = 1 \cdot 10^{-2} \text{ M}$, $[Fe(III)]_0 = 5 \cdot 10^{-6} \text{ M}$, $pH = 7$, $t = 25 \text{ }^\circ\text{C}$.

| Irradiation source [TGA] ₀ ·10 ⁴ , M | [·OH] ₀ · 10 ¹⁷ , M | | | |
|--|---|------|---------|-----------|
| | DRT-400 | AM0 | AM1.5 D | UVC-bloc. |
| 1.66 | 2.87 | 0.06 | 0.04 | 0.04 |
| 2.66 | 3.33 | 0.19 | 0.11 | 0.14 |
| 3.33 | 3.99 | 0.30 | 0.21 | 0.22 |
| 4.16 | 4.57 | 0.43 | 0.33 | 0.37 |
| 6.66 | 5.08 | 0.59 | 0.42 | 0.50 |

Thus, the OH radical concentration in the presence of Fe(III) ions decreases depending on the irradiation sources, in the following order: DRT-400 lamp $((2.9-5.1) \cdot 10^{-17} \text{ M}) > ((0.6-1.1) \cdot 10^{-17} \text{ M}) > \text{SS}$, AM0 filter $((0.6-5.9) \cdot 10^{-18} \text{ M}) > \text{SS}$, UVC-bl. filter $((0.4-5.0) \cdot 10^{-18} \text{ M}) > \text{SS}$, AM1.5D filter $((0.4-4.2) \cdot 10^{-18} \text{ M})$. The obtained findings thus demonstrate that TGA, on the one hand, induces the intensification of the processes of aquatic systems' self-purification, as a result of the regeneration of an additional quantity of OH radicals, which are the most active oxidative particles in aquatic systems. On the other hand, it was established that TGA forms complexes with Cu(II) and Fe(III) ions. The resulting compounds are significantly more reactive to OH radicals. As a result, hydrogen peroxide may be consumed completely and the "redox-toxicity" condition of natural waters may occur. Contrarily, the complexation of transition metals reduces their catalytic activity, which is crucial for the processes of radical self-purification of aquatic systems.

Influence of TU on the Radical Self-Purification Processes of Aquatic Systems

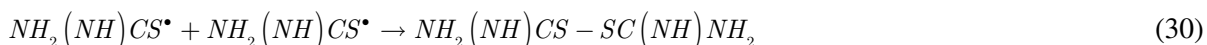
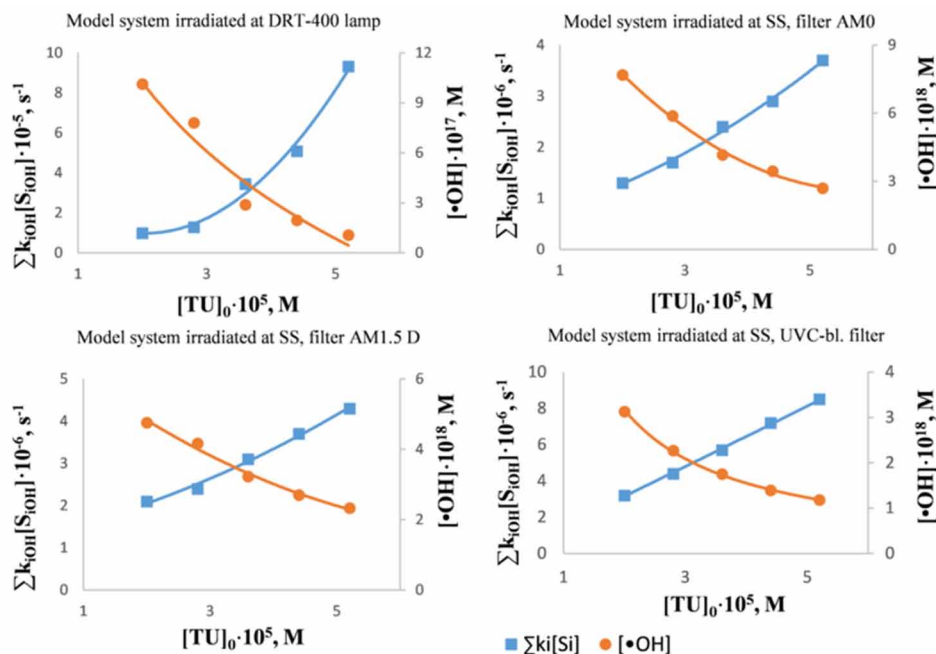
To determine the influence of TU on the self-purification capacity of aquatic systems, the TU initial concentration was varied while the concentrations of the other components were kept constant. The practical results were used to determine the inhibition capacity and steady-state concentrations of OH radicals. From the results shown in Figure 3, it is obvious that increasing the TU concentration in the system leads to increasing the inhibition capacity, regardless of the irradiation source used in the study. The inhibition capacity values are of the 10^6 s^{-1} order, and according to this parameter, they are classified as highly polluted waters for all irradiation sources used in the study. The DRT-400 lamp system, which has values of the 10^5 s^{-1} order and is listed as polluted waters, falls outside of this norm.

Hence, TU has a negative influence on aquatic systems and accordingly leads to the reduction of their self-purification capacity because it consumes an amount of OH radicals for its oxidation, according to Eqs. (29, 30), which is in agreement with previous studies (Duca et al., 2002; Lis, 2016; Sahu et al., 2011):



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Figure 3. The variation of the inhibition capacity and the steady-state concentrations of OH radicals depending on the TU concentration, at different irradiation sources; $[PNDMA]_0 = 1.1 \cdot 10^{-5} \text{ M}$, $[H_2O_2]_0 = 1 \cdot 10^{-2} \text{ M}$, $\text{pH} = 7$, $t = 25 \text{ }^\circ\text{C}$.



Although hydrogen peroxide has a broad absorption spectrum (190-400 nm), its decomposition rate with the generation of OH radicals is higher at lower wavelengths. The lowest values of the inhibition capacity were determined for the system irradiated with the DRT-400 lamp ($(0.9-9.3) \cdot 10^5 \text{ s}^{-1}$). This is explained by the fact that this lamp emits the highest amount of radiation with shorter wavelengths and in a fairly wide range (240-600 nm). So, the emission spectrum of this lamp best overlaps with the absorption spectrum of hydrogen peroxide. The highest values of the inhibition capacity were recorded for the systems irradiated upon the Solar Simulator, in the presence of all three filters. The values range between $(1.3-8.5) \cdot 10^6 \text{ s}^{-1}$ and are practically an order higher compared to the system irradiated with the DRT-400 lamp. This is explained by the fact that the Solar Simulator emits artificial sunlight and provides a very close approximation of natural solar radiation, the used filters block or allow the passage of a very small amount of radiation with wavelengths shorter than 290 nm. So, the emission spectra of SS, in the presence of all three filters, have less overlap with the absorption spectrum of hydrogen peroxide and, accordingly generate the smallest amounts of OH radicals upon irradiation (Gladchi et al. 2008; Duca et al. 2008; Bunduchi et al., 2006).

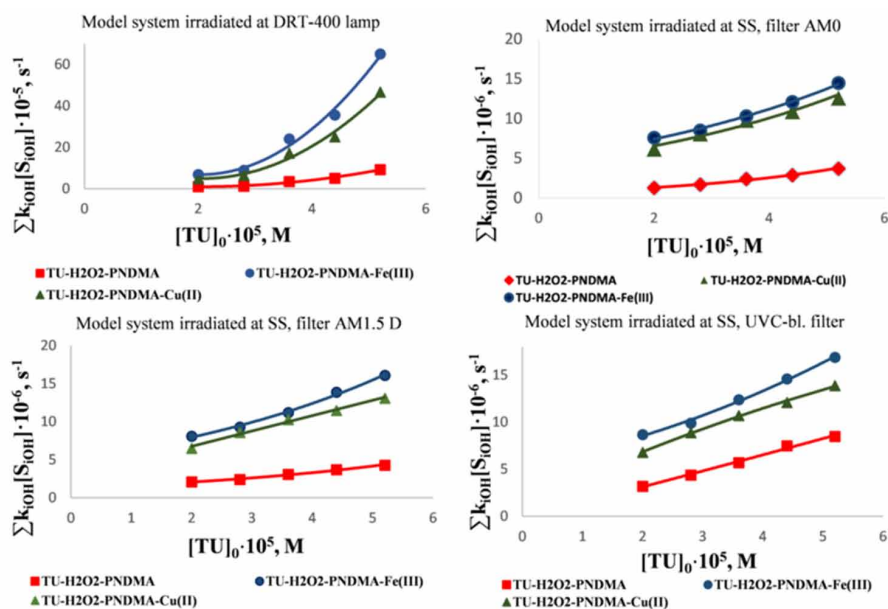
Another very important parameter used for determining the chemical self-purification capacity of aquatic systems is the steady-state concentration of OH radicals, which is inversely proportional to the inhibition capacity. As a result of the research, it was found that an increase in the TU concentration

leads to a decrease in the OH radical concentrations and is of the 10^{-18} M order, for all systems, except for the system irradiated with the DRT-400 lamp, for which the values are of the 10^{-17} M order. The OH radical concentrations decrease depending on the irradiation source, in the following order: DRT-400 lamp ($(10.1-1.1) \cdot 10^{-17}$ M) > SS, AM0 filter ($(7.7-2.7) \cdot 10^{-18}$ M) > SS, AM1.5D filter ($(4.8-2.3) \cdot 10^{-18}$ M) > SS, UVC-bl. filter ($(3.1-1.2) \cdot 10^{-18}$ M). Based on the obtained results, it was thus concluded that at TU concentrations of the 10^{-5} M order, according to the inhibition capacity parameter and the OH radical steady-state concentrations, the aquatic systems were included in the category of polluted and highly polluted waters.

The Influence of TU on the Radical Self-Purification Processes of Aquatic Systems in the Presence of Cu(II) and Fe(III) Ions

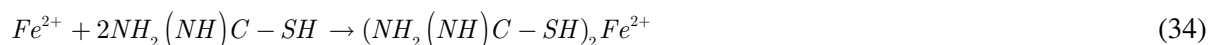
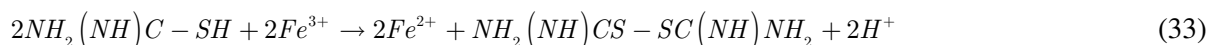
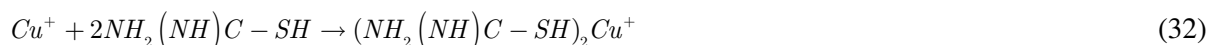
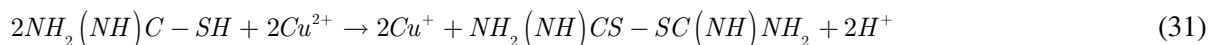
Starting from the fact that Fe(III) and Cu(II) ions play a very important role in the generation of OH radicals, and respectively in the self-purification processes of aquatic systems (Gladchi et al., 2008; Duca et al., 2008, 2002; Bunduchi et al., 2006), were studied the influence of TU in their presence on the processes of chemical self-purification of waters. Figure 4 shows the values of the inhibition capacity ($\sum k_{iOH}[S_{iOH}]$) in the presence of Cu(II) and Fe(III) ions, and Tables 5 and 6 show the steady-state concentration of OH radicals. From Figure 4, it was established that with the addition of Cu(II) and more obviously Fe(III) ions to the system, the self-purification capacity of aquatic systems suddenly worsens, increasing the inhibition capacity values. With the addition of Cu(II) ions, the inhibition capacity values increase by 1.6-5.7 times, and with the addition of Fe(III) ions, they increase by 1.9-7.3 times.

Figure 4. The variation of the inhibition capacity and the steady-state concentrations of OH radicals depending on the TU concentration, at different irradiation sources; $[PNDMA]_0 = 1.1 \cdot 10^{-5}$ M, $[H_2O_2]_0 = 1 \cdot 10^{-2}$ M, $[Cu(II)]_0 = 5 \cdot 10^{-6}$ M, $[Fe(III)]_0 = 5 \cdot 10^{-6}$ M, pH=7, $t=25$ °C

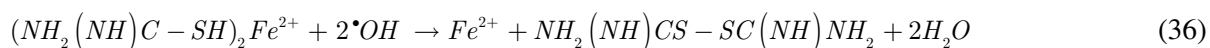


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It can be confirmed that TU binds Cu(II) and Fe(III) ions in complex compounds, the most probable ones being $(TU)_2Cu^+$ and $(TU)_2Fe^{2+}$, according to the mechanism described in Eqs. (31-34) (Duca et al., 2002):



The formed compounds $(TU)_2Cu^+$ and $(TU)_2Fe^{2+}$ possess a much higher reactivity towards OH radicals compared to TU and lead to their consumption according to Eqs. (35, 36) described in the literature (Duca et al., 2002):



So, it was concluded that TU in real conditions in aquatic systems has a negative influence on radical self-purification processes. On the one hand, it consumes oxidative agents from the aquatic systems, on the other hand, it binds Cu(II) and Fe(III) ions in complexes, thus neutralizing their capacity as catalysts in the processes of generation of OH radicals. On analysis of the inhibition capacity values obtained as a result of irradiation with all sources, similar legalities are attested, but the values of the inhibition capacity differ greatly. It was established that the inhibition capacity values increase with increasing TU concentration in the system and are of the 10^6 s^{-1} order, values characteristic of polluted and highly polluted waters. The lowest values of the inhibition capacity ($\sum k_{iOH}[S_{iOH}]$) were established for the systems irradiated with the DRT-400 lamp, which fell within the range $6.9 \cdot 10^5$ - $6.5 \cdot 10^6 \text{ s}^{-1}$ – for the system with Fe(III) ions addition and $4.9 \cdot 10^5$ - $4.7 \cdot 10^6 \text{ s}^{-1}$ – for the system with Cu(II) ions addition. This is because this lamp has the emission spectrum closest to the H_2O_2 absorption spectrum. Respectively, upon irradiation with this lamp, the largest amount of OH radicals is formed, and at the same time, the emission spectrum overlaps with the TU absorption spectrum, which is predominant in its thiol form (since this lamp emits radiation with longer wavelengths of 300 nm) (Lis, 2016).

The highest values of the inhibition capacity ($\sum k_{iOH}[S_{iOH}]$) were determined for the systems irradiated with SS, in the presence of the UVC-bl. filter, which took values between $8.7 \cdot 10^6$ - $1.7 \cdot 10^7 \text{ s}^{-1}$ – the system in which Fe(III) ions were present and $6.8 \cdot 10^6$ - $1.4 \cdot 10^7 \text{ s}^{-1}$ – the system in which Cu(II) ions were present. This can be explained by the fact that this filter blocks radiation with wavelengths shorter than 290 nm, so its emission spectrum less closely overlaps with the H_2O_2 absorption spectrum, and upon irradiation with this filter, fewer OH radicals are formed, which are then consumed to oxidize the substrate. At the same time, the emission spectrum of the UVC-bl. filter is closer to the emission spectrum of the Sun,

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so the processes occurring during irradiation with this filter better characterize the processes occurring in real aquatic systems. So, according to the inhibition capacity parameter in the presence of Cu(II) and Fe(III) ions, the values increase depending on the irradiation source, in the following order: DRT-400 lamp < SS, AM0 filter < SS, AM1.5D filter < SS, UVC-bl. filter.

It has been shown that the inhibition capacity values increase with increasing substrate concentration in the system and are of the order of 10^6 s^{-1} , values characteristic of polluted and highly polluted waters. At the same time, it was demonstrated that the inhibition capacity values depend very much on the quality of the emitted radiation. Extrapolating the results obtained on the model systems to natural aquatic systems, it is found that TU slows down the self-purification processes and, at concentrations $(2.0\text{-}5.2) \cdot 10^{-5} \text{ M}$, it led to the H_2O_2 total consumption, creating premises for a situation of “redox-toxicity”.

The steady-state OH radical concentrations, in the presence of Cu(II) and Fe(III) ions upon TU irradiation are shown in Tables 5-6. The steady-state concentration of OH radicals is inversely proportional to the inhibition capacity and was found to decrease with increasing TU concentration in the system. In the presence of Cu(II) ions, the OH radical concentrations are of the 10^{-18} M order, for all systems, except for the system irradiated with the DRT-400 lamp, for which the values were of the $10^{-18}\text{-}10^{-17} \text{ M}$ order. When analyzing the results presented in Table 5 and Figure 3, it was found that the OH radical concentrations in the presence of Cu(II) ions decreased sharply and were 2-6 times lower in their presence. This once again confirmed that TU complexes with Cu(II) ions have a much higher reactivity concerning OH radicals and consume a larger amount of them. It was established that the steady state OH radical concentrations generated in the analyzed systems also depended on the irradiation source. The highest concentrations of OH radicals are formed in the systems irradiated with the DRT-400 lamp, and the lowest concentrations are generated in the systems irradiated with SS, in the presence of the UVC-bl. filter. The OH radical concentrations, in the presence of Cu(II) ions, decreases depending on the irradiation source, in the following order: DRT-400 lamp $(2.0 \cdot 10^{-17}\text{-}2.1 \cdot 10^{-18} \text{ M}) >$ SS, AM0 filter $(1.6 \cdot 10^{-18}\text{-}7.9 \cdot 10^{-19} \text{ M}) >$ SS, AM1.5D filter $(1.5 \cdot 10^{-18}\text{-}7.6 \cdot 10^{-19} \text{ M}) >$ SS, UVC-bl. filter $(1.5 \cdot 10^{-18}\text{-}7.6 \cdot 10^{-19} \text{ M})$.

Table 5. Concentrations of OH radicals, generated in the system at different TU concentrations in the presence of Cu(II) ions; $[\text{PNDMA}]_0 = 1.1 \cdot 10^{-5} \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 1 \cdot 10^{-2} \text{ M}$, $[\text{Cu(II)}]_0 = 1 \cdot 10^{-6} \text{ M}$, $\text{pH} = 7$, $t = 25 \text{ }^\circ\text{C}$

| $[\text{OH}]_0 \cdot 10^{18}, \text{ M}$ | | | | |
|---|----------------|------------|----------------|------------------|
| Irradiation source [TU]₀ ·10⁵, M | <i>DRT-400</i> | <i>AM0</i> | <i>AM1.5 D</i> | <i>UVC-bloc.</i> |
| 2.00 | 20.40 | 1.61 | 1.54 | 1.47 |
| 2.80 | 15.60 | 1.23 | 1.16 | 1.12 |
| 3.60 | 5.81 | 1.02 | 0.97 | 0.93 |
| 4.40 | 3.98 | 0.92 | 0.87 | 0.83 |
| 5.20 | 2.14 | 0.79 | 0.76 | 0.76 |

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Based on the results presented in Table 6, it was found that for the systems in which Fe(III) ions were added, laws similar to those for Cu(II) ions were valid. However, the concentrations of OH radicals in the presence of Fe(III) ions are 1.3-1.5 times lower compared to those in the presence of Cu(II) ions. Analogous to Cu(II) complexes, Fe(III) complexes with TU have a higher reactivity towards OH radicals, and they consume a larger amount than the essential thiol.

Table 6. Concentrations of OH radical generated in the system at different TU concentrations, in the presence of Fe(III) ions; $[PNDMA]_0 = 1.1 \cdot 10^{-5} \text{ M}$, $[H_2O_2]_0 = 1 \cdot 10^{-2} \text{ M}$, $[Fe(III)]_0 = 1 \cdot 10^{-6} \text{ M}$, $pH = 7$, $t = 25 \text{ }^\circ\text{C}$

| | | $[^{\bullet}\text{OH}]_0 \cdot 10^{18}, \text{ M}$ | | | |
|---|---------|--|---------|-----------|--|
| Irradiation source [TU] ₀ ·10 ⁵ , M | | | | | |
| | DRT-400 | AM0 | AM1.5 D | UVC-bloc. | |
| 2.00 | 20.40 | 1.61 | 1.54 | 1.47 | |
| 2.80 | 15.60 | 1.23 | 1.16 | 1.12 | |
| 3.60 | 5.81 | 1.02 | 0.97 | 0.93 | |
| 4.40 | 3.98 | 0.92 | 0.87 | 0.83 | |
| 5.20 | 2.14 | 0.79 | 0.76 | 0.76 | |

Thus, the OH radicals concentration in the presence of Fe(III) ions decreases depending on the irradiation source, in the following order: DRT-400 lamp ($1.4 \cdot 10^{-17}$ - $1.5 \cdot 10^{-18} \text{ M}$) > SS, AM0 filter ($1.3 \cdot 10^{-18}$ - $6.9 \cdot 10^{-19} \text{ M}$) > SS, AM1.5D filter ($1.2 \cdot 10^{-18}$ - $6.2 \cdot 10^{-19} \text{ M}$) > SS, UVC-bl. filter ($1.1 \cdot 10^{-18}$ - $5.9 \cdot 10^{-19} \text{ M}$).

SOLUTIONS AND RECOMANDATIONS

The obtained data reveals the fact that thiols of anthropogenic origin, depending on their structure, can lead to a reduction in the intensity of radical self-purification processes in aquatic systems (for example TU). At the same time, thiols bind transition metals in complexes with low catalytic activity in the process of OH radicals' generation, thus disrupting the redox state of aquatic systems and having a negative impact on their self-purification processes. Based on the obtained results, it is recommended to systematically monitor the thiol concentrations in natural waters to prevent disruption of the redox state and their self-purification capacity. It is recommended to prohibit the discharge into surface waters of wastewaters with thiourea contents over $2 \cdot 10^{-5} \text{ M}$ to prevent their negative impact on the self-purification processes of natural waters. It is recommended to use the results obtained by the environmental control bodies to determine the self-purification capacity of natural waters.

FUTURE RESEARCH DIRECTIONS

Resulting from the fact that thiol substances have a strong reducing potential, they actively participate in the redox processes of natural waters, and to establish the biological value of hydrobionts' habitation, it becomes important to prevent water pollution with thiols in concentrations higher than their self-purification capacity. For this, it is necessary to continue studies on model systems using water from natural aquatic objects, because the self-purification capacity is also influenced by other factors, such as the presence and concentrations of other organic pollutants. It is also necessary to study the processes of wastewater treatment containing thiol, from the territories of enterprises, to prevent their penetration into natural aquatic systems. Identifying the effective methods and establishing the optimal conditions for their degradation to non-toxic compounds, so that they can be discharged into natural aquatic systems.

It is known that TGA in the presence of hydrogen peroxide reduces Fe(III) ions to Fe(II), even at a pH close to neutral, which would allow the use of a smaller amount of Fe(II) ions in the wastewaters treatment by the oxidation with the Fenton reagent. At the same time, this would allow the elimination of the water neutralization step in the treatment technology. So, another direction of research in the future would be the use of TGA in wastewater treatment, thus considerably reducing the required amounts of Fe(II) ions and H₂O₂, even at a neutral pH value. In this way, the costs of wastewater treatment can be reduced, and the treated water will be harmless for discharge into natural water bodies.

CONCLUSION

Based on the obtained results, it was concluded that TGA, on the one hand, leads to the intensification of the self-purification processes of aquatic systems because it conducts to the regeneration of an additional amount of OH radicals, which are the most active oxidative particles in aquatic systems. And on the other hand, it was confirmed that TGA interacts with Cu(II) and Fe(III) ions during the formation of complexes. Additionally, the newly formed compounds are much more reactive to OH radicals, which can result in the complete consumption of hydrogen peroxide and, correspondingly, the establishment of the "quasi-reduction" state of natural waters. At the same time, the binding of transition metals in complexes decreases their catalytic activity, which is of great importance in the processes of radical self-purification of aquatic systems.

Unlike TGA, TU in real aquatic systems has a negative influence on radical self-purification processes. On the one hand, it consumes oxidative agents from aquatic systems, on the other hand, like TGA, it binds Cu(II) and Fe(III) ions in complexes, thus neutralizing their capacity as catalysts in the processes of OH radicals generation. At the same time, it was demonstrated that the inhibition capacity values depend very much on the quality of the emitted radiation, and if the results obtained on the model systems are extrapolated to the natural aquatic systems, it is found that TU slows down the self-purification processes. The TU concentrations of $(2.0-5.2) \cdot 10^{-5}$ M, it are driven to the total consumption of H₂O₂ and create the premises for a "redox-toxicity" situation.

It has been shown that thiol substances, according to their behavior in the self-purification processes of aquatic systems, are divided into two groups: TU, which is an effective acceptor of OH radicals, respectively conducts to a decrease in the intensity of the self-purification processes of aquatic systems, and TGA, which regenerates an additional amount of OH radicals upon irradiation in the presence of hydrogen peroxide, respectively directs to an increase in the intensity of the self-purification processes.

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This particularity is related to the structure of the studied thiols, TGA has the -OH group in its structure, which breaks upon irradiation in the presence of hydrogen peroxide and thus regenerates an additional amount of OH radicals. Unlike TGA, TU does not have this group, and due to its reducing nature concerning oxidants in aquatic systems (such as OH radicals and H₂O₂), it leads to their consumption and creates the premises for establishing a redox-toxicity state.

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KEY TERMS AND DEFINITIONS

Inhibition Capacity: This is a kinetic parameter that involves the indirect determination of the OH radical's steady-state concentrations by using the “trap” of radicals, the dye N,N-dimethyl-4-nitrosodimethylaniline (PNDMA). This is calculated based on the photochemical destruction rates of the PNDMA dye in distilled and natural water. The destruction is achieved as a result of the dye's interaction with OH radicals, which are generated during the hydrogen peroxide photolysis added to the system.

Redox-Toxicity State: A state in which, in the presence of the pollutant, the hydrogen peroxide in the aquatic systems is considerably reduced or completely consumed.

Self-Purification of Surface Waters: This is a totality of biological, physical, and chemical processes within the water body that lead to the diminution of pollutants' concentrations to levels harmless for ecosystem functionality.