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**PHOTOCHEMICAL TRANSFORMATIONS OF SOME THIOLIC
SUBSTANCES AND THEIR PARTICIPATION IN CHEMICAL SELF-
PURIFICATION PROCESSES OF NATURAL WATERS**

145.02. ECOLOGICAL CHEMISTRY OF WATER

Abstract of the doctoral thesis in chemical sciences

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CONCEPTUAL GUIDELINES OF RESEARCH

The topicality and importance of the topic addressed

The accelerated development of recent economic activities, globally, has a decisive impact on the environment. Thus, man through his activities, pollutes most intensely aquatic ecosystems, thanks to the property of "universal solvent" of water. Between the aquatic systems, soil and atmosphere there is a permanent circulation of water, which involves a lot of chemical compounds in various states of aggregation, thus contributing to the migration of the latter in different components of the environment. This continuous movement of water represents the water circuit in nature, which has a major influence in the formation of the current biosphere on Earth.

The evolution of aerobic life over millions of years is generally due to a unique property of the environment called self-purification capacity, which means the set of hydrodynamic, physical, chemical and biological processes that contribute to reducing or removing harmful substances from the environment and the restoration of the initial physico-chemical parameters, adequate to the biological value of the habitat [1, 2]. In other words, the evolution of life is due to the dominance of aerobic ecochemical processes over anaerobic ones.

The component part of the environment, in which life appeared, is considered to be the hydrosphere, which is the main collector of various chemicals, thanks to the above-mentioned property. Due to the technical-scientific progress of the last decades, the intensity of the self-purification processes of the biosphere, especially of the natural waters, in which the chemical composition has significantly changed, has been considerably disturbed. Proof of this statement is the complete classification of the chemical components of aquatic systems, proposed by specialists in the field of hydrochemistry. Thus, it was complemented by a group of chemicals, namely toxic (xenobiotic) pollutants [2].

For the proper estimation of the ecological status of natural waters, it is necessary to use various research methods: physical, chemical, biochemical, due to their complex chemical composition. At the same time, in addition to the study of the chemical composition of water, it is necessary to investigate the processes that take place in water basins and that directly lead to the formation of the natural chemical composition. The study of the ecological state of the hydrosphere through the prism of ecological chemistry provides information about the chemical structure of the environment and more importantly about the processes that take place inside the water basins.

All water self-purification processes can be seen as being performed in an open type chemical reactor, in which all energy and substance flows are reduced to the flow of redox equivalents. The balance between the summary amount of oxidative equivalents (higher oxidation compounds) and reducing ones (lower oxidation compounds) is characterized by the parameter called water redox state [3, 4].

Under natural conditions, i.e. in the absence of pollution, the state of the environment is oxidizing, characterized by the dominance of oxidative equivalents, which determines the valuable biological state of any ecosystem, including aquatic.

Given that in the conditions of the environment the molecular oxygen is practically inert, in order for it to participate in chemical transformations it is necessary to activate it. Oxygen activators have a much higher reactivity, able to interact with reducing equivalents. Thus, all oxidative equivalents are reduced to reactive oxygen species. It is shown that in natural waters, the main active oxidative equivalent is hydrogen peroxide, which is an intermediate in the process of tetraelectronic reduction of dissolved oxygen. According to numerous studies, hydrogen peroxide has been identified in various natural water sources, such as rainwater, snow, surface water [3, 5].

As a result, the redox state has a dynamic character, at the same time as the flows of oxidative equivalents there must be the flow of reducing equivalents. Oxidative state disturbances involve the presence of reducer flows in increased quantities. Despite the fact that oxidative equivalents are well studied and their formation mechanisms are determined, compounds of a reducing nature are so far little studied, due to their enormous diversity in the aquatic environment.

A class of compounds, of reducing nature are thiols or mercaptans, with the general formula $R-SH$, which are characterized by a high reactivity, due to the thiol group ($-SH$) which easily yields electrons in redox transformations. Conventionally, thiol compounds are divided into two groups: native - those thiols that are formed as a result of biochemical processes inside the water basin (cysteine, glutathione) and allochthonous - thiols resulting from anthropogenic activity (thioglycolic acid, thiourea, etc.) [2, 6].

Although the processes of chemical self-purification, which are performed by hydrolysis, photolysis and oxidation, are in second place according to the intensity of the development, they still have a considerable impact on the redox state of aquatic systems [4]. It is important that in order to establish the influence of a compound on self-purification processes it is necessary to investigate its individual participation on all types of chemical self-purification.

Thus, the aim of this research is to evaluate the contribution of thiol substances in the processes of chemical self-purification of aquatic systems, by establishing the legitimacy of their photochemical transformation..

The proposed tasks for the goal achievement are as follows:

- ✓ systematization of research results on the place and role of thiols in the aquatic environment;
- ✓ establishing the legitimacy of photochemical transformation of cysteine on model systems;
- ✓ study of catalytic redox transformations with the participation of cysteine;
- ✓ establishing the influence of cysteine on the intensity of radical self-purification processes of aquatic systems;

- ✓ monitoring the content of thiol compounds and hydrochemical parameters in water bodies in the Dniester river basin and deducing correlations for assessing water quality through the redox state parameter;
- ✓ performing biotests with the use of cysteine and glutathione, to establish their influence on the biological activity of photoautotrophic hydrobionts on the example of cyanobacteria.

Research hypotheses

Given that the present study in the field of ecological water chemistry involves several research directions, both on model systems and the monitoring of water bodies, several hypotheses have been formulated.

Thus, one of the hypotheses put forward is that one of the classes of reducers in the composition of natural waters, which directly participates in the formation of the redox state, may be thiol compounds, respectively their role is not limited to products of organic matter decomposition processes.

The second hypothesis refers to the fact that thiol compounds participate in all self-purification processes, due to the increased reactivity of the -SH group. Moreover, by analogy with *in vivo* biochemical processes, where they play the role of antioxidants and regulate the bioavailability of heavy metals, it is assumed that thiols can play similar roles in the aquatic environment.

Interpreting the chemical composition of water as an open-type chemical reactor, it was proposed that based on classical hydrochemical parameters, ie macrocomponents, the presence of thiol compounds in natural waters, expressed by glutathione content, can be assessed, at least at the semiquantitative level.

Synthesis of the research methodology and justification of the chosen research methods

In the elaboration of the doctoral thesis, the methodological support is based on the fundamental principles of the theory of knowledge and materialist dialectics, the fundamental studies of ecological chemistry, physical chemistry, analytical chemistry, organic chemistry, natural water chemistry and other adjacent sciences that contribute to the description of environmental processes and propose solutions for environmental protection. This complex interdisciplinary nature of the study also argues for the diversity of methods, procedures and techniques used, including the following groups of methods: general methods (logic, analysis, systematic, modeling), analytical (qualitative and quantitative analysis), physico-chemical application of chemical kinetics apparatus with indication of specific parameters and various methods for determining or forecasting the mechanisms of ecochemical processes), mathematics (application of statistical analysis apparatus on data samples, based on determining indicators of centering / variation trend, and checking normal data distribution in series).

As a theoretical-scientific basis for the current paper were used the results of scientific research in the field of ecological chemistry and physical chemistry published in:

1. DUCA, Gh., SCURLATOV, Iu., MISITI, A., MACOVEANU, M., SURPĂȚEANU, M. *Chimie ecologică. Ediția a II-a, revăzută*. Chișinău: CE USM, 2003. 303 p.
2. СЫЧЕВ, А. Я., ДУКА, Г.Г. *Фундаментальные и прикладные аспекты гомогенного катализа металлокомплексами. Оксидные и пероксидные системы. Часть I*. Chișinău, 2002. 442 p.
3. Self-Purification Processes In Natural Waters, edited by Gh.Duca, Chișinău, 1995
4. СЫЧЕВ, А.Я., ТРАВИН, С.О., ДУКА, Г.Г., СКУРЛАТОВ, Ю.И. *Каталитические реакции и охрана окружающей среды*. Кишинев, 1983.
5. DUCA, Gh., GLADCHI, V., ROMANCIUC, L. *Procese de poluare și autoepurare a apelor naturale*. Chișinău: CEP USM, 2002. 167 p.
6. СИНЕЛЬНИКОВ, В. Е. *Механизм самоочищения водоемов*. М.: Стройиздат, 1980. 111 с.

To achieve the general goal requires a complex analysis algorithm, which involves the use of a number of research methods. All methods used can be classified into two groups: methods applied in the field and laboratory methods.

The analyzes performed at the water sampling site were selected from scientific sources of hydrochemistry field. The analysis of the water samples taken involved the use of analytical methods for determining the content of main ions, physico-chemical methods for determining pH, oxidation-reduction potential.

Research performed in laboratory conditions refers to the kinetic study of transformations on model systems, using formal kinetics quantified by classical analytical methods, including the method for determining the content of free -SH groups (Ellman method), the method for determining the concentration of ion ions. With (II) sodium diethyldithiocarbamate, spectrophotometric determination of ascorbic acid. Determination of the composition of complex compounds was performed using saturation methods and Ostromâslenskii-Job.

Biotesting of local thiol toxicity was performed using classical biochemical methods: determination of biomass, protein and phycobilin content.

Thesis includes introduction, six chapters, conclusions and recommendations, 125 bibliographical references, 9 annexes, 117 pages of basic text, 65 figures, 24 tables. The results are published in 15 scientific papers.

THESIS CONTENT

The introduction describes the topicality and novelty of the approached problem, defines the main purpose and objectives of the thesis, the synthesis of the research methodology, the dissemination and approval of the scientific results and the summary of the thesis chapters.

1. CHEMICAL COMPOSITION AND SOME PROPERTIES OF NATURAL WATERS

In this chapter, the bibliographic study of the specialized literature is presented. Chapter 1 consists of 4 subchapters, which describe the chemical composition and some properties of natural waters, including self-purification capacity and redox state. The study of the recent bibliography in the field argues the importance of photochemical processes of self-purification of aquatic systems and the role of redox equivalents in the formation of the valuable biological state of water as a living environment. At the same time, thiol compounds are being investigated as reducing equivalents in the formation of the redox state of water. The analysis of the situation in the chosen research field was the basis for identifying the problems and formulating the research hypotheses. The chapter ends with a brief synthesis of the issues addressed.

2. MATERIALS AND METHODS USED IN THE STUDY OF ECOCHEMICAL PROCESSES WITH THE PARTICIPATION OF THIOLS

Chapter 2 presents the methodology for researching the impact of thiol compounds on ecochemical processes in natural waters. Taking into account the specifics of the research, the methods used can be classified into 2 groups: experiments performed on model systems and monitoring of hydrochemical parameters in some aquatic objects. The empirical results obtained are the product of a wide range of methods in different fields. The research methodology can be presented in the form of a block diagram, which represents a combination of different hydrochemical, analytical, kinetic, physico-chemical, biochemical and statistical processing methods (Fig. 1).

Out of the total of 13 methods used, 2 of them were adapted: determination of the concentration of -SH groups by the Ellman method and determination of the inhibition capacity. The analysis of bibliographic sources denotes debatable data about the Ellman method [7, 8]. Therefore, it was initially verified. The actual value of the molar extinction coefficient of the reaction product between thiol and 5,5-dithiobis (2-nitrobenzoic acid) was determined. Subsequently, based on the high value of the established molar extinction coefficient ($14150 \text{ M}^{-1}\text{cm}^{-1}$) it was proposed to use the method for determining the thiol content in natural waters.

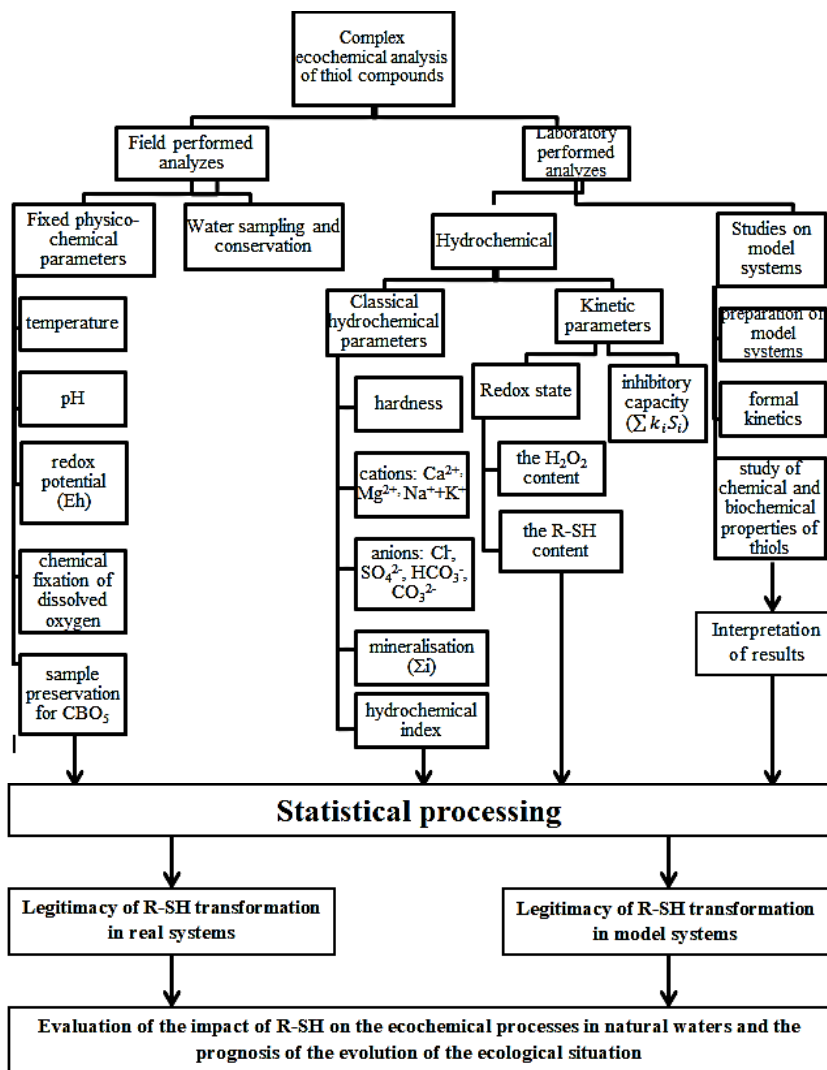


Fig. 1 . Block diagram of the complex ecochemical analysis of thiol compounds

The method involves adding EDTANa₂ to the preparation of the Ellman reagent, in order to eliminate the interferences caused by the precipitate formed between the ions of alkaline earth metals and the phosphate ions in the buffer solution. The addition of EDTANa₂ requires readjustment of the pH, which involves the use of the pH meter, which must be periodically calibrated. These operations

require time, which can become an impediment to the analysis of a large number of natural water samples. For this reason, another buffer solution with the same pH has been proposed, which does not require the addition of interference-free reagents. Thus, borax buffer was proposed. The reproducibility when using this buffer is 100%. Therefore, its use reduces the time for the preparation of reagents and the need to use complementary devices (pH-meter).

The second adapted method is the determination of inhibition capacity and radical concentration, which is an indirect kinetic method for estimating the intensity of radical self-purification processes of natural waters [9]. Thus, it was proposed to use a constant in the formula for calculating the inhibition capacity parameter [10]. The proposed constant for the interaction speed between the radicals generated at the H_2O_2 photolysis and the radical trap, the PNDMA dye, represents a multiannual average value of the respective speed, determined during 10 years of research, during the years 2008-2017 carried out within SCL of Ecological Chemistry and Modern Chemical Technologies. The results of the parameters obtained in the statistical processing of the experimental data reveal that the determined constant can be used to perform the experiment.

As a result, the composition of natural waters includes a large number of compounds that can interfere with the actual result of the thiol content, another change was proposed, namely the filtration of water samples through a filter with a pore diameter of $0.45\ \mu\text{m}$, to eliminate humic acids. Based on the literature, namely humic acids have a major influence on the veracity of the results, because they have the property of absorbing various compounds, including thiol [11, 12].

Therefore, the ecochemical study of some substrates requires the use of a wide range of methods. If research is also performed on real systems, accurate analytical methods are needed, but at the same time, which take a short time and require simple procedures with the use of small numbers of reagents and equipment..

3. PHOTOCHEMICAL TRANSFORMATIONS OF SOME THIOLS IN THE EXAMPLE OF CYSTEINE

Chapter 3 includes the experimental results obtained in modeling the photochemical transformations of cysteine. The systems were modeled taking into account the particularities of the chemical composition of natural waters. To rule out the probability that thiols can be oxidized by dissolved molecular oxygen, a process that takes place under conditions of advanced purity of reagents and at $\text{pH} > 7$ [13], the Tiol-O_2 system was modeled, using cysteine as a representative of native thiols. The results showed that the -SH group, quantified with the Ellman reagent, does not oxidize for a long time, at the concentration of thiol $\leq 10^{-5}\text{M}$. Therefore, the study of photochemical transformations of thiols, for example cysteine, was performed without adjusting the pH, given that the pH of the modeled systems is around 6.

Formal kinetics on model systems was used to deduce the photochemical transformation legitimacy of cysteine. 3 types of cysteine photolysis were modeled: direct, induced and sensitized. To adjust the modeled systems to natural water conditions, Cys was used as a substrate as a photoinitiator H_2O_2 as an oxidative equivalent, Cu(II) and Fe(III) ions as typical catalysts present in the composition of natural waters and humic acids in quality of photosensitizers.

In the case of *direct photolysis*, it was found that with the increase of the Cys concentration in the system, the photolysis speed also increases, being of the order of 10^{-9} - 10^{-8} M/s (Fig. 2).

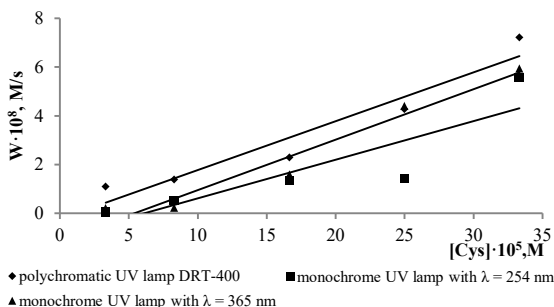


Fig. 2. Direct cysteine photolysis rates. pH=5.95, t=20⁰C

In order to explain the nonlinear increase in the photooxidation rate of thiol, the quantum yield (Φ) was calculated. The quantum yield allows to establish the complexity of the chemical transformations of the substrate. Based on the calculated monochrome lamp intensities, Φ of the direct photolysis process of Cys was calculated for its different concentrations (Tab. 1).

Table 1. Quantum yield values calculated on the basis of light intensity (I) for different cysteine concentrations

[Cys] · 10 ⁴ , M	Φ	
	lamp with monochrome filter with $\lambda = 365$ nm ($I=1.48 \cdot 10^{-8}$, E/s)*	lamp with monochrome filter with $\lambda = 254$ nm ($I=7.92 \cdot 10^{-9}$, E/s)*
0.33	0.08	0.11
0.83	0.14	0.65
1.67	0.64	1.80
2.50	1.53	2.65

*- experimentally determined light intensity values

At the concentration of -SH groups of the order of 10^{-5} M, the quantum yield is subunit, values that can be explained by the Frank-Rabinovici effect. For the other concentrations Φ it is supraunitary, which means that the chemical transformations of Cys take place after a complex mechanism, most probably radical, in which the photolysis represents only the initiation stage.

The effective constants of cysteine photolysis rates are within the order of 10^{-4} - 10^{-5}s^{-1} (Tab. 2). Their values show that the intensity of the irradiation source is decisive on the photolysis speed of the thiol, the most effective being the polychromatic lamp DRT-400.

Table 2. Values of the effective rate constants and the half-life of the direct cysteine photolysis process

Irradiation source	$k \cdot 10^4, \text{s}^{-1}$	$\tau_{1/2}, \text{ore}$
monochrome filter lamp with $\lambda = 254 \text{ nm}$	0.55 ± 0.08	3.50
monochrome filter lamp with $\lambda = 365 \text{ nm}$	0.65 ± 0.07	2.96
polychrome lamp model DRT-400	1.02 ± 0.14	1.89

According to the literature, the products of direct cysteine photolysis can be the following (Fig. 3):

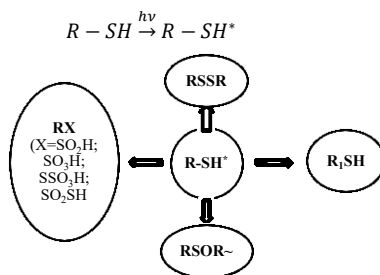


Fig. 3. Reaction products of direct photolysis of aliphatic thiols

Therefore, in the aquatic environment, cysteine will undergo direct photolysis in the upper layers, where the sun's rays penetrate, but with a very low intensity. The cysteine half-life is the shortest on irradiation with the DRT-400 lamp, 1.89 hours and the longest for the monochrome lamp with $\lambda = 254 \text{ nm}$, 3.5 hours.

The study of cysteine *induced photolysis* denotes the following. In the presence of hydrogen peroxide, a generator of radicals OH^\bullet , the rate of cysteine photolysis increases, and with the addition, separately, of Cu(II) and Fe(III) ions in the system, the rate increases even more (Fig. 4-6).

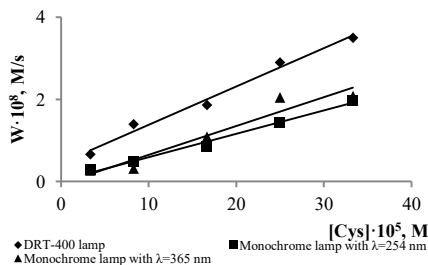


Fig. 4. Variation in the rate of oxidation of cysteine depending on its initial concentration.
[H₂O₂]=3.3·10⁻⁶M, pH=5.84, t=20°C

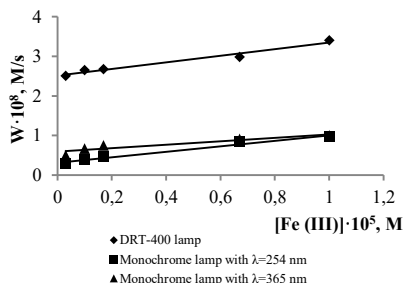
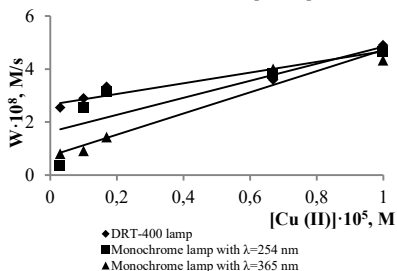


Fig. 5. Variation of Cys oxidation rate as a function of Cu (II) ion concentration.
[H₂O₂] = 3.3·10⁻⁶ M, [Cys] = 1.7·10⁻⁴ M, pH=5.39, t=20°C

Fig. 6. Variation of Cys oxidation rate as a function of Fe (III) ion concentration.
[H₂O₂] = 3.3·10⁻⁶ M, [Cys] = 1.7·10⁻⁴ M, pH=5.59, t=22°C

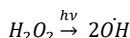
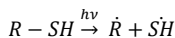
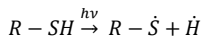
The calculated partial reaction orders indicate that the main substrate on which the intensity of induced photolysis processes depends is cysteine, followed by transition metal ions. Hydrogen peroxide has the lowest intake, even if it acts as a radical generator $\dot{O}H$ (Tab. 3) [3].

Table 3. Kinetic equations calculated for the cysteine induced photolysis process

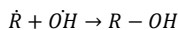
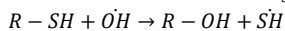
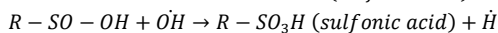
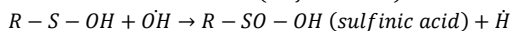
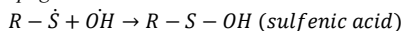
Irradiation source	The kinetic equation
Monochrome lamp with $\lambda = 254$ nm	$W = k \cdot [Cys]^{0.6} \cdot [H_2O_2]^{0.2}$
	$W = k \cdot [Cys]^{0.8} \cdot [H_2O_2]^{0.7} \cdot [Cu(II)]^{0.7}$
	$W = k \cdot [Cys]^{1.3} \cdot [H_2O_2]^{0.1} \cdot [Fe(III)]^{0.4}$
Monochrome lamp with $\lambda = 365$ nm	$W = k \cdot [Cys]^{0.8} \cdot [H_2O_2]^{0.4}$
	$W = k \cdot [Cys]^{0.8} \cdot [H_2O_2]^{0.3} \cdot [Cu(II)]^{0.5}$
	$W = k \cdot [Cys]^{0.5} \cdot [H_2O_2]^{0.2} \cdot [Fe(III)]^{0.2}$
DRT-400 lamp	$W = k \cdot [Cys]^{0.8} \cdot [H_2O_2]^{0.2}$
	$W = k \cdot [Cys]^{0.5} \cdot [H_2O_2]^{0.1} \cdot [Cu(II)]^{0.2}$
	$W = k \cdot [Cys]^1 \cdot [H_2O_2]^{0.1} \cdot [Fe(III)]^{0.1}$

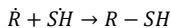
Based on the results of the kinetic parameters, the following hypothetical Cys photooxidation mechanism was proposed:

- initiation:*

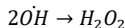
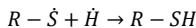
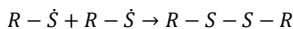


- propagation:*





- chain break:



The detected legitimacy could be explained by the complexation reactions of cysteine with transition metal ions, which occur at a higher rate than photolysis processes. [15, 16].

The results of modeling the processes of sensitized cysteine photolysis in the presence of humic acids (HA) showed that the process takes place only at the variation of cysteine in the system. When other components vary, there is no destruction of the free -SH groups in the cysteine composition (Fig. 7-8).

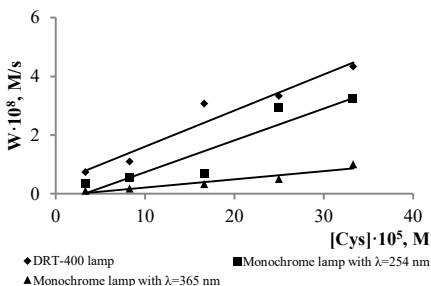


Fig. 7. Variation in the rate of oxidation of cysteine depending on its initial concentration.
[AH]=1.0 mg/L, [H₂O₂]=3.3·10⁻⁶ M, pH=6.46,
t=24°C

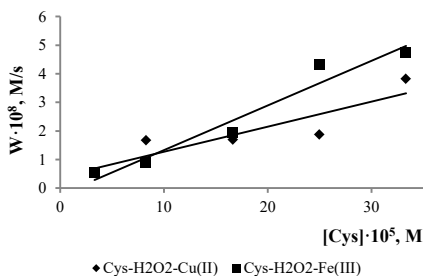


Fig. 8. Variation in the photooxidation rate of cysteine depending on its initial concentration in the system Cys-Mⁿ⁺-H₂O₂-AH.
[AH]=1.0 mg/L, [H₂O₂]=3.3·10⁻⁶ M, [Cu(II)]=
[Fe(III)]=3.3·10⁻⁷ M, pH₁=6.45; pH₂=6.50,
t=25°C

The observed phenomenon could be explained by the dual properties of humic acids, which act as photosensitizers and photoinitiators in the absence of oxidants and/or catalysts and antioxidants in their presence [17]. In systems in which Fe(III) ions have been added, the rates of photolysis are higher, thanks to the additional amounts of free radicals generated by the complex compounds of Fe(III) ions with humic acids [18, 19]. When irradiating with the DRT-400 lamp, the values of the speed constants are one order higher than when irradiating with the lamps with monochrome filters, but with the addition of the photoinitiator (H₂O₂), the values of the constants decrease. An even more pronounced decrease is attested when the catalysts are added (Tab. 4).

Table 4. Effective constants of the cysteine photolysis process, when irradiated with DRT-400 lamp

Model system	k·10 ⁴ , s ⁻¹	τ _{1/2}
Cys-AH-H ₂ O-hv	2.75±0.10	42 min
Cys-AH-H ₂ O ₂ -H ₂ O-hv	1.83±0.11	63 min 8 s
Cys-AH-H ₂ O ₂ -Cu (II)-H ₂ O-hv	1.65±0.09	70 min 1 s

Cys-AH-H ₂ O ₂ -Fe (III)- H ₂ O-hv	1.68±0.10	68 min 46 s
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Therefore, the legitimacies detected in the process of sensitized photolysis of Cys consist in the fact that the presence of hydrogen peroxide (photoinitiator) and catalysts (Cu(II) and Fe(III) ions), when irradiated with polychromatic lamp DRT-400, lead to the decrease cysteine photolysis intensity.

This decrease could be explained by the dual behavior of AH, at the same time they can be:

- ✓ *photosensitizers*, accumulate the absorbed radiation, go into the triplet excitation state and give it up after the collision,
- ✓ *photoinitiators*, generate different free radicals, following the absorption of radiation by the chromophore groups (-C=C-, -C=O etc.) from their structure,
- ✓ *antioxidants*, in the presence of other substrates with more pronounced free radical generation properties, they manifest as electron donors and/or radical traps.

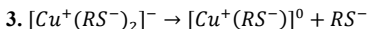
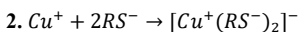
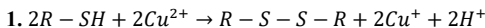
Overall, the research results showed that cysteine undergoes all types of photolysis. However, the lowest input at pH values equal to approximately 6 will have a direct photolysis, because the maximum absorption of thiol with the undissociated -SH group is at the wavelength $\lambda=200$ nm. The respective wavelength does not fall within the emission spectrum of solar radiation that reaches the Earth's surface. If natural waters pH is higher than 8, the contribution of direct photolysis increases, because the dissociation of the -SH group contributes to the bathochrome displacement of the absorption maximum up to the wavelength $\lambda=250$ nm.

Therefore, it has been established that cysteine undergoes photochemical transformations, the rate of which depends on the amount and nature of radiation emitted and the concentration of substrates in aqueous solutions. Under natural water conditions, cysteine will most likely be oxidized by sensitized photolysis, in the presence of humic acids and induced, in the presence of hydrogen peroxide, as radical OH generators.

4. THE INFLUENCE OF CYSTEINE ON CHEMICAL SELF-PURIFICATION PROCESSES OF AQUATIC SYSTEMS

The complexity of the composition of natural waters determines a large number of processes of different nature that take place simultaneously. In the previous chapter were deduced some laws of transformation of local thiols, for example cysteine, photochemically. However, it is obvious that thiols are also involved in other self-purification processes. Thus, in chapter 4 are presented the experimental data obtained for the modeling, in laboratory conditions, of the catalytic and radical redox processes. The establishment of the influence of cysteine on these two types of chemical self-purification processes occurred as a result of the legalities detected in the research of photochemical processes.

From the literature it is known that thiols, being of peroxidase nature, can interact with dissolved oxygen only in the presence of catalysts [2, 20]. The interaction mechanism is a specific one and consists of 3 stages, under anaerobic conditions [2]:



Since the photochemical transformations of cysteine were studied under aerobic conditions, the redox transformations were also investigated in the presence of dissolved oxygen. The results of the research obtained in modeling the Cys-Cu(II) -O₂ system confirmed that the interaction between thiol and metal ions occurs at much higher speeds than for photolysis. It has been established that at low concentrations of Cu(II) ions (10⁻⁶M), the interaction rate is proportional to their concentration in the system, thus indicating that Cu(II) ions are determinants of the intensity of the interaction process.

In order to verify the probability of complexation by the above mechanism, the isomolar series method was initially applied. The absorption spectrum of the mixture of cysteine and Cu(II) ions confirmed the formation of a complex compound at the wavelength $\lambda=215$ nm. The results of the applied method attest to the formation of two complex compounds, one with medium stability, in molar ratio, metal: ligand, 1:2 and the most stable corresponds to the molar ratio 1:1 (Fig. 9).

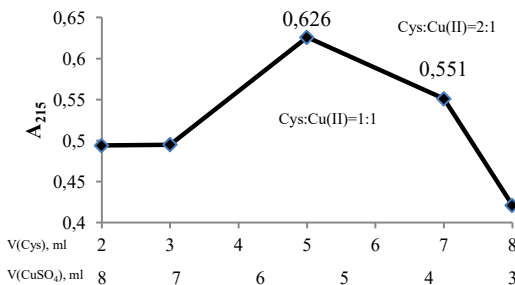
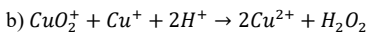
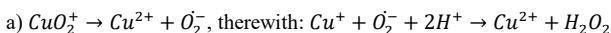
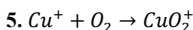
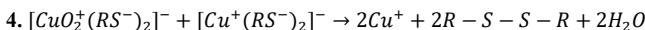
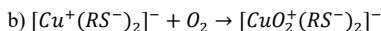
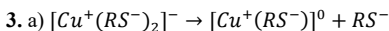


Fig. 9. Absorbance of the complex compound of Cu(II) ions with cysteine.
[Cys]₀=[Cu(II)]₀= 7·10⁻⁴ M

Thus, the detection of these complex compounds denotes that under aerobic conditions thiols interact with the ions of transition metals through a specific mechanism consisting of three stages. Taking into account the presence of molecular oxygen in the aqueous medium and data on the catalytic oxidation of thiols by dissolved oxygen, a physico-chemical method was applied to determine the residual concentration of Cu(II) ions with sodium diethyldithiocarbamate. At the quantitative level, after 10 minutes of reaction, the regeneration of 31% of Cu(II) ions takes place. Regeneration of Cu(II) ions denotes that the complex compound formed with cysteine, in a 2:1 molar ratio (ligand:metal) decomposes, with the oxidation of thiol and the regeneration of the metal ion.

Thus, it was found that under aerobic conditions, the mechanism of interaction of thiols, for example cysteine, with transition metal ions, for example Cu(II) ions, consists of 5 stages. The complexation reaction is unusual, having a redox character.

In the first stage, the reduction of Cu(II) ions to Cu(I) and the oxidation of thiols to disulfide takes place. The second stage involves the formation of unstable complex compounds, in molar ratio, ligand: 2:1 metal. In the presence of dissolved oxygen, in the 3rd stage there is another reaction concurrent with that of mercaptide formation. The concurrent reaction involves the formation of a complex compound with partial charge transfer of the superoxide type. The formation of this oxygenated complex invokes the oxidation of the ligand and the self-regeneration of the metal in the maximum degree of oxidation:



In order to form a clear image about the influence of thiols on chemical self-purification processes, their influence on radical self-purification processes was also studied. Thus, using an indirect kinetic method, using the specific trap for radicals, the dye PNDMA, the influence of cysteine on the processes of generation of these radicals was investigated. Because free radicals are formed in all types of self-purifying chemical processes (oxidation, photolysis), various non-catalytic systems have been modeled with the addition of Cu(II) ions, the main catalyst in ecochemical processes, which are in a homogeneous state.

Kinetic parameters calculated for systems in which thiol has been added indicate the ability of cysteine to inhibit radical processes. For the cysteine concentration range of $10^{-5}M$, according to the inhibition capacity parameter, the modeled systems correspond to heavily polluted waters (Tab. 5). In other words, the presence of cysteine in the given concentrations will have a negative impact on the radical processes of self-purification, because the thiol will consume the free radicals formed.

At the same time, it was observed that with the increase of cysteine concentration, the values of the same parameter decrease, respectively the stationary concentration of radicals \dot{OH} increases. This observation could be explained by the photolysis of cysteine, namely by the products of photooxidation, which could also be free radicals. This assumption is also reinforced by the values of the superunit quantum yield of cysteine photolysis.

Table 5. Inhibition capacity and concentration of radicals \dot{OH} calculated for modeled systems

System	<i>Cys-PNDMA-H₂O₂</i>		<i>Cys-Cu(II)-PNDMA-H₂O₂</i>	
$[-SH] \cdot 10^5, M$	$\sum k_i S_i \cdot 10^{-6}, 1/s$	$[OH] \cdot 10^{18}, M$	$\sum k_i S_i \cdot 10^{-6}, 1/s$	$[OH] \cdot 10^{18}, M$
3.0	1.50	6.7	1.43	7.1
5.0	1.67	6.0	1.61	6.2
8.0	1.33	7.5	1.10	9.1
10.0	1.04	9.6	0.90	11.1

Therefore, the mechanisms of cysteine interaction in catalytic redox processes have been established and it has been found that it can be oxidized by dissolved oxygen in the presence of transition metal ions. However, as a result of this reaction, about 70% of the metal ions are removed from their hydrochemical circuit, in the form of low soluble mercaptides, which are invariable by the action of dissolved oxygen. It has also been established that cysteine inhibits radical self-purification processes by consuming free radicals from the environment.

5. MONITORING OF THIOLIC SUBSTANCES CONTENT IN SURFACE WATERS

Chapter 5 presents the results of monitoring some parameters that characterize the redox state of some aquatic objects that are part of the Dniester river basin, during the years 2015-2019. As study objects were selected 3 lotic systems, the Dniester river, the rivers Raut and Ichel and 2 slow systems, the accumulation lakes Ghidighici and Danceni, in order to detect the legitimacy of transformation of thiol compounds and their influence on the redox state (Fig. 10).

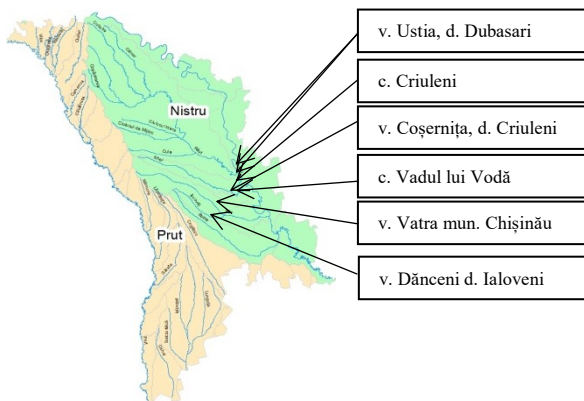


Fig. 10. Water sampling outlets.

Map of the Districts of the Hydrographic Basins of the Republic of Moldova

The monitored ecochemical parameters are: content of thiol compounds and hydrogen peroxide, oxidation-reduction potential (Eh), parameter rH, sulfate-ion content.

The detected concentrations of thiol compounds varied in all capture intakes within the limits of orders 10^{-5} - 10^{-6} M. The highest concentrations were found in the waters of the tributaries of the Dniester River, the rivers Raut and Ichel (Fig. 11). It is known from the literature that humic acids, present in the composition of surface waters, absorb a wide range of low molecular weight organic compounds. For this reason, all water samples were filtered, the pore size of the filter being $0.45\ \mu\text{m}$.

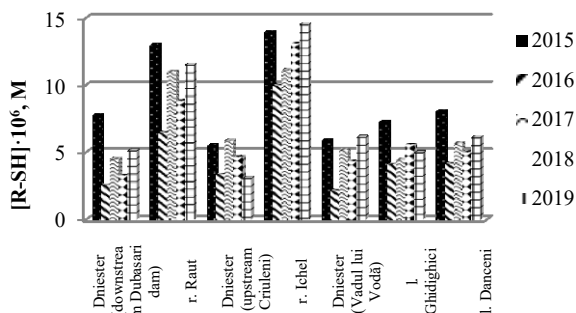


Fig. 11. Dynamics of the content of thiol compounds determined in the filtered samples, in the researched water basins, during the years 2015-2019

It has been established that humic acids influence the determination of the content of -SH groups in the composition of thiols by the Ellman method.

During the monitoring, in the waters of the Dniester River, the content of thiol compounds varied within an order (10^{-6} M), the multiannual averages in three catchments along the river being $4.65 \cdot 10^{-5}$ M; $4.49 \cdot 10^{-5}$ M and $5.35 \cdot 10^{-5}$ M. In all 3 capture intakes, the seasonal dynamics of thiol compounds was attested, attesting maximum concentrations during the summer, a period characterized by high biological activity of hydrobionts (Tab. 6). The years in which the seasonal variation was not detected, were characterized by specific meteorological conditions, such as abundant rainfall, during the summer, from 2019. Therefore, in the absence of the anthropogenic factor, characteristic of natural surface waters, is the dynamics of thiol compounds.

Table 6. Multiannual averages of thiol compounds content in capture points

Capture point	Multiannual average $\cdot 10^6$, M		
	Spring	Summer	Autumn
Dniester downstream Dubasari dam	3.33	8.21	3.94
r. Raut	5.87	9.60	15.47
Dniester upstream Criuleni city	4.15	6.54	2.67
r. Ichel	8.45	22.38	7.91
Dniester Vadul lui Vodă city	3.87	7.41	3.92
I. Ghidighici	4.02	8.36	3.91
I. Danceni	4.54	9.87	4.41

Seasonal variations of thiol compounds were found in the waters of the Dniester River, the Ichel River and Lake Ghidighici. In the waters of the Raut river and Danceni lake, the variation of the thiol content is low.

The linear correlations between the content of thiol compounds and the redox potential (Eh), the rH parameter, the H_2O_2 concentration and the stationary radical concentration $\dot{O}H$ were analyzed to evaluate the impact of thiols on the redox state of the monitored waters (Table 7, 8).

Table 7. Correlations between the concentration of thiol compounds and ecochemical parameters (Eh, rH, $[H_2O_2]$, $[OH]$), monitored during the years 2015-2019, in lotic systems

Capture point	Monitored parameter	Multiannual average			Coef. of linear correlation Pearson, R	The type of correlation
		Spring	Summer	Autumn		
Dniester downstream Dubasari dam	$[R-SH] \cdot 10^6$, M	3.33	8.21	3.94	-	-
	Eh, mV	289.20	255.18	299.08	- 0.95	very strong
	rH	27.10	25.33	27.30	-0.98	very strong
	$[H_2O_2] \cdot 10^7$, M	1.65	1.50	2.51	0.52	moderate
	$[OH] \cdot 10^{17}$, M	7.71	7.16	4.76	0.23	very weak
Dniester upstream Criuleni city	$[R-SH] \cdot 10^6$, M	4.15	6.54	2.67	-	-
	Eh, mV	290.23	304.35	327.70	-0.50	poorly moderate
	rH	26.84	27.75	28.43	-0.30	very weak
	$[H_2O_2] \cdot 10^7$, M	1.52	1.72	2.26	-0.61	moderate
	$[OH] \cdot 10^{17}$, M	88.89	5.18	6.80	-0.15	very weak
Dniester Vadul lui Vodă city	$[R-SH] \cdot 10^6$, M	3.87	7.41	3.92	-	-
	Eh, mV	290.76	291.68	318.46	-0.46	poorly moderate
	rH	26.99	26.44	27.86	-0.79	strong
	$[H_2O_2] \cdot 10^7$, M	1.44	1.84	2.12	0.10	very weak
	$[OH] \cdot 10^{17}$, M	4.44	4.72	12.47	-0.46	poorly moderate
r. Raut	$[R-SH] \cdot 10^6$, M	5.87	9.60	15.47	-	-
	Eh, mV	294.96	240.40	311.74	0.35	poorly moderate
	rH	27.75	26.22	28.12	0.31	poorly moderate
	$[H_2O_2] \cdot 10^7$, M	2.65	4.45	2.56	-0.17	very weak
	$[OH] \cdot 10^{17}$, M	5.14	4.77	4.90	-0.54	moderate
r. Ichel	$[R-SH] \cdot 10^6$, M	8.45	22.38	7.91	-	-
	Eh, mV	278.94	243.30	285.90	-0.99	very strong
	rH	26.45	24.79	26.89	-0.99	very strong
	$[H_2O_2] \cdot 10^7$, M	1.42	2.70	2.43	0.64	moderate
	$[OH] \cdot 10^{17}$, M	2.45	2.95	1.77	0.84	strong

Tabelul 8. Correlations between the concentration of thiol compounds and ecochemical parameters (Eh, rH, $[H_2O_2]$, $[OH]$), monitored during the years 2015-2019 in slow systems

Capture point	Monitored parameter	Multiannual average			Coef. of linear correlation Pearson, R	The type of correlation
		Spring	Summer	Autumn		
I. Ghidighici	$[R-SH] \cdot 10^6, M$	4.02	8.36	3.91	-	-
	Eh, mV	276.19	275.98	291.00	-0.53	moderate
	rH	28.27	27.97	29.22	-0.70	moderate
	$[H_2O_2] \cdot 10^7, M$	2.13	2.45	2.66	0.10	very weak
	$[OH] \cdot 10^{17}, M$	5.64	2.64	3.00	-0.58	moderate
I. Dancenii	$[R-SH] \cdot 10^6, M$	4.54	9.87	4.41	-	-
	Eh, mV	287.50	264.28	292.56	-0.99	very strong
	rH	28.08	27.93	28.99	-0.62	puternică
	$[H_2O_2] \cdot 10^7, M$	1.47	0.60	1.99	-0.94	very strong
	$[OH] \cdot 10^{17}, M$	1.29	2.29	1.56	0.96	very strong

Based on the detected correlations, the dominance of the chemical self-purification processes of thiol compounds was evaluated, which is achieved both by ion-molecular mechanisms and by radical processes.

Therefore, during the monitoring in all 7 catchments of the aquatic objects investigated, the concentrations of thiol substances varied within the limits of the orders 10^{-5} - 10^{-6} M. which confirms their indigenous nature. In the rest of the aquatic objects the seasonal variation of the thiols is either missing or very small.

The impact of thiol substances on other ecochemical parameters that determine the redox state of natural waters has been established. Thiol compounds do not significantly influence the redox potential (Eh) and rH, because the variation of these parameters does not deviate significantly.

However, it has been established that thiols have a significant influence on the concentration of H_2O_2 and the content of radicals OH , being of peroxidase nature, it contributes to the decrease of their content in chemical self-purification processes.

6. IMPORTANCE OF INDIGENOUS THIOLS IN THE BIOCHEMICAL PROCESSES OF HYDROBIONTS

In this chapter was confirmed the hypothesis that thiol compounds are not just the result of the processes of decomposition of organic matter in natural waters. The research was performed in 3 directions: comparative study of the reactivity of ascorbic acid and cysteine; establishing the toxicity of native thiols on photoautotrophic hydrobionts; dynamics of different forms of sulfur in some aquatic objects.

A comparative study of the reactivity of cysteine and ascorbic acid was performed. In *in vivo* biochemical processes, low molecular weight thiols, such as cysteine and glutathione, perform antioxidant functions, detoxifying agents, structural units in protein synthesis. However, the main antioxidant in most living organisms is ascorbic acid.

Starting from the fact that thiols participate in the *in vivo* biochemical mechanisms of detoxification, including heavy metals, it has been indirectly demonstrated that the different reactivity of ascorbic acid and thiols has played a decisive role in the use of the latter in various biological mechanisms *in vitro*.

So, it has been established that direct photolysis of ascorbic acid occurs 4.3 times faster than cysteine (Tab. 9).

Table 9. Some kinetic parameters of the cysteine and ascorbic acid photolysis processes

Photolysis is	direct		induced			
modeled system	Substrate-hv		Substrate-H ₂ O ₂ -hv		Substrate-H ₂ O ₂ - Cu(II)-hv	
Substrate -hv	$k \cdot 10^4, s^{-1}$	$\tau_{1/2}$	$k \cdot 10^4, s^{-1}$	$\tau_{1/2}$	k, s^{-1}	$\tau_{1/2}$
AA	4.36±0.34	26 min 30 s	2.45±0.09	47 min 9 s	$(5.62 \pm 0.09) \cdot 10^{-3}$	2 min 3 s
Cys	1.02±0.14	1 h 53 min 17 s	1.77±0.10	1 h 5 min 17 s	$(2.59 \pm 0.10) \cdot 10^{-4}$	44 min 37 s

In the presence of hydrogen peroxide, the intensity of ascorbic acid photolysis is 1.5 times higher, and with the addition of Cu(II) ions the difference increases up to 22 times. Therefore, ascorbic acid catalytically oxidizes 50% in just 2 minutes. The more pronounced stability of thiols positions them as suitable protective agents against external toxic factors in the aquatic system.

Once some organisms eliminate thiol compounds in the environment, they also assimilate them. But under some conditions, in response to external risk factors, the amount of thiol removed can increase considerably, in turn becoming toxic to the source organisms..

Spirulina was used as a typical representative of photoautotrophic hydrobionts. 3 biochemical parameters were determined to reflect the growth and development of these cyanobacteria [21]. As a substrate, potentially toxic, two native thiols were used separately: cysteine and glutathione. The results of the bioassay attested the occurrence of toxicity only in the presence of cysteine in the environment. Thus, at cysteine concentrations of 300 mg/L there is a 55% reduction in biomass content and protein content, respectively. According to the parameter phycobilin content, cysteine shows toxicity even at low concentrations, of 5 mg/L, and at the concentration of 300 mg/L there is inhibition of the synthesis of these photosensitizers by 56%. The toxicity of cysteine is also confirmed by some research, in which it was determined that cysteine causes the phenomenon of redox toxicity, decreasing

the activity of hydrobionts. The presence of glutathione did not show toxicity in the range of concentrations studied.

Therefore, possible contamination with thiol compounds, especially cysteine, can significantly reduce the intensity of biological self-purification processes, making favorable conditions for the pathogens development.

Given that the normal functioning of living organisms requires the supply of sulfur, it is obvious that some hydrobionts, especially autotrophs, consume some forms of sulfur and eliminate others. It is known that cyanobacteria use increased amounts of sulfate ions for the synthesis of thiols in vivo, used to inhibit reactive oxygen species formed in the process of photosynthesis. Unlike marine and ocean waters, in waters with low mineralization, sulfate ion content can become a limiting factor in the growth and development of photoautotrophic organisms.

Thus, in order to verify the existence of correlations between different forms of sulfur, during 2015-2019, the content of sulfate ions was monitored. In the statistical processing of data on the content of sulfate ions and thiols, only the water bodies in which the seasonal variation of thiols was detected were selected, in order to exclude the influence of the pollution factor on the results. The calculated Pearson coefficient values (Tab. 10), which reflect the correlation between the two forms of sulfur, indicated a moderate and strong dependence on water during the summer, when the activity of hydrobionts is maximum. Respectively, the higher the sulfate content, the higher the thiol content. In the colder periods, autumn and spring, the correlations vary from very weak to moderate, being mostly negative. This denotes the development of the processes of oxidation of thiols by chemical means, until, ultimately, the sulfate ions.

Table 10. Pearson coefficient values calculated based on seasonal variations of thiol and sulphate content

Capture point	Spring	Summer	Autumn
Dniester	-0.44 weak negative correlation	0.69 moderate positive correlation	-0.68 moderate negative correlation
River Răut	0.19 very weak positive correlation	0.85 strong positive correlation	-0.43 weak negative correlation
Ghidighici lake	-0.40 weak negative correlation	0.72 strong positive correlation	-0.32 weak negative correlation
Dancenilake	-0.09 very weak negative correlation	0.95 positive correlation close to perfect	0.20 very weak positive correlation

Therefore, these cyclic processes of transition of sulfur into organic forms (R-SH) from minerals and vice versa, indicate that thiols could participate in the hydrochemical circuit of sulfur.

To demonstrate that thiols are some of the main reducing equivalents in natural waters and also to predict thiol flows, two mathematical models were developed based on five monitored hydrochemical parameters: sulfate content, phosphates, calcium, total hardness, mineralization. The result of modeling by means of the bilinear function ($y=0.6032x+2.5297$; $R^2=0.6032$) shows, at a qualitative level, that the higher the reference value, the higher the calculated value. In other words, there is a certain relationship between the parameters used in modeling. Unlike the polynomial regression model, the neural network allows predictions for which the correlation coefficient $R^2=0.9945$ ($y=1.0083x$).

The modeling results showed, at a qualitative level, that there is a connection between the classic components of natural waters (macrocomponents) and those that characterize the redox state of water. Thus, based on the hydrochemical parameters, the thiol content, expressed by glutathione, can be calculated by means of prediction equations.

GENERAL CONCLUSIONS

1. Study of the photochemical transformation legitimacies of thiols, on the example of cysteine, established that it is subject to all types of photolysis, the effective rate constants being of the order of 10^{-5} - 10^{-4} s⁻¹. The speed of direct photolysis is proportional to its initial concentration in the system and depends on the quality and intensity of the emitted rays. In induced photolysis, the oxidation rates of cysteine increase with increasing concentration of Cu(II) and Fe(III) ions in the system and even more with increasing concentration of H₂O₂. Cu(II) ions have been shown to catalyze the cysteine oxidation process more efficiently compared to Fe(III) ions. It was found that in the presence of humic acids sensitized photolysis takes place. However, in the presence of oxidants, such as hydrogen peroxide and catalysts, Cu(II) and Fe(III) ions, humic acids also act as reducing agents, contributing to the decrease of free radicals generated. Thus, in complex modeled systems, the oxidation rates decrease, which indicates the dual character of humic acids. The quantum yield was calculated and it was observed that it is larger than unity, which means that cysteine generates radicals and only the first stage of its oxidation is photochemical.
2. The study of self-purifying catalytic redox transformations with the participation of cysteine and Cu(II) ions, the main catalysts in natural waters, showed that in the presence of dissolved oxygen cysteine forms complex compounds with Cu(II) ions after a cyclic mechanism consisting of 5 stages, in which the thiol initially reduces Cu(II) ions to Cu(I), then complexes it into slightly soluble and stable mercaptides, thus altering the bioavailability of complexed ions. The role of oxygen in this mechanism is limited to the self-oxidation of the catalyst. The ability of cysteine inhibition in radical self-purification processes was determined to explain the supraunit values of

quantum yield. The values of the inhibition capacity fall in the order of 10^6 s^{-1} , which corresponds to the highly polluted waters. The stationary content of radicals $\dot{\text{O}}\text{H}$ ($\approx 10^{-18}\text{M}$) is not sufficient to ensure a good development of radical self-purification processes. Therefore, under natural water conditions, cysteine will inhibit radical self-purification processes.

3. The concentration of thiol compounds was monitored, as well as other ecochemical parameters that characterize the redox state of the waters, in five water bodies that are part of the Dniester river basin. During the monitoring, in all 7 catchments of the aquatic objects investigated, the concentrations of thiol substances varied within the order of 10^{-5} - 10^{-6} M. During the Dniester River, the seasonal variation of thiol compounds was detected, which confirms their native nature. In the rest of the aquatic objects the seasonal variation of the thiols is either missing or very small. According to the chemical parameters: the concentration of thiol substances, hydrogen peroxide and the stationary concentration of radicals $\dot{\text{O}}\text{H}$ it was found that the rivers Raut and Ichel do not have a major influence on the redox state of the Dniester river. Based on the values of the Pearson linear correlation coefficients, it was found that during the Dniester River, the self-purification processes by ion-molecular mechanisms initially dominate, and in the region of or. Vadul lui Voda, through radical mechanisms. In the Raut river and Ghidighici lake, the self-purification processes take place according to radical mechanisms, and in Danceni lake the ion-molecular ones dominate. In the Ichel River, no inverse correlations were found between redox equivalents, which indicates the dominance of either biological or photochemical self-purification processes.
4. At the permissible limit concentrations for two native thiols (Cys, GSH) were established by applying biotests on photoautotrophic aquatic organisms (cyanobacteria). It was found that only cysteine shows toxicity, at a concentration of 300 mg/L, it inhibits the biochemical activity of spirulina by 50%. A positive linear correlation was found between two forms of sulfur in low mineralized waters, during the summer, which indicates that as the sulfate content increases, the thiol content also increases. In the autumn and spring periods, the linear correlations are negative, which indicates the oxidation of thiols in inorganic forms to sulfate, with the slowing down of the biological processes of hydrobionts. These cyclic processes of transition of sulfur into organic forms from minerals and vice versa, denote the fact that thiols could participate directly in the sulfur circuit in nature.
5. By applying 2 mathematical models, based on the results of hydrochemical parameters (total hardness, calcium content, sulfates, phosphates, mineralization) monitored in the mentioned period, prediction equations were deduced that will allow to establish, by calculations, based on parameters hydrochemical, thiol content in aquatic objects.

PRACTICAL RECOMMENDATIONS

1. It is proposed to use half-life values to estimate the stability of aquatic ecosystems in pollution with some thiol compounds and to assess the intensity of chemical self-purification.
2. It is recommended to monitor the content of thiol compounds in natural waters, the results of which can be used for indirect assessment of the redox state of water.
3. Seasonal monitoring of the content of thiol compounds can be used as an ecochemical indicator to identify the sources of pollution of aquatic objects, as well as their type, natural and/or anthropogenic.

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ADNOTARE

Date de identificare: Blonschi Vladislav, Transformări fotochimice ale unor substanțe tiolice și participarea acestora în procese de autopurificare chimică a apelor naturale, teză de doctor în științe chimice, Chișinău, 2021.

Structura tezei: introducere, șase capitole, concluzii generale și recomandări, bibliografie din 125 de titluri, 9 anexe, 117 de pagini de text de bază, 65 figuri, 24 tabele. Rezultatele obținute sunt publicate în 15 lucrări științifice.

Cuvinte-cheie: tioli, cisteină, autopurificare, fotoliză, starea redox, capacitate de inhibiție, mercaptidă, monitoring, spirulina, toxicitate.

Scopul lucrării: constă în evaluarea aportului tiolilor în procesele de autopurificare chimică a sistemelor acvatice, prin stabilirea unor legități de transformare fotochimică a tiolilor.

Sarcinile cercetării: stabilirea unor legități de transformare fotochimică, redox și radicalică a cisteinei pe sisteme model; monitoringul conținutului compușilor tiolici și a parametrilor hidrochimici în corpurile de apă din bazinul hidrografic al fluviului Nistru; efectuarea biotestelor cu utilizarea cisteinei și glutatationului, pentru stabilirea influenței acestora asupra activității biologice ale hidrobionților.

Noutatea și originalitatea științifică constă în studiul transformărilor fotochimice ale cisteinei în influența acesteia asupra stării redox a apelor. Extrapolarea legităților pe sisteme model la sistemele reale, având ca reper baza de date obținute în urma efectuării monitoringului compușilor tiolici în ape de suprafață.

Rezultatul obținut care contribuie la soluționarea unei probleme științifice importante constă în reconceptualizarea științifică despre locul și rolul compușilor tiolici autohtoni din apele naturale, ceea ce a condus la studiul complex a influenței acestora asupra capacității de autopurificare chimică, în special pe cale fotochimică, fapt ce a permis determinarea influenței tiolilor la formarea stării redox a apelor naturale de suprafață.

Semnificația teoretică a lucrării de cercetare constă în complementarea cunoștințelor fundamentale în domeniul chimiei ecologice despre influența compușilor tiolici asupra proceselor de autopurificare chimică.

Valoarea aplicativă a rezultatelor cercetării vizează utilizarea acestora în studiul ecochimic al apelor naturale de suprafață, posibilitatea depistării poluării cu substanțe biodegradabile de natură proteică.

Implementarea rezultatelor științifice: rezultatele obținute pot fi valorificate de instituțiile specializate în domeniul chimiei ecologice și protecției mediului pentru monitoringul apelor de suprafață de pe teritoriul țării, precum și în evaluarea nivelului de poluare a obiectelor acvatice și prognozarea consecințelor pentru ecosisteme acvatice.

АННОТАЦИЯ

Идентификационные данные: Блонски Владислав, Фотохимические превращения некоторых тиоловых веществ и их участие в процессах химического самоочищения природных вод, диссертация на соискания ученой степени кандидата химических наук, Кишинев, 2021.

Структура диссертации: введение, шесть глав, общие выводы и рекомендации, библиография из 125 наименований, 9 приложений, 117 страниц основного текста, 65 рисунка, 24 таблиц. Полученные результаты опубликованы в 15 научных трудах.

Ключевые слова: тиолы, цистеин, самоочищение, фотолиз, редокс состояние, ингибирующая способность, меркаптид, мониторинг, спиролина, токсичность.

Цель работы: оценить вклад тиолов в процессы химического самоочищения водных систем, установив закономерности фотохимического превращения тиолов.

Задачи: установление закономерностей фотохимических, окислительно-восстановительных и радикальных превращений цистеина на модельных системах; мониторинг содержания тиоловых соединений и гидрохимических параметров в гидрографическом бассейне реки Днестр; проведение биотестирования с использованием цистеина и глутатиона для установления их влияния на биологическую активность гидробионтов.

Научная новизна и оригинальность состоит в изучении фотохимических превращений цистеина, и его влияние на редокс состояние воды. Экстраполяция закономерностей в модельных системах на реальные системы с использованием базы данных, полученной в результате мониторинга содержания тиоловых соединений в поверхностных водах.

Полученный результат, который способствует решению важной научной проблемы, заключается в научном переосмыслении места и роли автохтонных тиоловых соединений в природных водах, что привело к комплексному изучению их влияния на процессы химического самоочищения, особенно фотохимическим путём, что позволило оценить влияние тиолов на формирование окислительно-восстановительного состояния поверхностных вод.

Теоретическая значимость работы заключается в дополнении фундаментальных знаний в области экологической химии о влиянии тиоловых соединений на химические процессы самоочищения.

Прикладное значение: результаты исследования направлены на их использование в экокхимическом изучении природных поверхностных вод, возможность обнаружения загрязнения биоразлагаемыми веществами белковой природы.

Внедрение научных результатов: полученные результаты могут быть использованы учреждениями, специализирующимися в области экологической химии и охраны окружающей среды, для мониторинга поверхностных вод в стране, а также при оценке уровня загрязнения водных объектов и прогнозирования последствий для водных экосистем.

ANNOTATION

Identification data: Blonschi Vladislav, Photochemical transformations of some thiol substances and their participation in chemical self-purification processes of natural waters,

PhD thesis in chemical sciences, Chisinau, 2021.

Thesis structure: introduction, six chapters, general conclusions and recommendations, bibliography of 125 titles, 9 annexes, 117 pages of basic text, 65 figures, 24 tables. The results obtained are published in 15 of scientific papers.

Keywords: thiols, cysteine, self-purification, photolysis, redox status, inhibitory capacity, mercaptide, monitoring, spirulina, toxicity.

The aim of the paper: consists in evaluating the contribution of thiols in the processes of chemical self-purification of aquatic systems, by establishing the legitimacy of photochemical transformation of thiols.

The objectives of the research: to establish the legitimacy of photochemical, redox and radical transformation of cysteine on model systems; monitoring the content of thiol compounds and hydrochemical parameters in the water bodies in the Dniester river basin; conducting bioassays using cysteine and glutathione, to establish their influence on the biological activity of hydrobionts.

Scientific novelty and originality: it consists in the study of photochemical transformations of cysteine and its influence on the redox state of water. Extrapolation of the legalities on model systems to the real systems, having as reference the database obtained following the monitoring of the thiol compounds in some surface waters.

The result obtained that contributes to solving an important scientific problem consists in the scientific reconceptualization about the place and role of native thiol compounds in natural waters, which led to the complex study of their influence on chemical self-purification capacity, especially photochemically. allowed to determine the influence of thiols on the formation of the redox state of natural surface waters.

Theoretical significance: of the research paper consists in complementing the fundamental knowledge in the field of ecological chemistry about the influence of thiol compounds on chemical self-purification processes.

Applicative value: of the research results aim at their use in the ecochemical study of natural surface waters, the possibility of detecting pollution with biodegradable substances of a protein nature.

Implementation of scientific results: the results obtained can be used by institutions specializing in ecological chemistry and environmental protection for monitoring surface water in the country, as well as in assessing the level of pollution of aquatic objects.

BLONCHI VLADISLAV

**PHOTOCHEMICAL TRANSFORMATIONS OF SOME THIOLIC SUBSTANCES AND
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145.02. ECOLOGICAL CHEMISTRY OF WATER

Abstract of the doctoral thesis in chemical sciences

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