

SENSITIZED PHOTOLYSIS OF THIOGLYCOLIC ACID IN AQUATIC ENVIRONMENT

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Abstract. It is known that thioglycolic acid (TgA) is widely used in industry and, unlike many other thiols, has a negative influence on organisms, similar to cysteine (Cys). The goal of this work was to study the TgA photochemical transformations in waters using model systems and to determine the kinetic parameters by varying the irradiation sources. It was found that TgA undergoes destruction on induced photolysis in the presence of humic substances (HSs), and its half-life can be estimated as 10-14 days, depending on weather conditions (cloudiness, time of day, season *etc.*). Results obtained in the course of this study on model systems were transferred to natural waters, and it was concluded that TgA has a positive influence on the chemical self-purification processes of water, in the natural aquatic environment. This is manifested by increasing the self-purification capacity of water, due to the generation of active oxygen species (ex.: $O_2^{\cdot-}$, $\cdot OH$, 1O_2), which lead to the degradation not only of this thiol, but of other pollutants present in aquatic environment, as well. At the same time, the products of the transformations are harmless to the aquatic environment and hydrobionts.

Keywords: photochemical transformation, thioglycolic acid, humic substance, kinetic parameter, natural water.

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Introduction

Photochemistry has become an important field in scientific research in recent years. Many photochemical transformations play an important role in the environment and are of interest, including those of various pollutants present in natural water bodies. Of all the pathways of abiotic degradation of pollutants, photochemical processes in the surface layer of the aquatic environment unfold with the highest rate. Understanding photolysis of pollutants in surface waters is essential to the assessment of potential exposures and risks to aquatic organisms as well as to humans *via* drinking water supplies [1-4].

Natural surface waters accumulate pollutants through wastewater discharges or stormwater runoffs following their use in agriculture, stockbreeding, medicine, and industry. It has been shown [2] that in surface waters, pollutants undergo direct, induced and sensitized photolysis, depending on several factors, such as: pH, mineralization of the natural waters, the presence of different forms of transition metal ions (Fe, Cu, Zn, Cd, Hg *etc.*),

the chemical nature of the pollutants, as well as the presence of dissolved organic matter [4-6]. Dissolved organic matter, predominantly humic substances (HSs), act as sensitizers, thus participating in the degradation of pollutants [2,5,7]. In natural waters, HSs act as photosensitizers: they reach an excited state by absorbing sunlight and then interact with dissolved oxygen in the water, photochemically producing reactive intermediate species that contribute to decomposition of pollutants [2,8-12]. To summarize the process, absorption of sunlight by HSs initially leads to the singlet-excited state $^1HSs^*$, which then undergoes intersystem crossing to the longer lived $^3HSs^*$ and may then return to the ground state, reacting directly with contaminants, or with ground state O_2 to form 1O_2 . Despite low steady-state concentrations of photochemically produced reactive intermediates, they effectively enhance the photochemical transformation of a wide range of contaminants. For this reason, it is important to study the influence of HSs on the processes of pollutants photolysis in aquatic environments.

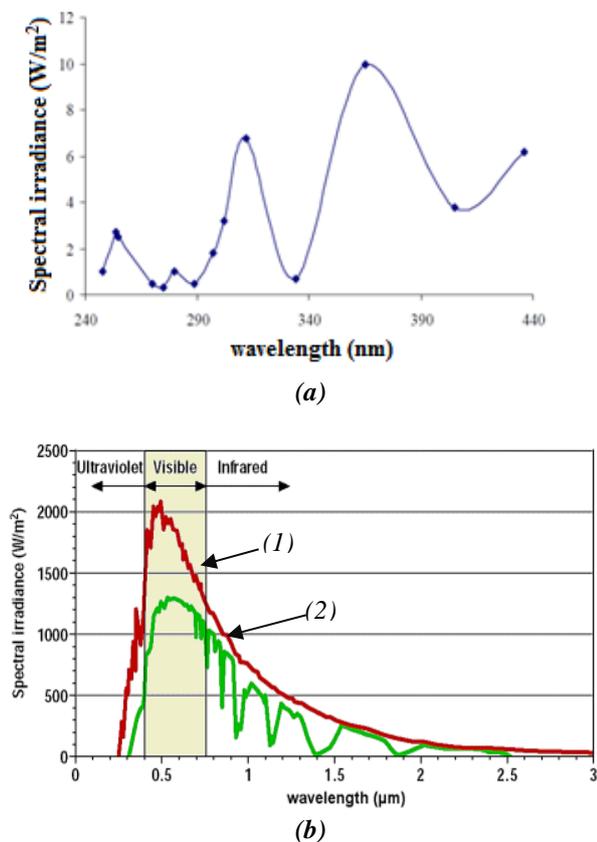


Figure 1. The emission spectra of DRT-400 lamp (a) and Solar Simulator Oriel 9119X (b) with AM0 (1) and AM1.5D (2) filters [15].

Previous studies have shown that thiols with the general formula RSH represent a class of reducing compounds, present in the composition of natural waters, that fulfil various functions in biogeochemical systems. Thiols are divided into two large subclasses: of natural and anthropogenic origin [1]. One representative of the thiols subclass of anthropogenic origin is thioglycolic acid (TgA). TgA has a wide range of applications: it is used as the main material for the synthesis of polyvinyl chloride stabilizers, as a corrosion inhibitor in oil field industry, in cosmetics (mainly in hair care products). In textile industry, TgA is used in shrink resistant treatment of wool, in fabric dyeing and in leather processing, thus easily reaching natural surface waters [13]. Despite its vast useful applications, TgA has negative effects on human health [14]. The negative influence of some thiols on living organisms has been studied in detail by Duca, Gh. *et al.* [1], who have shown that even some thiols of natural origin, such as cysteine (Cys), manifest toxicity to the aquatic organisms, like cyanobacterial species *Arthrospira platensis*. In this context, the transformations of that TgA undergoes in

natural environment become of great scientific interest and importance.

The goal of this work was to study the photochemical transformations of TgA in natural waters and to determine the transformation dependencies and kinetic parameters on irradiation with different light sources.

The study of the dependencies of pollutants transformation, in laboratory conditions, will be used to explain those that occur in natural aquatic environments. To achieve this, systems containing different components present in natural waters were simulated, in order to investigate the sensitized photolysis of TgA in the presence of HSs. Initially, photolysis was studied in the absence and presence of H₂O₂, by artificial exposure to UV radiation of various sources (UV-Vis DRT-400 lamp, the powerful UV lamp from Vilber Lourmat, VL-215.LC and the Solar Simulator (SS), Oriel Model 9119X, equipped with three filters, Figure 1 [15]). Further, the complexity of the systems was increased by the addition of Fe(III) and Cu(II) ions.

Experimental

Materials

Thioglycolic acid, humic acid sodium salt of technical grade, *p*-nitrosodimethylaniline (PNDMA) and oxygen peroxide were purchased from Sigma-Aldrich (Germany); iron(III) trichloride hexahydrate and copper(II) sulphate pentahydrate from Stanchem (Poland). All solutions were prepared with distilled water, Aqua D Distillers - 4 Pak.

Humic substances

All model solutions of humic substances were prepared using distilled water and humic acid sodium salt of technical grade. Subsequently, humic substances solutions with the concentration of 0.16-3.33 mg/L, were prepared by dilution. Higher concentrations would have increased the turbidity level of the solutions, thus hindering the determination of TgA concentration.

Thioglycolic acid determination

An amount of thioglycolic acid was dissolved in distilled water, to obtain a 1 M solution, subsequently all solutions were prepared by dilution.

The kinetic dependencies of the photochemical transformation process of TgA were studied using the UV-Vis spectroscopy method, by measuring the absorbance of the substrate solution on a T80+ UV-Vis Spectrometer, at 234 nm.

Method for determination of free •OH radical

The method is based on the interaction of •OH with PNDMA, resulting in solution discoloration, thus allowing the indirect determination of the free radicals using UV-Vis spectroscopy, according to the previously described method [16]. PNDMA was chosen as an indicator, since it acts as a trap of •OH formed during the photolysis of hydrogen peroxide. The employed model system consisted of phosphate buffer–PNDMA–H₂O₂, 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. Oxidation of PNDMA occurs as a result of its interaction with •OH generated by H₂O₂ under the action of light. When the rate of radicals initiation W_i and the rate constant of destruction are known, the stationary concentration of •OH may be determined by Eq.(1):

$$[\bullet OH] = \frac{W_i}{\sum k_i[S_i]} \quad (1)$$

where, W_i - rate of radicals' initiation, M·s⁻¹;
 $\sum k_i[S_i]$ - inhibitory capacity of the medium, s⁻¹.

Calculation of kinetic parameters

The process of TgA sensitized photolysis followed pseudo-first-order kinetics in all investigated solutions (according to the Eqs.(2-6)), with respect to the concentration of the substrate that was taken in excess of the concentrations of the other components, respectively [15].

$$[TgA] = \frac{A}{\epsilon} * F \quad (2)$$

where, $[TgA]$ - thioglycolic acid concentration, M;
 A - absorbance at $\lambda = 234$ nm;
 ϵ - molar extinction coefficient, L·mol⁻¹·cm⁻¹ (for TgA has been experimentally determined and is 294 L·mol⁻¹·cm⁻¹);
 F - dilution factor.

$$W = -\frac{d[TgA]}{dt} = -\frac{[TgA]_2 - [TgA]_1}{t_2 - t_1} = -k[TgA] \quad (3)$$

where, W - TgA photochemical transformation rate, M·s⁻¹;
 $[TgA]_1$ and $[TgA]_2$ - thioglycolic acid concentration at time t_1 and t_2 , respectively, M;
 t_1 and t_2 - irradiation time, s.

$$k = \frac{1}{t} \ln \frac{[TgA]_0}{[TgA]_t} \quad (4)$$

where, k - rate constant of TgA, s⁻¹;
 t - irradiation time, s;
 $[TgA]_0$ - thioglycolic acid initial concentration, M;
 $[TgA]_t$ - thioglycolic acid concentration at time t , M.

$$k(avg) = \frac{K_1 + K_2 + K_3 + K_4}{4} \quad (5)$$

where: k_1 - rate constant determined following the variation of the TgA initial concentrations;
 k_2 - rate constant determined following the variation of the HSs initial concentrations;
 k_3 - rate constant determined following the variation of the Fe(III) initial concentrations;
 k_4 - rate constant determined following the variation of the Cu(II) initial concentrations.

$$\tau_{1/2} = \frac{\ln 2}{k(avg)} \quad (6)$$

where, $\tau_{1/2}$ - half-life of TgA, s;
 $k(avg)$ - average rate constant of TgA, s⁻¹.

Irradiation sources

In this study, two lamps and a Solar Simulator (SS), Oriel Model 9119X, were used as irradiation sources, some technical parameters are presented in Table 1.

Experimental procedure

Four systems were modeled to simulate natural water conditions:

- 1) TgA–HSs– $h\nu$;
- 2) TgA–HSs–H₂O₂– $h\nu$;
- 3) TgA–HSs–H₂O₂–Fe(III)– $h\nu$;
- 4) TgA–HSs–H₂O₂–Cu(II)– $h\nu$.

The solutions were prepared using double distilled water and the reaction was carried out at pH 6.5, which was periodically monitored (before and after the photolytic session) using the WTW Inolab pH 720 pH-meter. All measurements were carried out under temperature control conditions, at 25°C. The solutions were contained in aerobic conditions, bringing the model closer to natural conditions. The 50 mL samples were placed in a thin-walled quartz glass of 100 mL and successively exposed to all irradiation sources mentioned above.

For each modeled system, step-by-step, the initial concentrations of one component were varied (according to the data presented in Table 2), and the initial concentrations of the other components were kept constant.

The absorbance of irradiated solutions was measured at $\lambda = 234$ nm, using a T80+ UV-Vis Spectrometer, every 5 minutes, for a total of 60 min. All systems were irradiated at the above-mentioned irradiation sources (Table 1), under the same conditions, in quartz glasses of the same size, for one hour, periodically measuring the absorbance of the irradiated solution.

The obtained results were used to calculate the TgA concentrations and the kinetic parameters of the modeled solutions, according to Eqs.(2-6). Calculation of kinetic parameters of the TgA sensitized photolysis shows that the reaction follows a pseudo-first-order kinetics in all modeled systems, with respect to the concentration of the excess substrate.

Table 1

The used irradiation sources and their general characteristics.			
<i>Irradiation source</i>	<i>Filters</i>	<i>Emitted wavelengths, nm</i>	<i>Comments</i>
DRT-400 lamp		240-440	Characterized by 3 intensive lines at 312 nm, 365 nm and 436 nm.
UV lamps, VL-215.LC	254 nm	254	Monochromatic light
	365 nm	365	Monochromatic light
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 of less than 290 nm.

Table 2

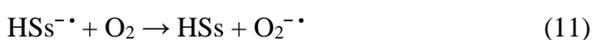
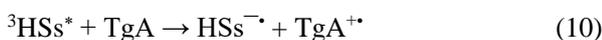
Initial concentrations of all components added to the modeled systems.						
<i>The modeled system</i>	<i>[TgA]₀ · 10³, M</i>	<i>[HSs]₀, mg · L⁻¹</i>	<i>[H₂O₂]₀ · 10⁴, M</i>	<i>[Fe(III)]₀ · 10⁵, M</i>	<i>[Cu(II)]₀ · 10⁵, M</i>	
TgA-HSs		0.16				
		1.66	0.33			
		2.66	1.00			
		3.33	1.66	-	-	-
		4.16	2.33			
		6.66	3.33			
TgA-HSs-H ₂ O ₂		0.16	0.33			
		1.66	0.33	0.66		
		2.66	1.00	1.00		
		3.33	1.66	1.60	-	-
		4.16	2.33	2.50		
		6.66	3.33	5.00		
TgA-HSs-H ₂ O ₂ -Fe(III)		0.16	0.33	0.33		
		1.66	0.33	0.66	1.00	
		2.66	1.00	1.00	1.66	
		3.33	1.66	1.60	6.60	
		4.16	2.33	2.50	10.00	
		6.66	3.33	5.00	12.50	
TgA-HSs-H ₂ O ₂ -Cu(II)		0.16	0.33		0.33	
		1.66	0.33	0.66	1.00	
		2.66	1.00	1.00	1.66	
		3.33	1.66	1.60	6.60	
		4.16	2.33	2.50	10.00	
		6.66	3.33	5.00	12.50	

Results and discussion

Previous studies have shown the presence of thiols in natural aquatic environment, in a concentration range of 10^{-6} - 10^{-5} M [1]. It was found that thiol concentrations depend on daytime and weather conditions, as well as on the location of the monitored aquatic object, which is related to the activity of hydrobionts [1]. The same study demonstrated that some thiols, such as Cys, show toxicity towards some microorganisms, depending on Cys concentration. As a continuation of the previous research, this work was focused on the study of photochemical transformations of an anthropogenic originating thiol (TgA).

The influence of HSs on the TgA photolysis

In the present study, the principle from-simple-to-complex was used, which implies a stepwise increase in the complexity of the investigated model systems. The irradiation of the first, simplest system, which consisted of TgA and HSs in aqueous solution, showed that TgA concentration decreases over time, and the substrate is subjected to sensitized photolysis with HSs, according to the mechanism (Eqs.(7-11)) [17].



Based on the obtained experimental data, the TgA transformation rates were calculated, which are shown in Figures 2 and 3.

Figure 2 shows that TgA undergoes induced photolysis in the presence of HSs and the rates of induced photolysis directly depend on the initial concentration of TgA added to the system, as well as on the quality of the emitted radiation. The values of induced photolysis rates in the presence of HSs proved to be ranging between 10^{-11} - 10^{-8} $\text{M}\cdot\text{s}^{-1}$. The highest values were recorded when irradiating with the DRT-400 lamp, which is due to the fact that the emission spectrum of the DRT-400 lamp coincides most closely with the absorption spectrum of HSs, which best absorbs radiation in the range of 220-365 nm [18]. When modeled systems were irradiated with the lamp emitting monochromatic light, the values of the TgA photolysis rates were lower than those obtained during irradiation with the DRT-400 lamp, but they were quite high compared to those for SS, because HSs has a maximum absorption at

$\lambda = 254$ nm and another peak at $\lambda = 365$ nm, respectively, and the first absorption maximum coincides with the emission spectrum of the monochromatic lamp [7,18].

The systems irradiated by SS demonstrated lower values of induced photolysis rates, which varied for the irradiated systems in function of employed filters. The highest rate values for SS irradiation were found when using the AM0 filter, which allowed the transition of the largest amount of radiation of $\lambda \leq 290$ nm, compared to other employed filters. The lowest rate values were recorded when using the AM1.5D filter, which blocked radiation $\lambda < 290$ nm, as well as decreases the intensity of the other emitted rays. Thus, the HSs absorption spectrum coincides less with the emission spectrum of SS, provided with this filter, but at the same time this filter allows the closest modeling of sun-emitted radiation. Therefore, for natural waters under these conditions, the values of sensitized photolysis rates with HSs would be ranging between 10^{-10} - 10^{-11} $\text{M}\cdot\text{s}^{-1}$. In order to demonstrate that the transformations are induced by irradiation, control experiments in the dark were carried out using the same solutions.

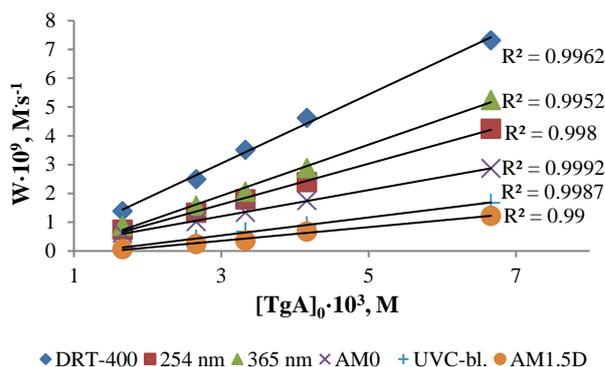


Figure 2. The influence of TgA concentration on its photochemical transformation, $[\text{HSs}]_0 = 1 \text{ mg}\cdot\text{L}^{-1}$, pH 6.5, 25°C.

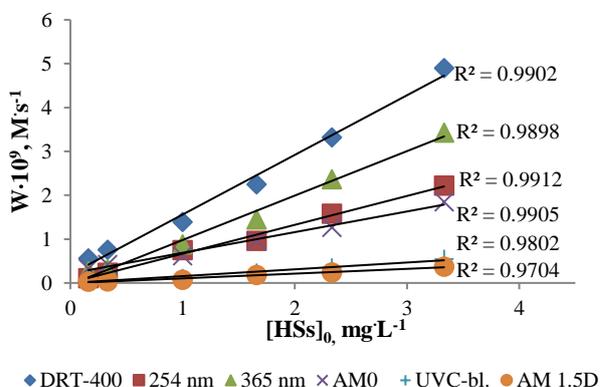
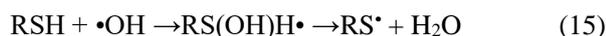
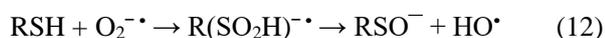


Figure 3. The influence of the HSs concentration on the TgA photochemical transformation, $[\text{TgA}]_0 = 1.66 \cdot 10^{-3} \text{ M}$, pH 6.5, 25°C.

It was found that TgA concentrations remain unchanged over time. Thus, it was demonstrated that HSs participate as sensitizers in photolysis, by absorbing radiation and reaching an excited state, further passing on the energy to the TgA, which is subsequently destroyed. On the other hand, reactive intermediates (ex.: $O_2^{\cdot-}$, $\cdot OH$, 1O_2 , H_2O_2 , $^3SH^*$) are produced photochemically and further react with TgA and contribute to its degradation [2,19].

Figure 3 shows that the rates of TgA induced photolysis are directly proportional to the initial concentration of HSs in the system, which is another confirmation of the fact that the irradiation process of HSs photochemically produces reactive intermediates, which lead to TgA destruction [20]. HSs can be considered as sensitizers for substrate destruction, which can occur according to the Eqs.(12-18) [21]:



where, RSH designates the general formula of thiols, in this particular case it is the CO_2HCH_2SH or TgA.

The values of the TgA photolysis rates ranged from 10^{-11} to $10^{-8} M \cdot s^{-1}$ and also depended on the quality of the emitted radiation. The highest values were recorded when irradiating with the DRT-400 lamp, and the lowest for the systems irradiated with the SS equipped with the AM1.5D filter. Although the SS is emitting some of the radiations that coincide with the HSs absorption spectrum, the TgA transformation rates are much lower, because the amount of UVB and UVC radiation is very small, of only up to 5-10% of the total radiation emitted by the SS, the most of the emitted radiation being in the UVA, VIS and IR regions [8].

The influence of H_2O_2 on the TgA induced photolysis

Previous studies have shown that the presence and amount of H_2O_2 in natural aquatic environments directly influences their quality [2]. Hydrogen peroxide, present in natural waters in concentrations of 10^{-7} - $10^{-5} M$ [8,22-25], was

introduced into the studied system, in order to make it more complex. The systems with added H_2O_2 were irradiated by the same irradiation sources, under the same conditions. One by one, the initial concentrations of one component were modified, and the initial concentrations of the other components were kept constant. The TgA photochemical transformation rates were calculated from the experimental results (Figures 4-6).

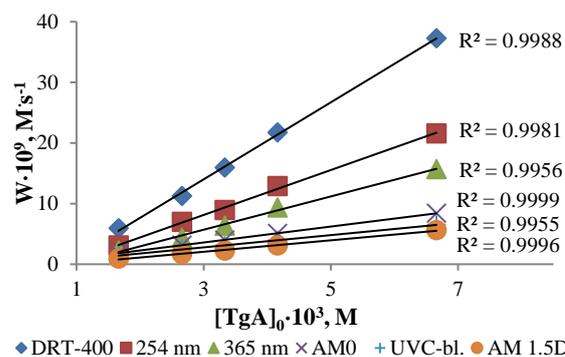


Figure 4. The influence of TgA concentration on its photochemical transformation, $[HSs]_0 = 1 \text{ mg L}^{-1}$, $[H_2O_2]_0 = 1 \cdot 10^{-4} \text{ M}$, pH 6.5, 25°C.

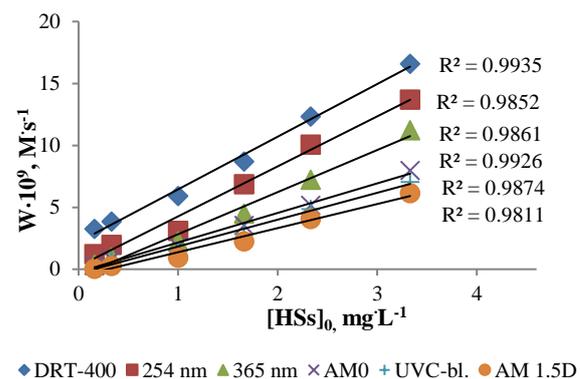


Figure 5. The influence of the HSs concentration on the TgA photochemical transformation, $[TgA]_0 = 1.66 \cdot 10^{-3} \text{ M}$, $[H_2O_2]_0 = 1 \cdot 10^{-4} \text{ M}$, pH 6.5, 25°C.

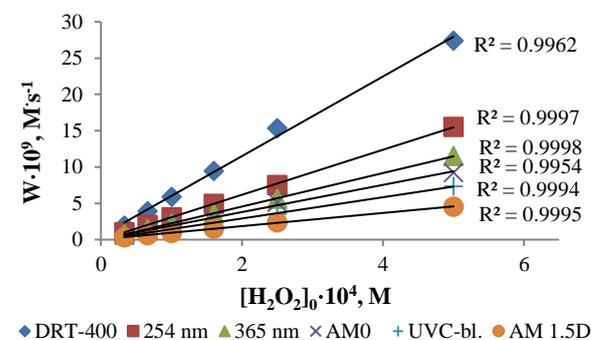


Figure 6. The influence of the H_2O_2 concentration on the TgA photochemical transformation, $[TgA]_0 = 1.66 \cdot 10^{-3} \text{ M}$, $[HSs]_0 = 1 \text{ mg L}^{-1}$, pH 6.5, 25°C.

Figures 4-6 show that the TgA photochemical transformation rates increase 3-5 folds upon H₂O₂ addition to the system which generates upon irradiation (Eq.(19)) •OH - the most reactive species in natural waters [2,16].



The TgA photochemical transformation rates directly depend on the concentrations of all parameters in the system, as well as on the quality and quantity of emitted radiation. It was found that the rates of induced photolysis in the presence of H₂O₂ increased with increasing TgA initial concentrations in the system and ranged between 10⁻¹⁰ and 10⁻⁸ M·s⁻¹ (Figure 4). As for the system that did not contain H₂O₂, the highest values were recorded upon irradiation with the DRT-400 lamp, and the smallest - for the systems irradiated with the SS equipped with AM1.5D filter.

Upon variation of HSs concentration in the system (Figure 5), the TgA photochemical transformation rates increased concomitantly with increasing HSs concentration. This shows that TgA photochemical transformations occur by two pathways: the first is its oxidation by •OH, generated by H₂O₂ photolysis added in the system, and the second - sensitized photolysis involving HSs. The values of the TgA photolysis rates ranged from 0.50·10⁻¹⁰ to 1.66·10⁻⁸ M·s⁻¹ and, as in previous cases, the highest values were recorded when irradiating with the DRT-400 lamp, and the lowest for the systems irradiated with SS equipped with AM1.5D filter, which allowed the passage of radiation identical to natural light.

For the systems in which the H₂O₂ initial concentration varied, the values of TgA photochemical transformation rates ranged from 3.10·10⁻¹⁰ to 2.74·10⁻⁸ M·s⁻¹, were the highest and increased with the increasing of the H₂O₂ initial concentrations in the system. Thus, the same dependencies were observed, with the highest values of TgA photochemical transformation rates

obtained when irradiating with the DRT-400 lamp, and the smallest for the systems irradiated with SS equipped with AM1.5D filter.

To demonstrate the generation of •OH, a “trap” was added to the system - the yellow solution of the PNDMA dye, which is discoloured upon interaction with the •OH, generated as a result of H₂O₂, HSs and TgA photolysis. Thus, the presence of •OH in the studied systems was proved and the values of its concentrations were in the range of 10⁻¹⁷–10⁻¹⁶ M (Table 3), which falls within the limits of OH radical concentrations present in natural waters of 10⁻¹⁷–10⁻¹⁴ M [26]. Their concentrations increased by increasing the TgA, HSs and, more obviously, H₂O₂ initial concentrations in the system.

Thus, the obtained results show that in the case of TgA sensitized photolysis in the presence of H₂O₂ with HSs, two parallel processes take place: direct destruction of TgA on its interaction with HSs in excited state, and its destruction on interaction with intermediate active particles, such as OH radicals, generated by irradiation of HSs and H₂O₂.

The influence of Cu(II) and Fe(III) on the TgA induced photolysis

Among the transition metals present in natural waters, Cu(II) and Fe(III) play an important role in the generation of free radicals. Transition metal ions are indispensable components of natural waters. Depending on the environmental conditions, transition metal ions exist in different oxidation states and are part of a variety of inorganic and organometallic compounds [27-28]. Dissolved oxygen in water leads to an oxidized state of metal ions participating in the activation of oxygen and hydrogen peroxide, giving species that further interact with various pollutants [29]. Based on this, the kinetics of TgA sensitized photolysis in the presence of Fe(III) and Cu(II) ions was studied. Experimental results are shown in Figures 7-10, Table 4.

Table 3

Concentrations of •OH, generated in the system, at various concentrations of TgA and various sources of irradiation.

[TgA]·10 ³ , M	[•OH]·10 ¹⁶ , M					
	DRT-400	254 nm	365 nm	AM0	UVC-bl.	AM1.5D
1.66	0.27	0.06	0.06	0.04	0.03	0.03
2.66	3.57	0.71	0.65	0.56	0.49	0.41
3.33	6.51	1.30	1.29	0.99	0.87	0.73
4.16	15.20	2.13	1.94	1.37	1.22	1.11
6.66	28.00	5.60	5.29	2.58	2.21	2.03

Experimental conditions: [PNDMA]₀ = 1.1·10⁻⁵ M, [HSs]₀ = 1 mg·L⁻¹, [H₂O₂]₀ = 1·10⁻⁴ M, pH 6.5, 25°C.

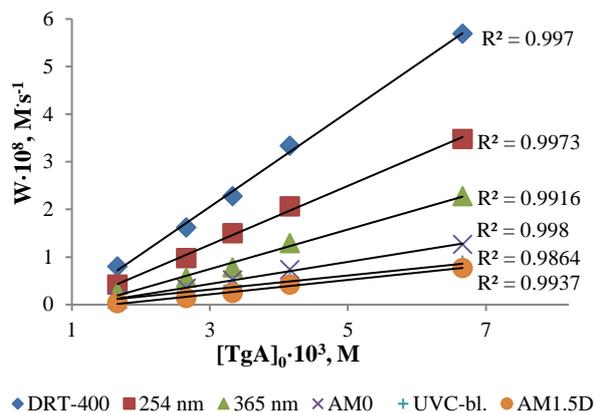


Figure 7. The influence of TgA concentration on its photochemical transformation, [HSs]₀ = 1 mg·L⁻¹, [H₂O₂]₀ = 1·10⁻⁴ M, [Fe(III)]₀ = 1·10⁻⁵ M, pH 6.5, 25°C.

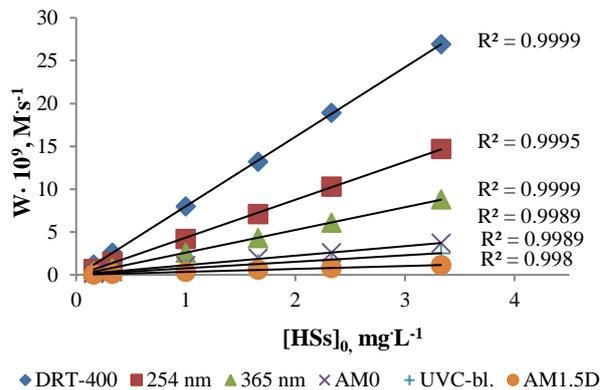


Figure 8. The influence of the HSs concentration on the TgA photochemical transformation, [TgA]₀ = 1.66·10⁻³ M, [H₂O₂]₀ = 1·10⁻⁴ M, [Fe(III)]₀ = 1·10⁻⁵ M, pH 6.5, 25°C.

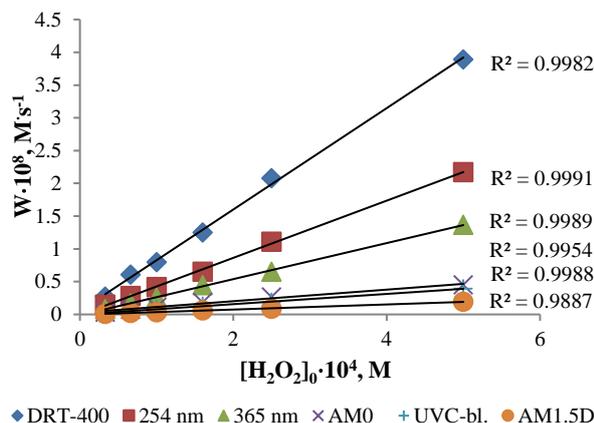


Figure 9. The influence of the H₂O₂ concentration on the TgA photochemical transformation, [TgA]₀ = 1.66·10⁻³ M, [HSs]₀ = 1 mg·L⁻¹, [Fe(III)]₀ = 1·10⁻⁵ M, pH 6.5, 25°C.

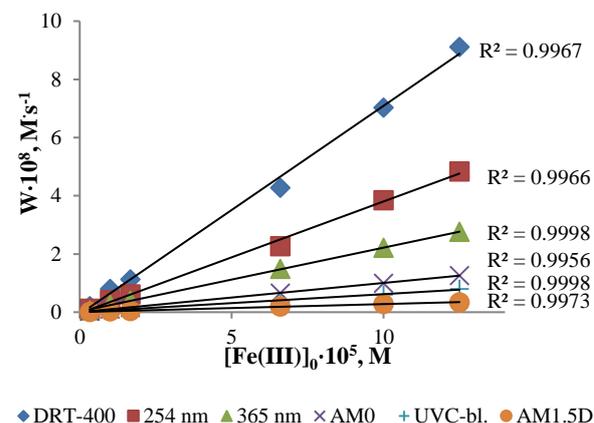


Figure 10. The influence of the Fe(III) ions concentration on the TgA photochemical transformation, [TgA]₀ = 1.66·10⁻³ M, [HSs]₀ = 1 mg·L⁻¹, [H₂O₂]₀ = 1·10⁻⁴ M, pH 6.5, 25°C.

Table 4

Concentrations of ·OH, generated in the system, at various concentrations of TgA and various sources of irradiation.

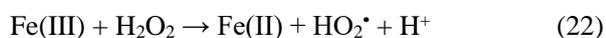
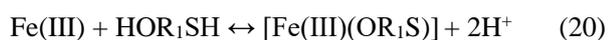
[TgA] ₀ · 10 ³ , M	[·OH] · 10 ¹⁵ , M					
	DRT-400	254 nm	365 nm	AM0	UVC-bl.	AM1.5D
1.66	0.36	0.08	0.07	0.04	0.03	0.03
2.66	0.63	0.13	0.09	0.07	0.05	0.05
3.33	2.00	0.41	0.40	0.23	0.19	0.16
4.16	4.57	0.96	0.82	0.45	0.39	0.35
6.66	13.90	2.30	2.19	1.10	0.98	0.86

Experimental conditions: [PNDMA]₀ = 1.1·10⁻⁵ M, [HSs]₀ = 1 mg·L⁻¹, [H₂O₂]₀ = 1·10⁻⁴ M, [Fe(III)]₀ = 1·10⁻⁵ M, pH 6.5, 25°C.

Photochemical transformation of TgA in the presence of Fe(III) ions

Iron is one of the most abundant transitional metal ions ubiquitously present in natural waters, in concentrations of 10^{-7} - 10^{-8} M. In order to elucidate the contribution of Fe(III) ions to the TgA induced photolysis, the system's complexity was increased by adding Fe(III) ions, which acted as a catalyst. Previous studies showed that the speciation of iron is highly pH dependent. In most natural waters (pH 6–8), the dominant species of iron is the photostable $\text{Fe}(\text{OH})^{2+}$. However, in acid conditions, Fe^{3+} and $\text{Fe}(\text{OH})^+$ could generate $\bullet\text{OH}$ under irradiation, which actively participates in pollutants oxidation in the aquatic environment [30]. In this case, a “trap” was also added to the system - the yellow solution of the PNDMA dye, which discolorates by interacting with the $\bullet\text{OH}$ generated as a result of H_2O_2 , HSs, Fe(III) and TgA photolysis. Thus, the presence of $\bullet\text{OH}$ in the studied systems was proved. The values of $\bullet\text{OH}$ concentrations were in the range of 10^{-16} - 10^{-15} M (Table 4), higher than in the absence of Fe(III) ions.

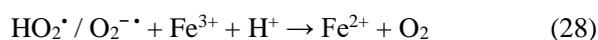
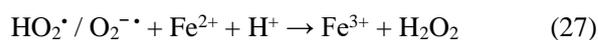
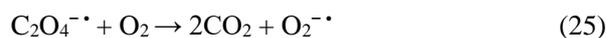
Obtained results clearly show that the values of the TgA photochemical transformation rates in the presence of Fe(III) ions were approximately 2-4 folds higher and were in the range of 10^{-10} - 10^{-8} $\text{M}\cdot\text{s}^{-1}$ (Figures 7-10). It is well known that TgA can bind with ferric and ferrous ions. TgA effectively binds with Fe(III) to form the ferric thioglycolate complex. In the presence of oxygen, this complex immediately decomposes to produce Fe(II) and dithioglycolate according to the Eqs.(20,21) [31]:



where: HOR_1SH is TgA.

It is known that in the presence of H_2O_2 , TgA forms a complex with Fe(III) (generated via reaction Eq.(20)), accelerates the reduction of Fe(III) to Fe(II) (Eqs.(20,21)), and promotes the Fenton reaction leading to complete degradation of some pollutants. Moreover, TgA has the ability to utilize iron species in the post-treatment solution for subsequent degradations, even at near neutral pH [31]. However, this fact has not been confirmed for other thiols, such as glutathione [2]. Previous studies show that the rate of GSH transformation in the presence of Fe(III), at

natural water pH, is very low and can be neglected [32]. At the same time, it is known that in the presence of Fe(III) ions, the irradiation of dissolved organic matter (in this case HSs), leads to the generation of $\bullet\text{OH}$ according to the Eqs.(23-29) [29].



Figures 7-10 show that the dependencies of induced photolysis of TgA are the same as for other systems. The values of the TgA photochemical transformation rates increase with increasing initial concentrations of HSs, TgA, H_2O_2 and, more obviously, of Fe(III) ions in the system.

It was also discovered that, similarly to the other studied systems, the values of the TgA photochemical transformation rates depend on the quality and quantity of the emitted radiation. The highest values were attested for the system irradiated by the DRT-400 lamp, which emits radiation in the range of 240-440 nm, thus coinciding the best with the absorption spectrum of HSs, H_2O_2 as well as the compounds of Fe(III). The lowest values were recorded for the system irradiated by SS, equipped with the AM1.5D filter, which emits radiation identical to the one that reaches the Earth's surface from the Sun.

Therefore, it can be concluded that the active particles which are formed during the TgA induced photolysis with HSs in the presence of H_2O_2 and iron ions, are generated with the involvement of Fe(III) ions as the catalyst.

Photochemical transformation of TgA in the presence of Cu(II) ions

Copper is an essential metal that participates in biochemical processes, therefore its presence in natural waters is obvious. Its concentration reaches 10^{-7} M, and it is present in various forms (soluble, colloidal and suspended). Many studies have shown that copper ions, unlike iron ions, participate actively as a catalyst in the processes of pollutants transformation in the aquatic environment [32].

For this reason, the influence of Cu(II) ions on TgA induced photolysis was studied, with HSs participation, in the presence of H₂O₂ upon irradiation with the same light sources. The irradiation conditions of this more complex system were the same as in the other cases. TgA photolysis rates were calculated in relation to all the components added to the system; the results are shown in Figures 11-14.

The highest values of TgA photolysis rates were attested in the systems where Cu(II) ions were added, and were of the order of 10⁻¹⁰-10⁻⁷ M·s⁻¹, one or two orders of magnitude higher than in their absence. The obtained results are in accordance with

previous studies, which show that Cu(II) ions effectively catalyze the photochemical transformation process of thiols [32].

Figures 11-14 show that the TgA photochemical transformation rates in the presence of Cu(II) ions were linearly dependent and increased with increasing initial concentrations of HSs, TGA, H₂O₂ and, more obviously, of Cu(II) ions in the system. This is explained by the fact that Cu(II) compounds, form reactive particles on irradiation, which oxidize TgA, according to Eq.(30) [33].

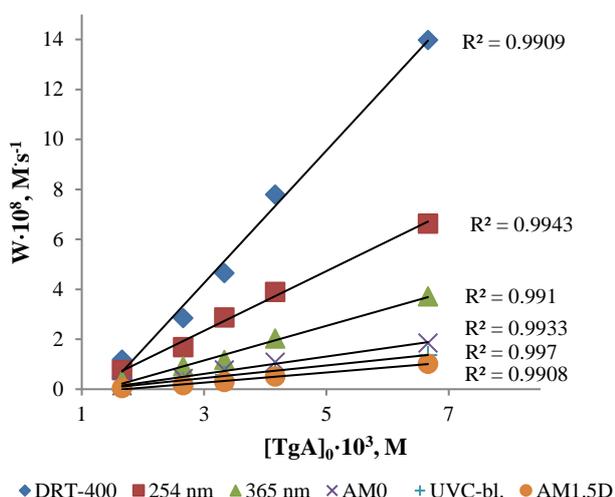
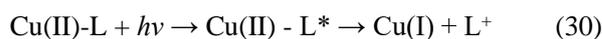


Figure 11. The influence of TgA concentration on its photochemical transformation, [HSs]₀ = 1 mg·L⁻¹, [H₂O₂]₀ = 1·10⁻⁴ M, [Cu(II)]₀ = 1·10⁻⁵ M, pH 6.5, 25°C.

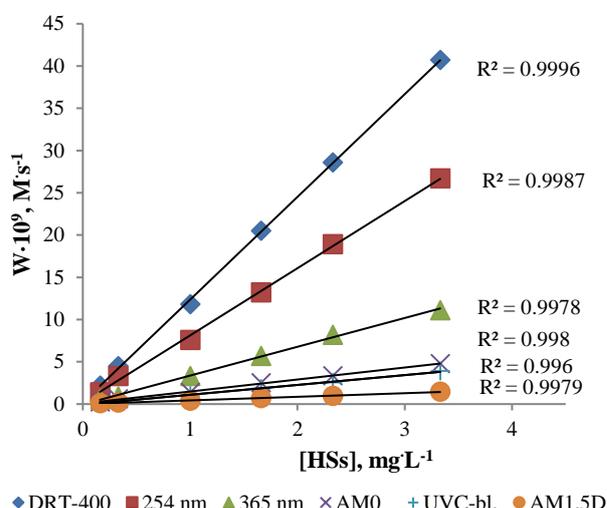


Figure 12. The influence of the HSs concentration on the TgA photochemical transformation, [TgA]₀ = 1.66·10⁻³ M, [H₂O₂]₀ = 1·10⁻⁴ M, [Cu(II)]₀ = 1·10⁻⁵ M, pH 6.5, 25°C.

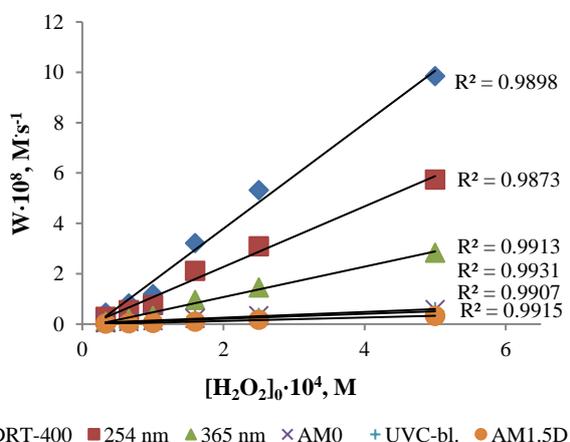


Figure 13. The influence of the H₂O₂ concentration on the TgA photochemical transformation, [TgA]₀ = 1.66·10⁻³ M, [HSs]₀ = 1 mg·L⁻¹, [Cu(II)]₀ = 1·10⁻⁵ M, pH 6.5, 25°C.

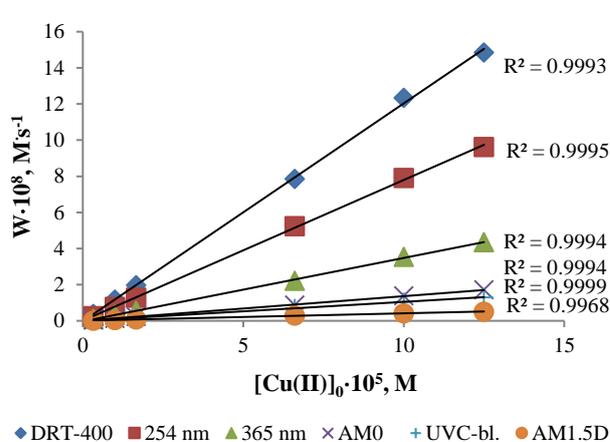


Figure 14. The influence of the Cu(II) ions concentration on the TgA photochemical transformation, [TgA]₀ = 1.66·10⁻³ M, [HSs]₀ = 1 mg·L⁻¹, [H₂O₂]₀ = 1·10⁻⁴ M, pH 6.5, 25°C.

On the other hand, thiols have the ability to reduce Cu(II) to Cu(I) [29], and in the presence of H₂O₂, Cu(I) generates OH radicals (Table 5), the most reactive particles in natural waters, according to Eq.(31) [34].



The yellow solution of the PNDMA dye was added to the system TgA-HSs-H₂O₂-Cu(II) to determine the concentrations of $\cdot\text{OH}$, generated as a result of H₂O₂, HSs, Cu(III) and TgA photolysis. Thus, the presence of $\cdot\text{OH}$ in the studied systems was proved, and the highest concentrations were in the range of 10⁻¹⁶-10⁻¹⁴ M (Table 5).

The same dependencies were attested in this system, similarly to previous cases, but the photochemical transformation rates were much higher. It was shown that the TgA photochemical transformation rates also depend on the quantity and quality of the emitted radiation. The highest values of the TgA photochemical transformation rates were attested for the system irradiated by the DRT-400 lamp, which emits radiation in the range

of 240-440 nm and the lowest values were for the system irradiated by SS, equipped with the AM1.5D filter, which blocks radiation with $\lambda < 290$ nm and the emitted radiation is closest to natural conditions.

For a better analysis of the kinetics of HSs-sensitized TgA photolysis, the TgA rate constants and half-life parameters were calculated, for all above-mentioned systems that proved to be of the pseudo-first order reaction.

Data presented in Table 6 show that the rate constants of the TgA induced photolysis in the presence of HSs, as sensitizers, were of the order of 10⁻⁷-10⁻⁵ s⁻¹. Analogically to the photochemical transformation rates, rate constants were linearly dependent on the initial concentrations of all components in the system, as well as on the quality of the radiation emitted by the irradiation bodies. The lowest values of the rate constants were characteristic for the system which consisted of only TgA and HSs, and ranged among 10⁻⁷-10⁻⁶ s⁻¹, irradiated at the same lamps and under the same conditions.

Table 5

Concentrations of $\cdot\text{OH}$, generated in the system, at various concentrations of TgA and various sources of irradiation.

[TgA] ₀ ·10 ³ , M	[$\cdot\text{OH}$]·10 ¹⁵ , M					
	DRT-400	254 nm	365 nm	AM0	UVC-bl.	AM1.5D
1.66	1.00	0.20	0.18	0.09	0.09	0.08
2.66	1.40	0.26	0.21	0.13	0.11	0.10
3.33	2.20	0.84	0.81	0.35	0.37	0.28
4.16	8.10	2.19	1.89	0.96	0.78	0.64
6.66	26.00	4.71	4.01	2.31	1.85	1.62

Experimental conditions: [PNDMA]₀ = 1.1 · 10⁻⁵ M, [HSs]₀ = 1 mg·L⁻¹,
[H₂O₂]₀ = 1 · 10⁻⁴ M, [Cu(II)]₀ = 1 · 10⁻⁵ M,
pH 6.5, 25°C.

Table 6

Kinetic parameters of the TgA sensitized photolysis in the presence of HSs in aqueous solution.

Irradiation source	TgA-HSs		TgA-HSs-H ₂ O ₂		TgA-HSs-H ₂ O ₂ -Fe(III)		TgA-HSs-H ₂ O ₂ -Cu(II)	
	K(avg), s ⁻¹	τ _{1/2}	K(avg), s ⁻¹	τ _{1/2}	K(avg), s ⁻¹	τ _{1/2}	K _{obs} (avg), s ⁻¹	τ _{1/2}
DRT-400	(1.18±0.08)·10 ⁻⁶	6.8 days	(5.42±0.13)·10 ⁻⁶	35.5 hours	(1.14±0.50)·10 ⁻⁵	16.9 hours	(2.16±0.41)·10 ⁻⁵	8.9 hours
254 nm	(5.64±0.04)·10 ⁻⁷	14.2 days	(3.29±0.11)·10 ⁻⁶	2.1 days	(6.30±0.47)·10 ⁻⁶	30.6 hours	(1.33±0.45)·10 ⁻⁵	14.5 hours
365 nm	(7.58±0.15)·10 ⁻⁷	10.6 days	(2.37±0.13)·10 ⁻⁶	3.4 days	(3.76±0.46)·10 ⁻⁶	2.1 days	(5.99±0.43)·10 ⁻⁶	32.1 hours
AM0	(4.75±0.15)·10 ⁻⁷	16.9 days	(1.77±0.17)·10 ⁻⁶	4.5 days	(2.26±0.44)·10 ⁻⁶	3.5 days	(2.29±0.43)·10 ⁻⁶	3.5 days
UVC-bl.	(1.58±0.13)·10 ⁻⁷	50.8 days	(0.89±0.23)·10 ⁻⁶	9.0 days	(1.18±0.35)·10 ⁻⁶	6.8 days	(1.75±0.45)·10 ⁻⁶	4.6 days
AM1.5D	(1.40±0.33)·10 ⁻⁷	57.3 days	(2.83±0.13)·10 ⁻⁶	28.3 days	(5.86±0.38)·10 ⁻⁷	13.7 days	(8.30±0.35)·10 ⁻⁷	9.7 days

Experimental conditions: [TGA]₀ = (1.66-6.66)·10⁻³ M, [HSs]₀ = 0.16-3.33 mg·L⁻¹,
[H₂O₂]₀ = (0.33-5.00)·10⁻⁴ M, [Cu(II)]₀ = (0.33-12.50)·10⁻⁵ M,
[Fe(III)]₀ = (0.33-12.50)·10⁻⁵ M, pH 6.5, 25°C.

The highest value of the rate constant of $1.18 \pm 0.08 \cdot 10^{-6} \text{ s}^{-1}$ (Table 6) is characteristic for the systems irradiated by the DRT-400 lamp, and the lowest value of $1.40 \pm 0.33 \cdot 10^{-7} \text{ s}^{-1}$ for the systems irradiated by SS with the AM1.5D filter.

When H_2O_2 was added to the system, the rate constants increased 2-4 times, for all irradiation sources, which is explained by the fact that in addition to the photoinitiation process of HSs, which generates active particles leading to TgA degradation, $\bullet\text{OH}$ were generated by H_2O_2 under the action of light, which also lead to the degradation of TgA [10]. The same dependences were attested for this system and also the highest value of the rate constant was found for the systems irradiated to the DRT-400 lamp ($5.42 \pm 0.13 \cdot 10^{-6}$), which was 4.5 times higher than for the H_2O_2 free system and the lowest on irradiation with SS, equipped with the AM1.5D filter ($2.83 \pm 0.13 \cdot 10^{-7} \text{ s}^{-1}$), which was twice higher than for the H_2O_2 free system.

When Fe(III) ions were added to the system, the values of the rate constants for all irradiation sources increased by 2-3 times, which is explained by the fact that TgA reduces Fe(III) to Fe(II) thus increasing the rate of formation of $\bullet\text{OH}$ in the presence of H_2O_2 [30]. As in previous cases, the highest value of the rate constant was found for the systems irradiated by the DRT-400 lamp ($(1.14 \pm 0.50) \cdot 10^{-5} \text{ s}^{-1}$), being twice higher than in the Fe(III) ions free system and the lowest on irradiation with SS, equipped with the AM1.5D filter ($5.86 \pm 0.38 \cdot 10^{-7} \text{ s}^{-1}$), also being twice higher than in the Fe(III) ions free system.

For the last system in which Cu(II) ions were added, the same dependencies were attested, the values of the rate constants proved to be the highest and were in the range of 10^{-6} - 10^{-5} s^{-1} , approximately 2 folds higher than in the presence of Fe(III) ions, once again demonstrating the importance of Cu(II) ions in the generation of $\bullet\text{OH}$, and in the degradation of pollutants in natural waters. The highest value of the rate constant was found for the systems irradiated by the DRT-400 lamp ($(2.16 \pm 0.41) \cdot 10^{-5} \text{ s}^{-1}$), which was 4 times higher than in the Cu(II) ions free system and the lowest value of the rate constant was estimated for the systems irradiated by the SS, equipped with the AM1.5D filter ($(8.30 \pm 0.35) \cdot 10^{-7} \text{ s}^{-1}$) the values being 3 times higher than in the system without Cu(II) ions.

The obtained results show that under natural water conditions, the estimated half-life of TgA is of 10-14 days, a value that is also influenced by the weather forecast (cloudiness, time of the day, season, *etc.*), Table 5.

Therefore, in the natural aquatic environment, TgA has a positive influence on eco-chemical processes, by increasing the water self-purification capacity, due to the generation of active species, which lead to the degradation of not only the substrate, but of other natural waters pollutants, as well. At the same time, the reaction products are harmless to the aquatic environment and to hydrobionts. On the other hand, TgA can be used successfully in wastewater treatment, considerably reducing the required amounts of iron ions and H_2O_2 , even at a neutral pH of the solutions. This would reduce the costs of wastewater treatment and the treated water would be harmless for discharge into the natural aquatic environment.

Conclusions

The results of this study show that thioglycolic acid (TgA) undergoes induced photolysis with humic substances (HSs) and the rate of photolysis linearly depends on the initial concentrations of TgA and HSs in the system, as well as on the emitted spectrum of irradiation.

The rate constants of TgA photolysis increased 4-6 folds in the presence of H_2O_2 , due to the additional generation of $\bullet\text{OH}$ during hydrogen peroxide photolysis. The presence of $\bullet\text{OH}$ was demonstrated by using the indirect PNDMA method and it was found that the concentrations of $\bullet\text{OH}$ in the studied systems ranged between 10^{-16} - 10^{-15} M , values similar to those of natural waters.

The influence of transition metals such as Fe(III) and Cu(II) proved to be positive, by increasing the generation rate of $\bullet\text{OH}$, and the degradation of pollutants in model systems. The rate constants of TgA in the presence of Fe(III) ions increased by 2-3 times, for all used irradiation sources. In the presence of Cu(II) ions, the values of TgA photochemical transformation rate constants were the highest.

The use of several sources of irradiation in this study allowed concluding that the rate of TgA photolysis also depends on the emitted spectrum of irradiation. Transferring the results obtained in laboratory conditions onto real conditions it can be stated that under the conditions of natural waters, the half-life of TgA may be estimated at 10-14 days, a value that is also influenced by the weather (cloudiness, time of the day, season, *etc.*).

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