PHOTOCHEMICAL DEGRADATION OF SULFADIAZINE

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Abstract: The photochemical degradation of the sulfadiazine (SDZ) was studied. The photochemical processes used in degradation of SDZ were UV and UV/H₂O₂. In the experiments hydrogen peroxide was applied at different concentrations: 10 mg/dm³ ($2.94 \cdot 10^{-4}$ M), 100 mg/dm³ ($2.94 \cdot 10^{-3}$ M), 1 g/dm³ ($2.94 \cdot 10^{-2}$ M) and 10 g/dm³ ($2.94 \cdot 10^{-1}$ M). The concentrations of SDZ during the experiment were controlled by means of HPLC. The best results of sulfadiazine degradation, the 100% removal of the compound, were achieved by photolysis using UV radiation in the presence of 100 mg H₂O₂/dm³ ($2.94 \cdot 10^{-3}$ M). The determined rate constant of sulfadiazine reaction with hydroxyl radicals k_{OH} was equal $1.98 \cdot 10^9$ M⁻¹s⁻¹.

INTRODUCTION

Several authors and reports have shown that the amount of pharmaceuticals in the environment strongly increases [10, 27, 28, 35]. For many years, a great proportion of research has been related to the presence of these substances in the aqueous environment [9, 11, 16, 23], however their occurrence in soil [19], milk [18], meat [24], wastewater [26] and drinking water [11] has also been confirmed. The development of new analytical techniques enabled the determination of pharmaceuticals at concentration of even few ng/dm³ [9, 12, 17, 34].

The first antimicrobial agents were sulphonamide drugs, where sulphonamide paved the way for the antibiotic revolution in medicine [14]. However, due to their high toxicity, sulphonamides are now replaced by other chemotherapeutics such as quinolones and metronidazole. Nevertheless, antimicrobial agents from sulphonamide group are still currently used in animal husbandry, for veterinary purposes or as growth promoters (particularly in large-scale animal farming and intensive livestock treatment) [20].

Sulfadiazine (SDZ) is a sulphonamide widely used as a veterinary antibiotic to prevent and treat diarrhoea and other infectious diseases. This substance infiltrates into the land with manure during the fertilization of agricultural soils [15].

Sulfadiazine (Fig. 1) was detected in sea water in concentration of 2.5 µg/dm³, and different drugs from sulphonamide group occurred over wide range: 3–41 µg/dm³ in sewage sludge, 0.48–2.64 µg/dm³ in cow's milk and 16–39 µg/dm³ in poultry and pork meat. Other examples are shown in Table 1.

Fig. 1. Chemical structure of sulfadiazine

Table.1. Selected antimicrobial agents concentrations detected in the various sectors of the environment

Substance	Medium	Concentration	Literature
ciprofloxacin	surface water	0,3–0,4 mg/dm ³	[12]
chloramphenicol	wastewater	0,56 µg/dm ³	[35]
erythromycin	water	0,02 µg/dm ³	[15]
macrolides	surface water treated wastewater	20 ng/dm ³	[15]
	river sediment	0,4–8 ng/dm ³	[23]
sulfadiazine	sea water	2,5 µg/dm ³	[31]
sulphonamides	sewage sludge	3–41 µg/dm ³	[10]
	cow's milk	0,48–2,64 µg/dm ³	[18]
	poultry and pork meat	16–39 µg/dm ³	[24]
trimethoprim	sea water	2,5 µg/dm ³	[31]

Some authors suggest a correlation between the presence of antibiotic substances in the environment and the problem of antibiotic drug resistance of pathogenic bacteria. The requirement to reduce the environmental risk resulting from the occurrence of these substances necessitates the development of relevant methods for their elimination [1, 2, 3, 7, 8]. Many drugs, including sulfadiazine, are resistant to chemical degradation and biodegradation. Their elimination during the processes of wastewater treatment and water self-purification occurs only to a little extent, or does not occur at all, due to their high persistence [36].

In those cases, advanced oxidation processes (AOPs) are efficient novel methods for water treatment, which have afforded very good results. Radicals generated during AOPs can lead to the remediation of an extensive variety of organic pollutants [29].

The purpose of this study was to verify non-photochemical and photochemical methods: H₂O₂, UV and UV/H₂O₂ – processes to remove sulfadiazine (a substance belonging to the group of antimicrobial agents) from aqueous solution. Advanced oxidation technologies are characterized by the production of the highly oxidative

hydroxyl radical at ambient temperatures for oxidative destruction of organic compounds, which can ultimately lead to complete mineralization with the formation of CO_2 , H_2O and mineral acids [29].

The study on sulfadiazine (SDZ) photolysis was documented by far and the SDZ solution was exposed to light of a xenon lamp for 100 h in the presence of H_2O_2 at μL level. Furthermore, the equation for determination of quantum yield was based on measuring the number of irradiating photons by means of spectrophotometer. The calculated values of quantum yields of photochemical decay of SDZ by means of xenon lamp were in the range of $2.0\text{--}3.5 \times 10^{-4}$ (photon^{-1}) [32]. The aim of this work was to study the UV photodegradation of SDZ in the absence and presence of H_2O_2 and to determine kinetic parameters of this process using mathematical model.

MATERIALS AND METHODS

Chemicals

Sulfadiazine (SDZ – molecular mass 250) was purchased from Sigma Aldrich (Germany). Acetonitrile (POCH, Poland) was the organic solvent used in the experiment at the HPLC technique quality. Hydrogen peroxide (30%) was purchased from Fluka (Switzerland).

Analytical methods

Measurements of the current concentration of sulfadiazine in the samples were made using high performance liquid chromatography HPLC UltiMate 3000 from Dionex, working in reversed-phase (RP HPLC – Reverse Phase High Performance Liquid Chromatography). Sulfadiazine analysis was performed in the presence of water and acetonitrile in a volume ratio of 60:40, with a steady flow of mobile phase through a chromatographic column RP C 18 Hypersil GOLD Polygen, of $1 \text{ cm}^3/\text{min}$. The analysis time of one injection lasted 5 minutes. The Chromeleon® computer software was used for the acquisition and processing of the data obtained from the analysis [25].

The “dark reaction”

For the preliminary tests, termed as the “dark reaction” (without the use of a polychromatic medium pressure mercury lamp) a system consisting of beakers with a capacity of 1 litre and magnetic stirrers was used. Aqueous solutions of an initial concentration of sulfadiazine $10 \text{ mg}/\text{dm}^3$ ($4 \times 10^{-5} \text{ M}$) were placed in beakers, with the corresponding dose of oxidant – hydrogen peroxide (H_2O_2). Hydrogen peroxide solution of 30% with a density of $1.11 \text{ g}/\text{cm}^3$ was used as an oxidant. The study was performed using the following concentrations of hydrogen peroxide: $10 \text{ mg}/\text{dm}^3$ ($2.94 \times 10^{-4} \text{ M}$), $100 \text{ mg}/\text{dm}^3$ ($2.94 \times 10^{-3} \text{ M}$), $1 \text{ g}/\text{dm}^3$ ($2.94 \times 10^{-2} \text{ M}$) and $10 \text{ g}/\text{dm}^3$ ($2.94 \times 10^{-1} \text{ M}$). The experiment was done in duplicate. In order to assess the instantaneous concentration of sulfadiazine during the “dark reaction”, samples were taken at fixed intervals (0, 5, 10, 15, 20, 30, 45, 60 minutes). The measurement of the actual concentration of sulfadiazine was determined by high performance liquid chromatography (HPLC).

UV process

The process of photochemical decomposition of aqueous solution of sulfadiazine was carried out in an UviLab P400 reactor (Vita Tec GmbH, Germany). The sulfadiazine

solution was placed in the reaction chamber (2), of 350 cm³ capacity. The initial concentration of sulfadiazine was approximately 10 mg/dm³ ($4 \cdot 10^{-5}$ M).

The reaction chamber was irradiated with ultraviolet rays from the UV produced by the polychromatic medium pressure mercury vapour lamp (1), with a maximum power of 400 W, connected to an external power supply and placed in its housing of a quartz glass reaction chamber.

The mercury vapour lamp was set to a half of its maximum power (200 W). The test system was cooled with tap water, circulated in the outer mantle (3). In addition, the solution of sulfadiazine was mixed by a magnetic stirrer. Samples of 1 cm³ were collected with a syringe (from the point of sampling (5)) at specified intervals from the start of the irradiation (0, 1, 2, 5 min. and every 5 minutes to 60 minutes of the experiment).

UV/H₂O₂ process

Sulfadiazine photolysis using UV radiation in the presence of hydrogen peroxide was carried out using the same system as previous one. The only difference was the addition of appropriate amounts of hydrogen peroxide to the sulfadiazine solution before irradiation.

As in the preliminary study 30% solution of hydrogen peroxide with a density of 1.11 g/cm³ was used. In the experiments the oxidant was applied in three different doses: 10 mg/dm³ ($2.94 \cdot 10^{-4}$ M), 100 mg/dm³ ($2.94 \cdot 10^{-3}$ M) and 1 g/dm³ ($2.94 \cdot 10^{-2}$ M).

RESULTS AND DISCUSSION

Degradation of sulfadiazine by hydrogen peroxide

The purpose of the preliminary tests was to determine the effect of hydrogen peroxide on the stability of the sulfadiazine molecule. The initial concentration of SDZ solution was 10 mg/dm³ ($4 \cdot 10^{-5}$ M). This solution was subjected to the influence of different concentrations of an aqueous solution of hydrogen peroxide. The addition of hydrogen peroxide in concentrations of 10 mg/dm³ ($2.94 \cdot 10^{-4}$ M), 100 mg/dm³ ($2.94 \cdot 10^{-3}$ M) and 1 g/dm³ ($2.94 \cdot 10^{-2}$ M) did not cause significant degradation of sulfadiazine. A dose of 10 g H₂O₂/dm³ ($2.94 \cdot 10^{-1}$ M) only decreased sulfadiazine concentrations by less than 1 mg/dm³. These data allow for the conclusion that the sulfadiazine is not degraded by hydrogen peroxide.

Photolysis of sulfadiazine using UV

The next stage of the experiment was to determine the effects of UV radiation on an aqueous solution of sulfadiazine (the process of direct photolysis). The direct photolysis occurred after five minutes of the experiment (Fig. 2). The graph shows that sulfadiazine concentrations decreased less than 42% after 60 minutes of the experiment. The effect of the direct photolysis process can be assessed as inefficient because the SDZ removal is less than 50%, and therefore it would have little chance of being used on an industrial scale.

Photolysis of sulfadiazine using UV radiation in the presence of H₂O₂

The efficiency of photolysis and oxidation with hydrogen peroxide processes applied separately was unsatisfactory as illustrated in the previous subsections. Therefore, a combination of both methods was applied for the experiments that followed.

A number of studies demonstrate a rapid removal of substrate with the addition of hydrogen peroxide to the UV irradiated solution [2, 21, 32].

Fig. 2. Average removal of sulfadiazine during the direct photolysis

The process is based on induced photoionization of the substrate by absorption of light and the generation of free radicals. The photo-initiated $\text{OH}^\bullet$ occurred normally through electron excitation of the auxiliary chemical oxidant, for example H_2O_2 or O_3 . The oxidant starts a complex chain of radical reactions, which provides suitable conditions for substances' degradation [21].

Consequently, the experiment was carried out in order to examine the impact of hydrogen peroxide in various doses (10 ($2.94 \cdot 10^{-4}$ M), 100 ($2.94 \cdot 10^{-3}$ M), 1000 ($2.94 \cdot 10^{-2}$ M) H_2O_2 mg/dm^3) during photolysis of sulfadiazine using UV radiation over the wide range from 190 to 820 nm.

Photolysis of sulfadiazine using UV radiation in the presence of 10 mg/dm^3 ($2.94 \cdot 10^{-4}$ M) H_2O_2

An initial measure of 10 mg/dm^3 ($2.94 \cdot 10^{-4}$ M) hydrogen peroxide was used. Even such a low concentration resulted in a significant loss of sulfadiazine to less than 2 mg/dm^3 after 60 minutes of the process. Changes in SDZ concentration during the study are illustrated in Fig. 3. The addition of the oxidant – hydrogen peroxide (10 mg/dm^3 ($2.94 \cdot 10^{-4}$ M)) increases the efficiency of sulfadiazine removal to 80% after 60 min of irradiation with UV. The UV/ H_2O_2 process gives much better results in comparison to the UV radiation process.

Therefore, even the addition of low concentrations of hydrogen peroxide, such as 10 mg/dm^3 ($2.94 \cdot 10^{-4}$ M), resulted in a synergistic effect on sulfadiazine decomposition.

Sulfadiazine photolysis using UV radiation in the presence of 100 mg/dm^3 ($2.94 \cdot 10^{-3}$ M) H_2O_2

An alternative dose of oxidant used in the study was 100 $\text{mg H}_2\text{O}_2/\text{dm}^3$ ($2.94 \cdot 10^{-3}$ M). The changes in the concentration of sulfadiazine are shown in Fig. 4. It is noteworthy that the decrease of the concentration of the test substance (SDZ) after 25 minutes of the experiment reached 90%, and after 40 minutes the sulfadiazine was removed completely.

Fig. 3. Average removal of sulfadiazine during the UV photolysis in the presence of 10 mg/dm³ ($2.94 \cdot 10^{-4}$ M) H₂O₂

This was achieved due to the greater amount of hydrogen peroxide. The amount of hydroxyl radicals increased and contributed to the process of the drug removal (free-radical oxidation chain reaction) from the aqueous solution. In addition, at the beginning of the irradiation very rapid decomposition of sulfadiazine was observed.

Photolysis of sulfadiazine using UV radiation in the presence of 1 g/dm³ ($2.94 \cdot 10^{-2}$ M) H₂O₂

The hydrogen peroxide dose was increased to a concentration of 1 g H₂O₂/dm³ ($2.94 \cdot 10^{-2}$ M). Based on the data presented in Figure 5, one can observe the efficiency of the process,

Fig. 4. Average removal of sulfadiazine during the UV photolysis in the presence of 100 mg/dm³ ($2.94 \cdot 10^{-3}$ M) H₂O₂

from the very beginning of the experiment. Over 90% removal of the investigated drug was achieved by the 30th minute and the total elimination of substances from the solution resulted after 55 minutes of exposure. The result of the percentage removal for a dose of 1 g $\text{H}_2\text{O}_2/\text{dm}^3$ ($2.94 \cdot 10^{-2}$ M) is not as satisfactory as for a concentration of 100 mg $\text{H}_2\text{O}_2/\text{dm}^3$ ($2.94 \cdot 10^{-3}$ M). The removal of sulfadiazine is inhibited by the reaction of hydroxyl radicals with hydrogen peroxide still present in the reaction solution. When the H_2O_2 concentration in the reaction solution is too high, H_2O_2 absorbs all emitted photons from the UV-spectrum. Because the H_2O_2 is more susceptible to degradation by hydroxyl radicals than the sulfadiazine, there is limited photochemical decay of the sulfadiazine in the reaction solution due to the presence of too high concentration of H_2O_2 [1, 2, 3, 5, 8].

Fig. 5. Average removal of sulfadiazine during the UV photolysis in the presence of 1 g/dm³ ($2.94 \cdot 10^{-2}$ M) H_2O_2

The kinetics of photolytic decomposition of sulfadiazine

In the kinetic of photolytic decomposition of sulfadiazine the concentration of 100 mg $\text{H}_2\text{O}_2/\text{dm}^3$ ($2.94 \cdot 10^{-3}$ M) resulted in the best decay of the test substance – sulfadiazine. Concentration of 100 $\text{H}_2\text{O}_2/\text{dm}^3$ ($2.94 \cdot 10^{-3}$ M) results in the 100% removal of sulfadiazine from aqueous solution in a short time period and any inhibitory effect was noted.

The medium-pressure Hg lamp emitted photons from the region of 254 nm to 579 nm. The absorption spectrum of SDZ (sulfadiazine) extends in the range from 190 nm to 354 nm peaking at 204 and 265 nm. This means that during the performed investigations radiation at the range from 254 nm to 354 nm was actively used (Fig. 6). The lamp irradiance (E_0) was determined by an actinometric investigation and it was equal to 2708.61 W/m³ ($6.89 \cdot 10^{-6}$ Einstein /dm³*s). The average molar extinction coefficient of SDZ (ϵ) was calculated as a weighted average of single molar extinction coefficients determined at selected wavelengths (λ = every 2 nm, in the range of active spectrum from 254 nm to 354 nm) [4, 13, 29]. The value of the ϵ coefficient was equal to $2.19 \cdot 10^4$ dm³/mol*cm. The initial molar concentration of SDZ during the direct photolysis process was equal to $4 \cdot 10^{-5}$ M (10 mg/dm³).

Fig. 6. The relative intensity of the medium-pressure Hg lamp and the SDZ (sulfadiazine) absorption spectrum

Fig. 7. Decrease of sulfadiazine molar concentration during the direct photolysis process and the UV/H₂O₂ process (100 mg H₂O₂/dm³ (2.94*10⁻³ M))

The initial reaction rate of SDZ photodegradation (r_{UV}) was calculated by differentiating exponential curve that fitted experimental points (Fig. 7) and it was equal to $3.35 \cdot 10^{-7} \text{ M} \cdot \text{s}^{-1}$. Because the absorbance of SDZ is above the 0.1 value and it is equal to $A = \varepsilon b C = 0.8764$, the reaction rate should be expressed as (1) [30]:

$$r_{UV} = - \frac{dC}{dt} = \varphi_{SDZ} * E_0 * (1 - 10^{-\varepsilon b C}) \quad (1)$$

where:

- C SDZ molar concentration,
- φ_{SDZ} SDZ quantum yield,
- E_0 lamp irradiance,
- b – average light path into the solution,
- ε weighted average molar extinction coefficient [30].

Based on equation (1) the quantum yield (ϕ_{SDZ}) [30] of SDZ was calculated as:

$$\Phi_{SDZ} = \frac{r_{uv}}{E_0 * (1 - 10^{-b\epsilon C})} = 0.056 \quad (2)$$

The initial molar concentration of SDZ during the UV/H₂O₂ – process was equal to 4*10⁻⁵ M (10 mg/dm³) and the H₂O₂ molar concentration was at the level of 2.94*10⁻³ M (100 mg/dm³). The reaction rate (r) was calculated in the same way as the initial reaction rate of SDZ photodegradation r_{UV} (Fig. 7) and was equal to 3,70*10⁻⁶. The reaction rate (r) of the SDZ decay in the UV/H₂O₂ – process may be expressed also by the equation (3) and (4) [4]:

$$r = -\frac{dC}{dt} = r_{OH} + r_{UVI} + r_d \quad (3)$$

$$\text{then: } r_{OH} = r - r_{UVI} - r_d \quad (4)$$

where:

- r_{OH} SDZ reaction rate with hydroxyl radicals,
- r initial SDZ rate in the UV/H₂O₂-process,
- r_{UVI} initial SDZ direct photolysis rate,
- r_d initial “dark reaction” rate.

Because the estimated value of r_d was relatively small ($r_d = 3.81 \cdot 10^{-8} \text{ M} \cdot \text{s}^{-1}$), it was omitted from further calculations.

Applying the assumption of the quasi-stationary concentration of OH[•], the reaction of SDZ decay proceeded as pseudo first order reaction [4], the apparent rate constant (k_{app}) of the reaction with OH[•] can be presented by means of expression (5) [4]:

$$k_{app} = k_{OH} * [OH] \quad (5)$$

where:

- $[OH]$ quasi-stationary concentration of OH[•],
- k_{OH} rate constant of SDZ with OH[•]

The reaction rate of SDZ with OH[•] may be expressed as follows:

$$r_{OH} = k_{OH} * [OH] * C = k_{app} * C \quad (6)$$

The rate of SDZ direct photolysis (r_{UVI}) was calculated from a modified equation (1), taking into account the distribution of UV radiation between SDZ and hydrogen peroxide. It may be expressed as (7):

$$r_{UVI} = \phi_{SDZ} * E_0 * f_{SDZ} * (1 - 10^{-b \sum \epsilon_i C_i}) \quad (7)$$

where:

$b\sum \varepsilon_i C$ absorbance of reaction solution (sulfadiazine + H_2O_2),

i substances taking part in the reaction,

f_{SDZ} fraction of radiation absorbed by sulfadiazine

The absorbance of the reaction solution–sulfadiazine and H_2O_2 ($b\sum \varepsilon_i C_i$) and the fraction of absorbed irradiation by sulfadiazine (f_{SDZ}) were calculated as follows [4, 13]:

$$b\sum \varepsilon_i C_i = b^*(\varepsilon_H C_H + \varepsilon_{SDZ} C_{SDZ}) = 0.9117 \quad (8)$$

$$f_H = \frac{\varepsilon_H C_H}{\sum \varepsilon_i C_i} = 0.0415 \quad (9)$$

$$f_{SDZ} = 1 - \frac{\varepsilon_H C_H}{\sum \varepsilon_i C_i} = 0.9585 \quad (10)$$

where:

f_H fraction of absorbed irradiation by H_2O_2 ,

ε_H hydrogen peroxide weighted average molar extinction coefficient (12, 9)[8],

C_H H_2O_2 molar concentration.

The calculated value of r_{UV1} was equal to $3.25 \cdot 10^{-7} \text{ M} \cdot \text{s}^{-1}$. According to equation (4), the value of r_{OH} was evaluated ($r_{OH} = 3.37 \cdot 10^{-6} \text{ M} \cdot \text{s}^{-1}$). Based on equation (6), the apparent rate constant (k_{app}) reaction with $OH^\bullet$ may be calculated as [4]:

$$k_{app} = \frac{r_{OH}}{C} = 8.45 \cdot 10^{-2} \text{ s}^{-1} \quad (11)$$

The reactions occurring in the UV/H_2O_2 – system and their reaction rates are presented by the following equations [4]:

where:

φ_H H_2O_2 quantum yield (0.5) [22]), $k_2 = 2.7 \cdot 10^7 \text{ s}^{-1}$ and $k_4 = 7.5 \cdot 10^9 \text{ s}^{-1}$ [6],
 E_{aH} and E_{aSDZ} irradiance absorbed by H_2O_2 and SDZ , respectively,
 K equilibrium constant [4].

Applying the assumption that the rate of hydroxyl radicals' generation is equal to the rate of their disappearance (a stationary state $\rightarrow r_1 = r_2 + r_4 + r_{OH}$), the quasi-stationary concentration of $OH^\bullet$ may be expressed as [4]:

$$[OH] = \frac{2\phi_H E_0 f_H (1 - 10^{-b \sum \epsilon_i C_i})}{k_2 [H_2O_2] + k_4 [HO_2^-] + k_{OH} C} \quad (18)$$

The combination of the equation (18) with (5) allowed calculating the rate constant of SDZ reaction with hydroxyl radicals (k_{OH}) [4]:

$$k_{OH} = \frac{k_{app} * (k_2 [H_2O_2] + k_4 [HO_2^-])}{2\phi_H E_0 f_H (1 - 10^{-b \sum \epsilon_i C_i}) - k_{app} C} = 1.98 * 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (19)$$

It is assumed that the susceptibility to degradation by hydroxyl radicals ($OH^\bullet$) shows the rate constant above 10^3 – $10^4 \text{ M}^{-1} \text{ s}^{-1}$ [29]. The determined rate constant of sulfadiazine reaction with hydroxyl radicals ($k_{OH} = 1.98 * 10^9 \text{ M}^{-1} \text{ s}^{-1}$) allows the conclusion that the substance is susceptible to degradation by hydroxyl radicals ($OH^\bullet$).

SUMMARY AND CONCLUSIONS

Basing on the results obtained from this investigation it is concluded that the efficiency of sulfadiazine's photochemical decomposition can be enhanced by a UV process combined with the use of an oxidizer, such as hydrogen peroxide.

The best results of sulfadiazine degradation were achieved by photolysis using UV radiation in the presence of $100 \text{ mg H}_2\text{O}_2/\text{dm}^3$ ($2.94 * 10^{-3} \text{ M}$). Lower concentrations of oxidant do not have a significant effect, and higher concentrations of oxidant inhibit the decomposition of sulfadiazine.

Because of the need to develop a new solution to complement conventional methods of sewage treatment, further concerns are associated with the assessment of the quality and efficiency of the applied processes. Therefore, the purpose of this study was to investigate some of the more widely used methods for the pre-treatment of wastewater – the photochemical degradation and advanced oxidation to remove sulfadiazine, a widely-used sulphonamide. The presented analysis of the photochemical decomposition of sulfadiazine leads to the following conclusions:

- The results show no significant effect of hydrogen peroxide on the test substance.
- The decomposition of sulfadiazine after 60 minutes of direct photolysis processes is 42%.
- The experiment confirmed the synergistic effect of hydrogen peroxide on UV radiation in the degradation of sulfadiazine.
- Concentration value $10 \text{ mg H}_2\text{O}_2/\text{dm}^3$ ($2.94 * 10^{-4} \text{ M}$) during photolysis using UV radiation removes the test substance by 80% after 60 minutes.
- The use of hydrogen peroxide in a dose of $100 \text{ mg}/\text{dm}^3$ during photolysis using UV radiation results in the acceleration of the photolysis reaction and the complete removal of sulfadiazine in 40 minutes.

- An excessive amount ($1 \text{ g H}_2\text{O}_2/\text{dm}^3$ ($2.94 \cdot 10^{-2} \text{ M}$)) of hydrogen peroxide during photolysis using UV radiation caused a decrease in the efficiency of sulfadiazine's rate of decay.
- The calculated value of quantum yield of SDZ photodegradation (ϕ_{SDZ}) was equal to $5.6 \cdot 10^{-2}$ and it is about two order of quantity higher than the value presented the reference.
- The order of magnitude of the rate constant of SDZ reaction with hydroxyl radicals ($k_{\text{OH}} = 1.98 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$) indicates that sulfadiazine is susceptible to decay by means of hydroxyl radicals ($\text{OH}^\bullet$).

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REFERENCES

- [1] Andreozzi, R., Caprio, V., Marotta, R., & Radovicovic, A. (2003a). Ozonation and H_2O_2 /UV treatment of clofibrac acid in water: a kinetic investigation. *Journal of Hazardous Materials*, 103, 233–246.
- [2] Andreozzi, R., Caprio, V., Marotta, R., & Vogna, D. (2003b). Paracetamol oxidation from aqueous solutions by means of ozonation and H_2O_2 /UV system. *Water Research*, 37, 994–1004.
- [3] Beltrán, F.J., Gonzalez, M., & Gonzalez, J.F. (1997). Industrial wastewater advanced oxidation. Part 1: UV radiation in the presence and absence of hydrogen peroxide. *Water Research*, 31, 2405–2414.
- [4] Błędzka, D., Gryglik, D., Olak, M., Gębicki, J.L., & Miller, J.S. (2010). Degradation of n-butylparaben and 4-tert-octylphenol in H_2O_2 /UV system. *Radiation Physics and Chemistry*, 79, 409–416.
- [5] Borowska, E. (2010). *Photochemical degradation of sulfamethoxazole*. Gliwice: Politechnika Śląska.
- [6] Christensen, H.S., Sehested, H., & Corfitzan, H. (1982). Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures. *J. Phys. Chem.*, 86, 15–68.
- [7] Esplugas, S., Gimenez, J., Contreras, S., Pascual, E., & Rodriguez, M. (2002). Comparison of different advanced oxidation processes for phenol degradation. *Water Research*, 36, 1034–1042.
- [8] Felis E., Ledakowicz, S., & Miller, J.S. (2011). Degradation of bisphenol A using UV and $\text{UV}/\text{H}_2\text{O}_2$ processes. *Water Environmental Research*, 83 (12), 2154–2158.
- [9] Goebel, A., Thomsen, A., McArdell, C., Alder, A., Giger, W., & Theib, N. (2005a). Extraction and determination of sulfonamides, macrolides, and trimethoprim in sewage sludge. *Journal of chromatography*, A. 1085, 179–189.
- [10] Goebel, A., Thomsen, A., McArdell, C., Joss, A., & Giger, W. (2005b). Occurrence and sorption behavior of sulfonamides, macrolides and trimethoprim in activated sludge treatment. *Environmental Science & Technology*, 39 (11), 3981–3989.
- [11] Golet, E., Alder, C., & Giger, W. (2002). Environmental exposure and risk assessment of fluoroquinolone antibacterial agents in wastewater and river water of the Glatt Valley watershed, Switzerland. *Environmental Science & Technology*, 36, 3645.
- [12] Golet, E.M., Alder, A.C., Hartmann, A., Ternes, T.A., & Giger, W. (2001). Trace determination of fluoroquinolone antibacterial agents in urban wastewater by solid-phase extraction and liquid chromatography with fluorescence detection. *Anal. Chem.*, 73, 3632–3638.
- [13] Gryglik, D., Olak, M., & Miller, J.S. (2010). Photodegradation kinetics of androgenic steroids boldenone and trenbolone in aqueous solutions. *Journal of Photochemistry and Photobiology A: Chemistry*, 212, 14–19.
- [14] Hager, T. (2006). *The Demon Under the Microscope: From Battlefield Hospitals to Nazi Labs, One Doctor's Heroic Search for the World's First Miracle Drug*. Crown Publishing Group.
- [15] Heuer, H., Focks, A., Lamshöft, M., Smalla, K., Matthies, M., & Spiteller, M. (2008). Fate of sulfadiazine administered to pigs and its quantitative effect on the dynamics of bacterial resistance genes in manure and manured soil. *Soil Biology & Biochemistry*, 40, 1892–1900.
- [16] Hirsch, R., Ternes, R., Haber, K., & Kratz, K.-L. (1999). Occurrence of antibiotics in the aquatic environment. *The science of the total environment*, 225, 109–118.

- [17] Hirsch, R., Ternes, Th., Haberer, K., Mehlich, A., Ballwanz, F., & Kratz, K.-L. (1998). Determination of antibiotics in different water compartments via liquid chromatography – electrospray tandem mass spectrometry. *Journal of Chromatography A.*, 815, 213–223.
- [18] Koesukwiwat, U., Jayanta, S., & Leepipatiboon, N. (2007). Validation of a liquid chromatography-mass spectrometry multi-residue method for the simultaneous determination of sulfonamides, tetracyclines, and pyrimethamine in milk. *Journal of chromatography A.*, 1140, 147–156.
- [19] Kreuzig, R., Hoßlge, S. (2005). Investigations of the fate of sulfadiazine in manured soil: laboratory experiments and test plot studies. *Environ. Toxicol. Chem.*, 24, 771–776.
- [20] Kümmerer, K. (2009). The presence of pharmaceuticals in the environment due to human use – present knowledge and future changes. *Journal of Environmental Management*, 90, 2354–2366.
- [21] Kümmerer, K. (2008). Pharmaceuticals in the environment: sources, fate, effects and risks. *Springer.*, 455–463.
- [22] Legrini, O., Oliveros, E., & Braun, A.M. (1993). Photochemical Processes for Water Treatment. *Chem. Rev.*, 93, 671–698.
- [23] Löffler, D., & Ternes, Th. (2003). Determination of acidic pharmaceuticals, antibiotics and ivermectin in river sediment using liquid chromatography – tandem mass spectrometry. *Journal of chromatography A*, 1021, 133–144.
- [24] Lu, K.-H., Chen, C.-Y., & Lee, M.-R. (2007). Trace determination of sulfonamides residues in meat with a combination of solid-phase microextraction and liquid chromatography-mass spectrometry. *Talanta*, 72, 1082–1087.
- [25] Lemańska, N. (2008). *Methodics of determination of chosen chemotherapeutic agents in the aqueous solutions*. Gliwice: Politechnika Śląska.
- [26] McArdeell, C., Molnar, E., Suter, M.J., & Ginger, W. (2003). Occurrence and fate of macrolide antibiotics in wastewater treatment plants and in the Glatt River watershed, Switzerland. *Environmental Science & Technology*, 37 (24), 5479–86.
- [27] Miao, X.-S., Bishay, F., Chen, M., & Metcalfe, C.D. (2004). Occurrence of antimicrobial compounds in the final effluents of sewage treatment plants in Canada. *Environmental Science & Technology*, 38 (13), 3533–41.
- [28] Miksch, K., Rychta, U., & Woźniak (Felis), E. (2001). *Obecność farmaceutyków w środowisku*. VII Ogólnopolskie Sympozjum Naukowo-Techniczne, Wisła-Jarzębata, 4–7 grudzień 2001.
- [29] O'Shea, K.E., & Kim, D.K. (2004). *Advanced oxidation technologies radical processes for water treatment*. Status of Industrial scale radiation treatment of wastewater and its future, 61–66.
- [30] Paszyc, S. (1992). *Podstawy fotochemii*. Warszawa: PWN.
- [31] Sørensen, L.K., & Hansen, H. (2002). Determination of sulfadiazine and trimethoprim in marine sediment by LC-APCI-MS. *Journal of Liquid Chromatography R.*, T., 25 (7), 1063–1075.
- [32] Sukul, P., Lamshöft, M., Zuhlke, S., Spiteller, M. (2008). Photolysis of ¹⁴C-sulfadiazine in water and manure. *Chemosphere*, 71, 717–725.
- [33] Ternes, Th., & Joss, A. (2006). *Human pharmaceuticals, hormones and fragrances. The challenge of micropollutants in urban water management*. London–New York: IWA Publishing.
- [34] Ternes, Th. (2001). Analytical methods for the determination of pharmaceuticals in aqueous environmental samples. *Trends in analytical chemistry*, 20 (8), 419–433.
- [35] Ternes, Th. (1998). Occurrence of drugs in german sewage treatment plants and rivers. *Water Research*, 32 (11), 3245–3260.
- [36] Zaleska-Radziwił, M., Łebkowska, M., Affek, K., & Zarzeczna, A. (2011). Environmental risk assessment of selected pharmaceutical present in surface waters in relation to animals *Archives of Environmental Protection* 37 (3), 31–42.

FOTOCHEMICZNY ROZKŁAD SULFADIAZYNY

W ramach niniejszego eksperymentu przeprowadzono fotochemiczny rozkład sulfadiazyny (SDZ). Rozkład sulfadiazyny był realizowany z wykorzystaniem procesów UV oraz UV/H₂O₂. W badaniach użyto nadtlenu wodoru w następujących stężeniach: 10 mg/dm³ (2.94*10⁻⁴ M), 100 mg/dm³ (2.94*10⁻³ M), 1 g/dm³ (2.94*10⁻² M) oraz 10 g/dm³ (2.94*10⁻¹ M). Zmiany stężenia SDZ obserwowano przy wykorzystaniu HPLC. Najlepsze rezultaty rozkładu sulfadiazyny, 100% usunięcie badanej substancji, zaobserwowano w procesie fotolizy przy obecności 100 mg H₂O₂/dm³ (2.94*10⁻³ M). Stała szybkości reakcji sulfadiazyny z rodnikami hydroksylowymi k_{OH} wyniosła 1.98*10⁹ M⁻¹s⁻¹.