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PHOTOCATALYTIC DEGRADATION OF THE SELECTED SULFONAMIDES IN WASTEWATER

FOTOKATALITYCZNA DEGRADACJA WYBRANYCH SULFONAMIDÓW W ŚCIEKACH

Abstract: Sulfonamides are antibacterial drugs, the most commonly used in veterinary prophylaxis. To the environment, these drugs are being introduced in several ways. Sulfonamides have the capacity to accumulate in various organisms, for which they may be toxic. Even low concentrations of these drugs may lead to the formation of microbial drug resistance. The aim of this study was to determine the applicability of the process of photocatalysis for the degradation of selected sulfonamides applied to real wastewater and optimization of this method. The process of photocatalytic degradation was studied in real municipal wastewater, synthetic sewage and in distilled water. The process was carried out in open reactors that were UV-A irradiated, with the participation of TiO_2-P25, a mixture of $FeCl_3$ and $TiO_2/FeCl_3$. It was found that use of the $TiO_2/FeCl_3$ mixture brings the best results in the removal of selected sulfonamides. Influence of selected wastewater treatment processes, pH and concentrations of reagents on the efficiency of degradation of sulfonamides from wastewater has been determined. In addition, orders were designated as well as kinetics of studied reaction.

Keywords: photocatalysis, sulfonamides, wastewater

Environment is an essential part of human's life. Therefore, it is very important to avoid pollution of water, soil and air. In most cases, progressing pollution of the environment is a result of human's activity. The main sources of environmental pollution are mostly households, industry and agriculture, where various organic compounds can pass to wastewater. However, after treatment, the wastewater can become a serious threat to a whole biosphere. Ones of the particularly hazardous components of these wastewater are drugs and their metabolites. *Sulfonamides* (SNs) are an example of such compounds. It is estimated that most of them is stable in the environment, and some are also highly toxic, or ecotoxic [1, 2].

The threat caused by antimicrobial drugs is mainly based on the fact that even in trace amounts, they may generate drug resistance in microorganisms [3, 4]. Then, the resistance genes can be transferred between different strains of bacteria, for example by conjugation.

In consequeance, these genes may occur in pathogens in ecosystems not previously exposed to contact with antibiotics [4]. According to the authors of the National Programme for the Protection of Antibiotics [5], relatively few pathogenic microorganisms through acquired resistance mechanisms may be major factors threatening the health and human life. In result, diseases commonly considered to be "defeated" may be re-spread again.

The above discussed reasons cause that different methods to remove of these compounds from wastewater have been intensively studied in recent years. The efficiency

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of traditional methods, eg, biodegradation, coagulation and sedimentation, is often low or very low [1, 6-8]. Researchers have high expectations with regard to *advanced oxidation processes* (AOP) such as a photocatalytic degradation [9-15]. The use of this technique for treatment of municipal and domestic wastes enables the degradation of organic substances, including drugs, as a result of oxidation by hydroxyl radicals (HO•) generated in the reaction medium. Partially treated wastewater without pharmaceuticals and their metabolites could be used for example to fertilize the fields.

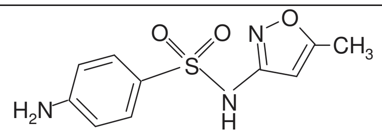
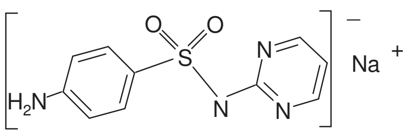
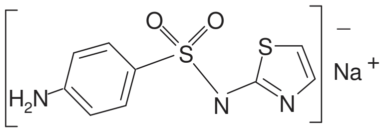
The aim of this study was to determine the possibility of the use of photocatalytic process for degradation of the selected sulfonamides added to real wastewater and this method optimization.

Materials and methods

The investigated SNs are characterized in Table 1.

Table 1

The characteristics of the used SNs

Sulfonamides	**Abbr. in text**	**Structure**	**Manufacturer**	**Initial concentration in samples [mmol dm^{-3}]**
Sulfamethoxazole	SMX		Sigma	0.050
Sulfadiazine (natrium salt)	SDZ		Sigma	0.025
Sulfathiazole (natrium salt)	STZ		Sigma	0.025

Titanium oxide (IV) (TiO_2-P25) from Evonic Degussa GmbH and ferric chloride ($FeCl_3$) from POCH were used as photocatalysts. They were selected based on the results of previous studies on the photocatalytic degradation of sulfonamides in aqueous solutions. If necessary, the HCl was added to samples in order to decrease the pH values.

Wastewater samples

The characteristics of wastewater used in experiments are presented in Table 2. Wastewater samples were stored for 1 hour at room temperature before their use in experiments. The investigated drugs at concentrations above the limit of detection were not detected in wastewater. The determination of wastewater parameters were performed according to the standard operating procedures for water and wastewater.

Table 2

The characteristics of the used wastewater samples

	Wastewater[a]	**Influent II**[b]	**Wastewater from septic tank**	**Landfill leachate**	**Effluent after WWTP**[b]
Collection date	04.2009	09.2009-02.2010	29.12.2010	8.06.2010	09.2009-02.2010
pH	7.63	7.58÷7.92	8.69	8.37	7.10÷7.66
COD [mg O_2 dm^{-3}]		611÷902	820	>2000	137÷774
BOD_5 [mg O_2 dm^{-3}]		152÷199	368	360	60÷89
Conductivity [mS cm^{-1}]	0.799	0.508÷1.789	2.56	8.25	1.204÷1.722
Turbidity [FTU]	117	40÷145	352	-	4÷50
Absorption λ = 254 nm		0.380÷0.752	1.77	-	0.196÷0.346

[a)] illegal discharge of wastewater drain into the river Bobrek, Sosnowiec (Poland), [b)] from sewer system that convey domestic and urban waste to wastewater treatment plant (WWTP) Zagorze, Sosnowiec (Poland)

Before the irradiation process, a mixture of SNs (Table 1), solid TiO_2 and / or $FeCl_3$ were added to wastewater samples (100 cm^3). They were irradiated with 4 UV lamps (Philips TL W/05). During irradiation, samples were mixed using magnetic stirrers and had free contact with air.

Determination of drugs in samples

The concentration of selected drugs in samples were determined by HPLC method [16] (Waters detector - TAD-486, wavelength - 254 nm, pump - Knauer 64, column Supelcosil LC-18, 250x4.6 mm, grain - 5 μm, mobile phase: buffer containing 20 mmol dm^{-3} K_2HPO_4, pH 8.2: acetonitrile - 95:5, flow - 1.0 cm^3/min, sample volume - 20 cm^3).

In order to estimate the efficiency of the investigated photocatalytic reactions, the dynamics of changes in SNs concentrations during the irradiation was compared in relation to the stock solutions prepared according to previously described procedure (without the addition of catalysts and before the beginning of irradiation). On this basis, the percentage degree of the removal of SNs after a definite, in the experiment, irradiation time of their solutions was determined. *The degree of removal* (*DR*) was calculated according to the equation:

$$DR = \left(1 - \frac{C_i}{C_o}\right) \cdot 100\%$$

where C_i/C_o is the ratio of determined and initial concentration of each sulfonamide.

The average degree of removal of SNs in a mixture was calculated as a weighted average value of DR.

Studied the kinetics of photocatalytic processes were evaluated based on the value of the regression coefficients

$$\ln\frac{C_i}{C_o} = -k^I t + b \quad \text{(for the first-order reaction)}$$

$$\frac{1}{C_i} = k^{II} t + b \quad \text{(for the second-order reaction)}$$

where t is the irradiation time, b is the intercept.

The half-life time ($T_{1/2}$) was determined by the graphical method.

Dynamics of photocatalytic reaction

The process of photocatalytic degradation of SNs was studied in the presence of TiO_2 (0.5 g dm^{-3}) and $FeCl_3$ (1.0 mmol dm^{-3}) and mixtures containing these two compounds. Their used concentrations and the pH of the irradiated solutions was established in preliminary studies using the SNs solutions in distilled water. Figure 1 shows the average half-times of SNs to added to wastewater samples during irradiation in the presence of TiO_2 and / or $FeCl_3$. Additionally, the results obtained in processes carried out in distilled water are presented in Figure 1.

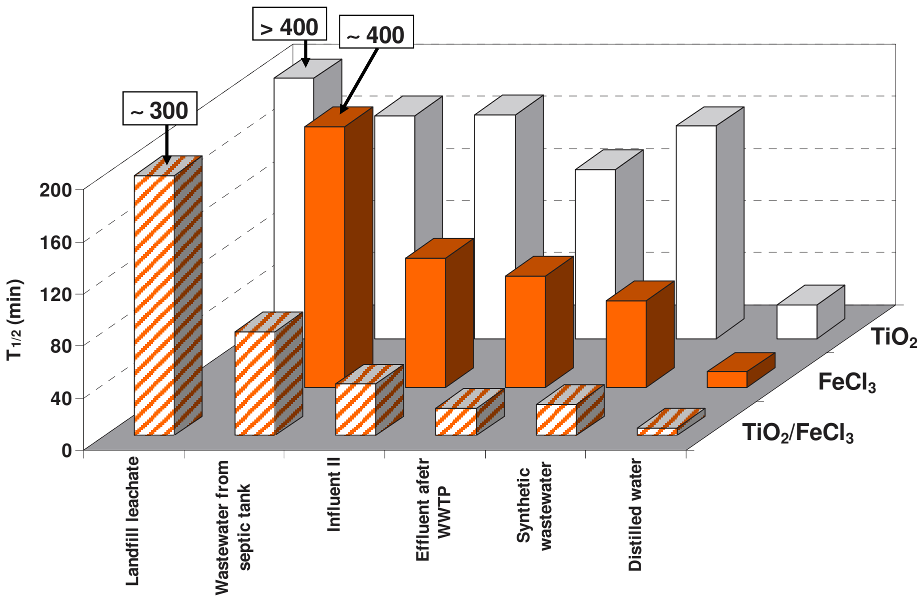


Fig. 1. The average half-times of SNs added to samples during irradiation in the presence of TiO_2 (0.5 g dm^{-3}) and/or $FeCl_3$ (1.0 mmol dm^{-3})

Before the beginning of irradiation, a slight decrease in SNs concentration (about 10%) was observed in all samples at pH ~3. Further decrease in SNs concentration occurred during the irradiation of samples. It can be an evidence of the drugs degradation. As expected, the values of $T_{1/2}$ determined for SNs in wastewater samples are much longer than in distilled water. It means that in order to carry out an effective degradation of drugs in wastewater, the irradiation time should be prolonged.

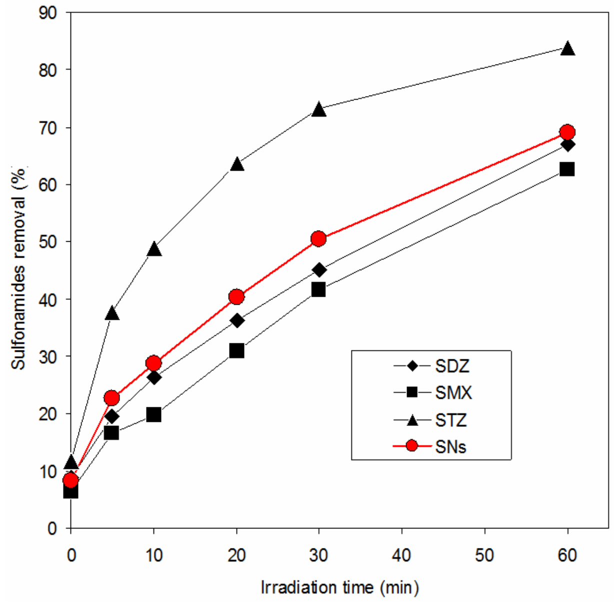


Fig. 2. The dynamics of the SNs degradation in influent in the presence of $TiO_2/FeCl_3$ mixture

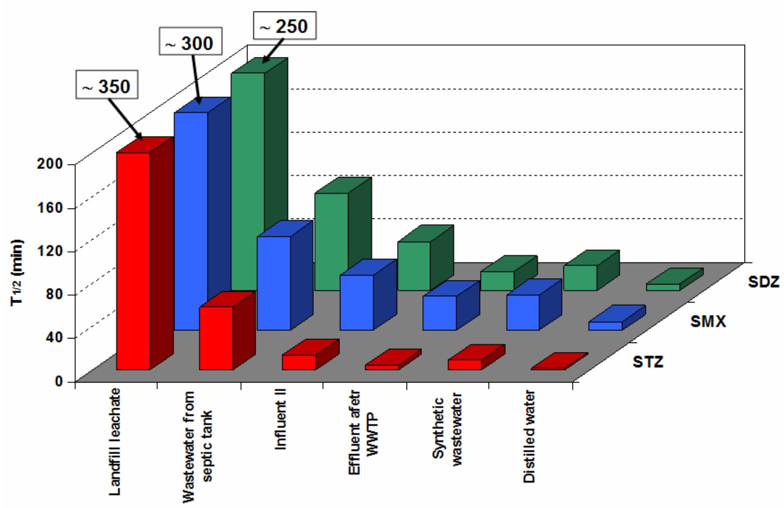


Fig. 3. The half-life times of SNs in wastewater samples and in distilled water. The values were determined during the photocatalytic degradation carried out in the presence of a mixture of TiO_2 (0.5 g dm^{-3}) and $FeCl_3$ (1.0 mmol dm^{-3})

By comparing the half-times of individual SNs, the mixture $TiO_2/FeCl_3$ was settled as the optimal photocatalyst in this process (Fig. 1). This mixture has high initial rate of photodegradation, especially in the case of sulfathiazole (STZ) and the process occurs most likely in accordance with the second-order reaction kinetics (Fig. 2). In all other cases, the process of photodegradation follows the first-order kinetics.

Figure 3 presents the weighted average of $T_{1/2}$ determined for all SNs in the investigated samples.

It was found that all investigated SNs, added to wastewater samples underwent the photocatalytic degradation. However in practice, the photocatalysis has only little use in the case of leachate from landfills because it proceeded much slower than in the other wastewater studied.

Additionally, the effect of concentration of individual components of the most active photocatalytic system ($TiO_2/FeCl_3$) and the pH of the irradiated samples on the $T_{1/2}$ value of SNs added to the influent II were also determined. The results obtained were similar to those observed in distilled water. It was found that in wastewater the photocatalytic degradation of SNs carried out at pH = 3 and at concentrations of TiO_2 and $FeCl_3$ established in earlier experiments was the most preferred process. However, the results obtained for STZ differed from the others. For example, the efficiency of STZ degradation increased with increasing concentration of TiO_2 above 0.5 g dm^{-3} and at pH < 3. It means that the reaction mechanisms for SDZ, SMX and STZ may vary.

Conclusions

1. Sulfonamides (SNs) added to wastewater, may be removed by the photocatalytic degradation process.
2. Photocatalytic degradation of SNs is ineffective in the case of leachate from landfills.
3. The process of photocatalytic degradation is the most favourable when a mixture of $TiO_2/FeCl_3$ and pH = 3 are used.
4. Photocatalytic reaction mechanisms may vary in the case of individual SNs.

Acknowledgements

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References

[1] Eintrag von Arzneimitteln und deren Verhalten und Verbleib in der Umwelt Literaturstudie Fachbericht 2, Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen. Recklinghausen 2007.

[2] Environmentally Classified Pharmaceuticals 2009. Stockholm County Council. http://www.janusinfo.org/imcms/servlet/GetDoc?meta_id=10205.

[3] Phuong Hoa PT, Nonaka L, Viet PH, Suzuki S. Sci Total Environ. 2008;405:377-384. DOI: 10.1016/j.scitotenv.2008.06.023.

[4] Pallecchi L, Lucchetti C, Bartoloni A, Bartalesi F, Mantella A, Gamboa H, Carattoli A, Paradisi F, Rossolini GM. Antimicrob Agents Chemother. 2007;51:1179-1184.

[5] Narodowy Program Ochrony Antybiotyków na lata 2006-2010, Ministerstwo Zdrowia, http://www.mz.gov.pl/wwwfiles/ma_struktura/docs/zal_ochr_antybiotyk_26032007.pdf

[6] Ternes T. Assesment of technologies for the removal of pharmaceuticals and personal care products in sawage and drinking water facilities to improve the indirect portable water reuse: POSEIDON detailed report related to the overall duration, 2005: www.eu-poseidon.com

[7] Sukul P, Spiteller M. Environ Contam Toxicol. 2006;187:67-101.
[8] Batt AL, Kim S, Aga DS. Chemosphere. 2007;68:428-435. DOI: 10.1016/j.chemosphere.2007.01.008.
[9] Klavarioti M, Mantzavinos D, Kassinos D. Environ Int. 2009;35:402-417. DOI: 10.1016/j.envint.2008.07.009.
[10] Calza P, Medana C, Pazzi M, Baiocchi C, Pelizzetti E. App Catal B Environ. 2004;53:63-69. DOI: 10.1016/j.apcatb.2003.09.023.
[11] Kaniou S, Pitarakis K, Barlagianni I, Poulios I. Chemosphere. 2005;60:372-380. DOI: 10.1016/j.chemosphere.2004.11.069.
[12] Hu L, Flanders PM, Miller PL, Strathmann TJ. Water Res. 2007;41:2612-2626. DOI: 10.1016/j.watres.2007.02.026.
[13] Beltran FJ, Aguinaco A, Garcia-Araya JF, Oropesa A. Water Res. 2009;43:1359-1369. DOI: 10.1016/j.watres.2008.12.015.
[14] Abellan MN, Gimenez J, Esplugas S. Catal Today. 2009;144:131-136. DOI: 10.1016/j.cattod.2009.01.051.
[15] Baran W, Adamek E, Sobczak A, Sochacka J. Catal Comm. 2009;10:811-814. DOI: 10.1016/j.catcom.2008.12.026.
[16] Baran W, Adamek E, Sobczak A, Makowski A. Appl Catal B Environ. 2009;90:516-525. DOI: 10.1016/j.apcatb.2009.04.014.

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Abstrakt: Sulfonamidy są lekami przeciwbakteryjnymi najczęściej używanymi w profilaktyce weterynaryjnej. Do środowiska leki te dostają się różnymi drogami. Sulfonamidy mają zdolność kumulowania się w różnorodnych organizmach, wobec których mogą okazać się toksyczne. Nawet małe stężenie tych leków może prowadzić do wytworzenia się lekooporności drobnoustrojów. Celem pracy było określenie możliwości zastosowania procesu fotokatalizy do degradacji wybranych sulfonamidów aplikowanych do rzeczywistych ścieków oraz optymalizacja tej metody. Proces fotokatalitycznej degradacji badany był w rzeczywistych ściekach komunalnych, w ściekach syntetycznych oraz w wodzie destylowanej. Proces prowadzony był w otwartych reaktorach, które były naświetlane promieniowaniem UV-A, przy udziale TiO_2-P25, $FeCl_3$ i mieszaniny $TiO_2/FeCl_3$. Stwierdzono, iż zastosowanie mieszaniny $TiO_2/FeCl_3$ przynosi najlepsze efekty w usunięciu wybranych sulfonamidów. Określono wpływ wybranych procesów oczyszczania ścieków, pH oraz stężeń reagentów na efektywność degradacji sulfonamidów ze ścieków. Zostały wyznaczone ponadto rzędy badanych reakcji oraz ich kinetyka.

Słowa kluczowe: fotokataliza, sulfonamidy, ścieki