

Justyna ZIEMIAŃSKA \*, Ewa ADAMEK \*, Andrzej SOBCZAK \*,  
Ilona LIPSKA \*, Andrzej MAKOWSKI \*, Wojciech BARAN \*

## THE STUDY OF PHOTOCATALYTIC DEGRADATION OF SULFONAMIDES APPLIED TO MUNICIPAL WASTEWATER

*Received March 16, 2010; reviewed; accepted May 4, 2010*

A photocatalytic process of degradation of the selected sulfonamides (sulfathiazole, sulfamethoxazole and sulfadiazine) added to real wastewater was studied in this work. The process was initiated by UV-a irradiation and TiO<sub>2</sub>-P25, FeCl<sub>3</sub> and mixtures of TiO<sub>2</sub>-P25 with FeCl<sub>3</sub> were used as photocatalysts. The effect of pre-treatment of wastewater and the influence of process parameters on the efficiency of sulfonamides removal were also determined. It was found that the highest efficiency of degradation was achieved in the process carried out in the presence of TiO<sub>2</sub>-P25/FeCl<sub>3</sub> mixture, in full scale effluent wastewater treatment plant..

*keywords: sulfonamides, photocatalysis, wastewater treatment, TiO<sub>2</sub>, FeCl<sub>3</sub>*

### 1. INTRODUCTION

Recently, there has been an increasing concern, particularly in highly developed countries, about penetration of pharmaceuticals into the environment and related risks [1-6]. This penetration is caused, among others, by a very high consumption of drugs by societies in these countries and by the growing, unfavourable results of

---

\* Medical University of Silesia, Faculty of Pharmacy Chemistry, 4 Jagiellońska Str.,41-200 Sosnowiec, bw-xxl@wp.pl (W. Baran)

pharmaceuticals' presence in the environment [2]. It is estimated that there are approx. 200 000 pharmaceuticals on the world market, and the quantity of available preparations in individual countries can even achieve the number of 10 000 [7]. At present, the world consumption of pharmaceuticals in medicine and veterinary medicine is estimated at 100 000 t annually [8]. According to other sources, only the antibiotics use ranges from 100 000 to 200 000 t annually in the world, of which 50 to 75% is used in the veterinary prophylaxis and/or as growth promoters in animal breeding [6]. Sarmah et al. [9] have reported that in different countries, sulfonamides (SNs) represent from 2% (USA) to 22% (UK, Kenya) of used veterinary antibiotics. Particular concern is growing from the fact that residues of these pharmaceuticals can easily penetrate to the environment, which has been proved by the data derived from systematic monitoring [2,3,6,7,9]. Almost 100% of samples taken recently from various parts of the hydrosphere contained trace concentrations (mostly below  $1 \mu\text{g l}^{-1}$ ) of sulfonamides [6]. Antibiotics, including sulfonamides, in the concentrations below the lethal level are a serious risk to health and to the environment due to the generation of drug-resistance of pathogenic bacteria and bacterial resistance to disinfection products [10].

The reasons described above caused that the methods for elimination of antibiotics from sewage have been intensively sought for several years. The effectiveness of traditional methods (biodegradation, coagulation, sedimentation) is often low or very low [2,3,5,11]. Simultaneously, Turkdogan and Yetilmezsoy [12] have found that the removal efficiency of antibacterial drugs from biosphere during the routine, biological processes was estimated a little above 20%. Scientists have great hopes for the techniques of advanced oxidation processes (AOP) particularly in ozonation [2,13,14] and photocatalytic degradation [13-20]. The use of this technique for treatment of municipal or farm sewage allows to decompose organic substances and medicines present in this type of waste, as a result of oxygenation using hydroxyl radicals ( $\text{HO}^{\bullet}$ ) generated in the reaction environment. Many researches have described a mechanism and a kinetics of sulfonamides degradation in the presence of hydroxyl radicals [16,17,20]. It was found that during the initial step of photocatalytic process a decrease in toxicity and a significant increase in biodegradability of solutions containing sulfonamides were observed [21]. Since intermediates of photocatalytic process are chemically and biologically less stable than the initial substrates, the increase of COD and  $\text{BOD}_5$  is often observed in the irradiated solutions [22]. The photocatalytic process can lead to the total mineralization of organic substances however it is unfounded from the economic point of view. The further biodegradation of the residual organic products seems to be more correct and well founded. A combination of both processes, namely photocatalysis and biodegradation, should lead to a decrease in the toxicity, the microbial activity as well as to a decrease of COD and  $\text{BOD}_5$  in wastewater containing antibiotics [21]. The above mentioned results were obtained in the experiments using sulfonamides solutions in distilled water.

Many of the cited papers have presented the results of experiments concerning the photocatalytic degradation of sulfonamides in the presence of commercial TiO<sub>2</sub>-P25 as a catalyst. However, our previous results showed that the efficiency of sulfonamides photodegradation can be considerably higher using Fe(III) salts as a photocatalyst (e.g. FeCl<sub>3</sub> [19,20]) than in the presence of TiO<sub>2</sub> alone. In these solutions, Fe(III) ions are partly hydrolyzed and in the result, the photoactive Fe(OH)<sup>2+</sup> ions are formed. After absorption of UVa light by these ions, hydroxyl radicals are generated in solutions [20,23]. The high photocatalytic activity of Fe(III) salts was confirmed in the experiments reported by other researchers [24,25]. According to Mestankova et al. [26] the simultaneous use of TiO<sub>2</sub> and FeCl<sub>3</sub> mixture probably cause an increase in efficiency of the photocatalytic system due to the synergic effect. This fact was confirmed experimentally during the photocatalytic decoloration of real tannery wastewater [22].

The aim of the work was determination of the possibility of using photocatalytic process to degradation of selected sulfonamides added to real wastewater and this method optimization.

## 2. MATERIALS AND METHODS

### 2.1. Reagents

The characteristics of the investigated sulfonamides are presented in Table 1.

Table 1. The characteristics of investigated SNs

Sulfonamides	Abbr. in text	Structure	pKa <sub>1</sub> <sup>a</sup>	pKa <sub>2</sub> <sup>a</sup>	k <sub>OH</sub> <sup>b</sup> (l mol <sup>-1</sup> s <sup>-1</sup> )	C <sub>0</sub> <sup>c</sup> (mmol l <sup>-1</sup> )	t <sub>R</sub> <sup>d</sup> (min)	LOD <sup>e</sup> (mmol l <sup>-1</sup> )
Sulfamethoxazole	SMX		1.60	5.81	(5.8 ± 0.2) · 10 <sup>9</sup>	0.050	7.49	1.7 · 10 <sup>-5</sup>
Sulfadiazine (natrium salt)	SDZ		2.00	6.48	3.7 · 10 <sup>9</sup>	0.025	3.48	1.1 · 10 <sup>-5</sup>
Sulfathiazole (natrium salt)	STZ		2.36	7.23	(7.1 ± 0.2) · 10 <sup>9</sup>	0.025	12.66	2.0 · 10 <sup>-5</sup>

a)  $\text{SNsH}_2^+ \xrightleftharpoons{K_{a1}} \text{SNsH} \xrightleftharpoons{K_{a2}} \text{SNs}^-$  b) reaction rate constant for SNs with HO<sup>•</sup> [27,28]

c) initial concentration of SNs in experiments

d) retention time for mobile phase flow 1.0

ml min<sup>-1</sup>

e) limit of detection for injection samples at volume 50 μl

All SNs used throughout this study were of analytical grade and were manufactured by Sigma. Just before experiments, weighed amounts of each sulfonamide were added to wastewater or distilled water and samples were intensively mixed. The theoretically initial concentrations of sulfonamides in samples are shown in Table 1. Titanium(IV) dioxide (TiO<sub>2</sub>-P25) obtained from Evonic Degussa GmbH and iron(III) chloride (FeCl<sub>3</sub>) purchased from POCH were used as photocatalysts. These compounds were selected based on preliminary experiments concerning the photocatalytic degradation of sulfonamides in aqueous solutions [20,21]. Hydrochloric acid (HCl) was added to wastewater samples in order to adjust the pH at a desire value. In our earlier studies, we did not observe significant changes in the sulfonamides concentration in solutions irradiated in the presence of HCl.

## 2.2. Wastewater samples

The wastewater samples were taken from sewer system that conveys domestic and urban waste to wastewater treatment plant (WWTP) Zagórze in Sosnowiec (Poland). Samples were stored at temperature below -18°C. The characteristics of used wastewaters are presented in Table 2. The synthetic wastewater was prepared on the base ISO 9887:1992(E) (Table 3) [29].

Table 2. The characteristics of used wastewater samples

	Influent	Effluent
pH	7.58-7.92	7.10-7.66
COD (mg O <sub>2</sub> l <sup>-1</sup> )	611-902	137-774
BOD <sub>5</sub> (mg O <sub>2</sub> l <sup>-1</sup> )	152-199	60-89
Conductivity (mS cm <sup>-1</sup> )	0.508-1.789	1.204-1.722
Turbidity (FTU)	40-145	4-50
Ab <sub>S<sub>254</sub> nm</sub>	0.380-0.752	0.196-0.346

Table 3. Chemical composition of the synthetic municipal wastewater

Chemicals	Concentration (mg l <sup>-1</sup> )
Peptone	160
Meat extract	110
Urea	30
K <sub>2</sub> HPO <sub>4</sub>	28
NaCl	7
CaCl <sub>2</sub> ·2H <sub>2</sub> O	4
Mg <sub>2</sub> SO <sub>4</sub> ·7H <sub>2</sub> O	2

Before beginning the experiments, the samples were stored at room temperature for 1 day. The investigated SNs were not detected in wastewater in the concentration above the detection limit (LOD).

### 2.3. Conditioning of wastewater samples

The wastewater samples (before SNs addition) were stored in glass adsorption bulbs (250 ml) enabling barbotage for 7 days at  $20.4 \pm 0.9^\circ\text{C}$ . During the whole experiments, samples were aerated by a continuous airflow ( $0.41 \pm 0.14 \text{ ml s}^{-1}$ ). The concentration of oxygen dissolved in wastewater was about  $\sim 100\%$ .

### 2.4. Microfiltration of wastewater samples

The wastewater samples (without SNs) were vacuum-filtered using vacuum filtration system (J.T.Baker) with z Milipore HVPL membrane filter ( $0.45 \mu\text{m}$ , 47 mm) and vacuum pump AgaLabor PL2. The mean speed of filtration was  $2.8 \text{ ml s}^{-1}$  and the maximum partial vacuum was 0.09 MPa.

### 2.5. Coagulation of wastewater samples

The coagulation of wastewater samples (before SNs addition) was carried out in beakers (250 ml). Aliquots (4 ml) of the coagulant ( $\text{FeCl}_3$  stock solution at concentration of  $1 \text{ mol l}^{-1}$ ) were added to 200 ml of wastewaters and mixtures were mixed using compressed air. After the addition of the coagulant, pH of samples was 6.26. After 5 min, the mixing was finished and samples were left in order to settle the sediments. Aliquots of solution were collected from above the sediment and were used in further experiments

### 2.6. Irradiation

Before irradiation a solid  $\text{TiO}_2$  and/or  $\text{FeCl}_3$  stock solution was added to wastewater or distilled samples containing sulfonamides (Tab. 1). The pH of the irradiated samples was adjusted with concentrated HCl or NaOH solutions ( $<1 \text{ ml}$ ). Next, mixtures were homogenized in dark for 30 min by means of magnetic stirrers. The catalyst concentrations are presented in Table 4. In all experiments, open glass crystallizers (volume: 500 ml, exposed surface:  $102 \text{ cm}^2$ ) containing 100 ml of samples were irradiated by four UV lamps (Philips TL-40 W/05 at  $\lambda_{\text{max}} 366 \text{ nm}$ ). The intensity of radiation, determined by Parker's actinometer was  $5.25 \cdot 10^{-7} \text{ Einstein min}^{-1} \text{ cm}^{-2}$  [30]. During the irradiation, mixtures were magnetically stirred and had free contact with air. The temperature of samples was  $21\text{-}24^\circ\text{C}$ .

## 2.7. Analytical methodology

After the appropriate irradiation time samples were centrifuged (30 min, 4000 RPM). Before and after irradiation, the concentration of sulfonamides in mixtures was determined using HPLC (column Supelcosil Suplex pKB-100 LC-18, 5 mm, 250 mm x 4.6 mm, detectors Waters TAD 486,  $\lambda = 254$  nm) and mobile phase  $\text{K}_2\text{HPO}_4$  (pH 8.2)/ $\text{CH}_3\text{CN}$  in the ratio 95:5. The retention time and LOD value of SNs are shown in Table 1. The pH and concentration of oxygen dissolved in irradiated samples were measured by multimeter HD22569.2 (Delta OHM).

## 2.8. Analysis of results

Removal of individual SNs was calculated according to the equation:

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

where:  $Y_i$  is the removal of SDZ, SMX or STZ (%),  $C_o$  is the initial concentration of SDZ, SMX or STZ (in standard solution),  $C_i$  is the final concentration of SDZ, SMX or STZ (in samples). Removal of SNs sum was calculated as follows:

$$Y_{SNs} = \sum x_i Y_i$$

where  $x_i$  is the mole fraction of investigated sulfonamides. The reaction rate constant ( $k$ ) values were determined as a slope of linear relationship:

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

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

where  $t$  is the irradiation time,  $b$  is a free term of the equation. The initial reaction rate ( $r_o$ ) values were calculated using the formula:

$$r_o^I = k^I C_o \quad (\text{the first-order kinetics})$$

$$r_o^{II} = k^{II} C_o^2 \quad (\text{the second-order kinetics}).$$

## 3. RESULTS AND DISCUSSIONS

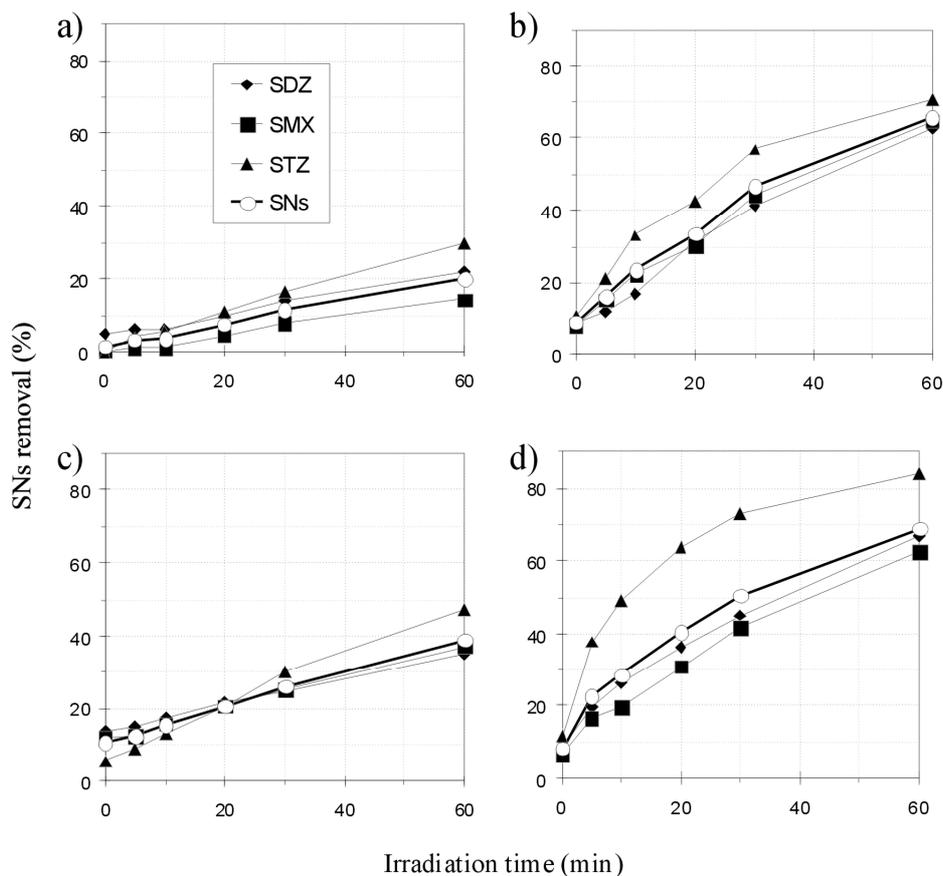
3.1. The comparison of photocatalytic activities of selected photocatalytic systems ( $\text{TiO}_2$ ,  $\text{TiO}_2/\text{HCl}$ ,  $\text{FeCl}_3/\text{HCl}$ , and  $\text{TiO}_2/\text{FeCl}_3/\text{HCl}$ )

Fig. 1. The dynamics of photocatalytic degradation of SNs added to influent samples during irradiation with  $\text{TiO}_2$  (a);  $\text{TiO}_2/\text{HCl}$  (b);  $\text{FeCl}_3/\text{HCl}$  (c); and  $\text{TiO}_2/\text{FeCl}_3/\text{HCl}$  (d)

The dynamics of photodegradation of SNs in the spiced samples of influent in the presence of  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{HCl}$ ,  $\text{FeCl}_3/\text{HCl}$  and  $\text{TiO}_2/\text{FeCl}_3/\text{HCl}$  were also studied. The results are showed in Fig. 1. Table 4 shows the reagent concentrations, pH and the initial reaction rate.

HCl was added in order to adjust the optimal pH value for the photoactivity of Fe-salts (based on the literature data [20,23]). No significant changes in the sulfonamides

concentration were observed after irradiation of samples with HCl only.

The decrease in sulfonamides concentration by about 10% was observed in all samples at pH~ 3 (Fig. 1b,c,d), before the beginning of irradiation. Since the influent samples were centrifuged before analysis, the decrease in their concentration was caused by the adsorption of SNs on the suspension particles.

Table 4. The results of initial photocatalytic degradation rate of sulfonamides in spiced influent

Concentration			pH	Initial photocatalytic degradation rate (mmol l <sup>-1</sup> min <sup>-1</sup> )			
TiO <sub>2</sub> (g l <sup>-1</sup> )	FeCl <sub>3</sub> (mmol l <sup>-1</sup> )	HCl <sup>a</sup> (mmol l <sup>-1</sup> )		SDZ	SMX	STZ	SNs
0.5	-	-	7.86	(0.83±0.10)·10 <sup>-4</sup>	(1.35±0.15)·10 <sup>-4</sup>	(1.45±0.15)·10 <sup>-4</sup>	(3.63±0.40)·10 <sup>-4</sup>
0.5	-	5-20	3.00	(3.83±0.38)·10 <sup>-4</sup>	(8.05±0.80)·10 <sup>-4</sup>	(1.18±0.10)·10 <sup>-3</sup>	(2.36±0.21)·10 <sup>-3</sup>
-	1.0	2-14	3.01	(1.18±0.05)·10 <sup>-4</sup>	(2.90±0.20)·10 <sup>-4</sup>	(5.00±0.25)·10 <sup>-4</sup>	(9.08±0.50)·10 <sup>-4</sup>
0.5	1.0	2-13	2.98	(4.10±0.30)·10 <sup>-4</sup>	(7.60±0.40)·10 <sup>-4</sup>	(2.13±0.07)·10 <sup>-3</sup> b	(3.30±0.10)·10 <sup>-3</sup>
2.5	1.0	2-12	3.00	(4.56±0.33)·10 <sup>-4</sup>	(7.12±0.79)·10 <sup>-4</sup>	(7.15±0.29)·10 <sup>-3</sup> b	(8.32±0.40)·10 <sup>-3</sup>
0.5	3.0	~5 <sup>c</sup>	3.00	(2.21±0.15)·10 <sup>-4</sup>	(2.40±0.10)·10 <sup>-4</sup>	(1.83±0.11)·10 <sup>-3</sup> b	(2.29±0.14)·10 <sup>-3</sup>

<sup>a</sup>) HCl was added in order to adjust pH values in samples

<sup>b</sup>) calculated based on the second-order kinetics equation

<sup>c</sup>) one sample of wastewater was examined only

Further decrease in the SNs concentration occurred during the longer irradiation time. In this case it is most probably caused by the degradation of SNs only. It was found that the photodegradation of SNs in the presence of TiO<sub>2</sub>/HCl (Fig. 1b) and TiO<sub>2</sub>/FeCl<sub>3</sub>/HCl (Fig. 1d) was the most effective. Second of the catalytic system is characterized by the high initial rate of STZ photodegradation that follows the second-order kinetics. In the cases of SDZ and SMX, the photocatalytic process is described by first-order reaction kinetics. Similar results were obtained during studies concerning the photocatalytic degradation of SNs in aqueous solutions [20]. The comparison of the propagation rate with the use of SNs and HO• radicals (Table 1) does not explain these differences. Most probably, the photodegradation of STZ in the presence of TiO<sub>2</sub>/FeCl<sub>3</sub>/HCl differs from the degradation of SDZ and SMX with the use of the same catalyst during the initiation step. However, unequivocal explanation of this effect

requires further studies. The described above change in the reaction order causes that the comparison of the photocatalytic process based on the estimation of the initial reaction rate only may be incorrect. During irradiation, the second-order reaction rate slows down more than the first-order one. At the beginning of irradiation the STZ photodegradation was about 6 times faster in the presence of  $\text{TiO}_2/\text{FeCl}_3/\text{HCl}$  than with  $\text{TiO}_2/\text{HCl}$ . However, after 60 min of irradiation the change in the removal degree of STZ from wastewater was 13% only (Figs. 1b and 1d). It is worth to mention that the high degradation level of all SNs will be very possible after long-lasting irradiation time. Based on the theoretical calculations and determined experimentally the reaction rate constants it was estimated that the irradiation time necessary to degrade SDZ, SMX and STZ on the level of 90% in influent irradiated with  $\text{TiO}_2/\text{FeCl}_3/\text{HCl}$  under the used conditions may be 133, 146 and 105 min, respectively. Moreover, based on the comparison of the initial rate of SNs degradation (Table 4) and the time necessary to obtain the high degradation level,  $\text{TiO}_2/\text{FeCl}_3/\text{HCl}$  was selected as the optimum photocatalytic systems for this photodegradation process. It is also important that this catalyst system can be easily separated from the reaction medium [31].

An increase of  $\text{TiO}_2$  concentration in  $\text{TiO}_2/\text{FeCl}_3/\text{HCl}$  mixture caused a significantly increase in the degradation rate of STZ but it did not observe a large effect on the  $r_0$  values for SDZ and SMX. This phenomenon is thoroughly explained in the next section. On the other hand, the increase of  $\text{FeCl}_3$  concentration (to  $3.0 \text{ mmol l}^{-1}$ ) in  $\text{TiO}_2/\text{FeCl}_3/\text{HCl}$  mixture caused only decrease in the reaction rates of all selected SNs. In the case of SMX the  $r_0$  value decreased almost 3 times (Table 4) but at present no clear explanation to observed dependence may be given. .

### 3.2. Influence of pH on the photocatalytic degradation rate of SNs

In photocatalytic processes carried out under heterogeneous conditions, the pH of irradiated mixtures has an influence on the surface charge of the catalyst. Moreover, this value decides about products of  $\text{FeCl}_3$  hydrolysis and the charge of sulfonamides. Potentially, the best results for heterogeneous catalysis can be achieved in process in which substrates and the photocatalyst surface have opposite charges. Figure 2 shows the influence of pH on the photodegradation of SNs in the presence of  $\text{TiO}_2$  or  $\text{TiO}_2/\text{FeCl}_3$  in wastewater influent. The pH values were corrected by the addition of concentrated solutions of HCl or NaOH.

The results for wastewater influent samples are significantly different from results for distilled water [20]. In experiments with the use of distilled water, a decrease in pH caused a decrease in the photodegradation rate of sulfonamide in the presence of  $\text{TiO}_2$  while in the presence of  $\text{TiO}_2/\text{FeCl}_3$  it was showed the apparent maximum rate at pH about 3. On the other hand in wastewater the  $r_0$  values increased with the increase of acidification of irradiated samples. The decrease in pH had a strong effect on the

degradation rate of STZ and only slight influence on the  $r_0$  value for SDZ. In turn, in the presence of  $\text{TiO}_2$  the photodegradation of SMX proceeded with the constant rate in the pH range of 3-5.5 but in the presence of  $\text{TiO}_2/\text{FeCl}_3$  a high degradation rate was observed only at pH about 3.

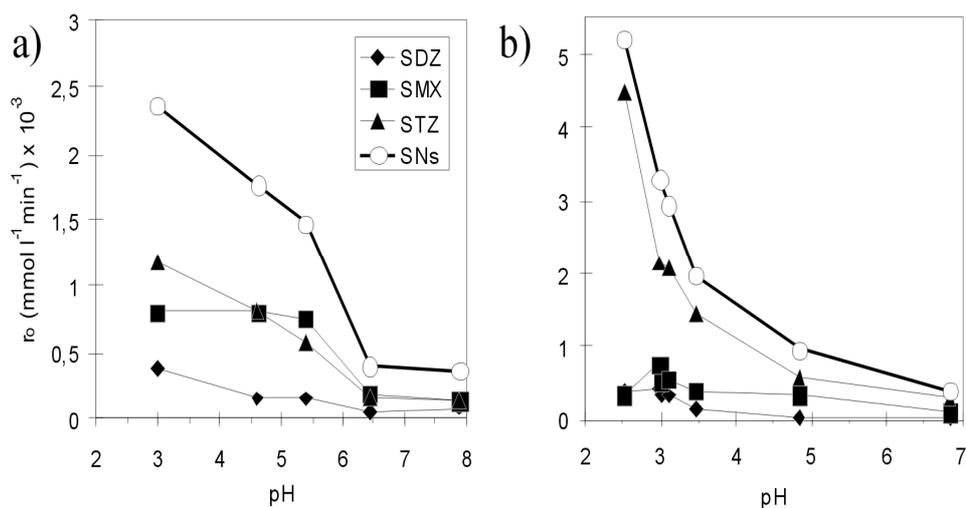


Fig. 2. The effect of pH on the photocatalytic degradation of SNs added to influent samples during irradiation with  $\text{TiO}_2$  (a) and  $\text{TiO}_2/\text{FeCl}_3$  (b)

The results described above imply that mainly  $\text{H}^+$  ions effect on the degradation rate of STZ. Based on the comparison of  $\text{pK}_{a1}$  for the selected SNs (Table 1) it is clear that the concentration of  $\text{SNsH}^+$  ions in the acidic medium increases from SMZ to STZ. Moreover, it is possible that  $\text{STZH}^+$  ions after adsorption onto  $\text{TiO}_2$  surface take part in a direct photocatalytic process as acceptors of excited electrons. Fujishima et al. have reported that cations can undergo the sorption onto  $\text{TiO}_2$  surface [32]. It confirms our results (Table 4) concerning the increase in the degradation rate of SMX after the increase in  $\text{TiO}_2$  concentration. However, this hypothesis should be confirmed by further experiments, including identification and quantitative determination of products of SMX degradation. Results obtained for SMZ and SDZ photodegradation in the presence of  $\text{TiO}_2/\text{FeCl}_3$  implies that  $\text{Fe}(\text{OH})^{2+}$  ions have a significant effect on their degradation. STZ, as distinct from SMX and SDZ, is relatively easy to biodegrade. Thus from the practical viewpoint, the more important is the choice of suitable conditions for the effective removal of SMX and SDZ. Therefore, the following process conditions were selected as the optimum ones for the degradation of SNs:  $\text{TiO}_2$  ( $0.5 \text{ g l}^{-1}$ ),  $\text{FeCl}_3$  ( $1.0 \text{ mmol l}^{-1}$ ),  $\text{pH} \sim 3$ . The economic disadvantage is high consumption of HCl necessary for acidification of samples (Table 4). This effect is caused by high

buffer capacity of wastewater. In experiments with the use of distilled water, the appropriate pH value (about 3) was obtained without the addition of HCl but as a result of FeCl<sub>3</sub> hydrolysis. From this reason the search for other methods of modification of the investigated process in order to reduce the consumption of HCl, without the decrease in the photodegradation efficiency, seems to be well founded.

### 3.3. Effect of preliminary wastewater treatment on the efficiency of photodegradation of sulfonamides

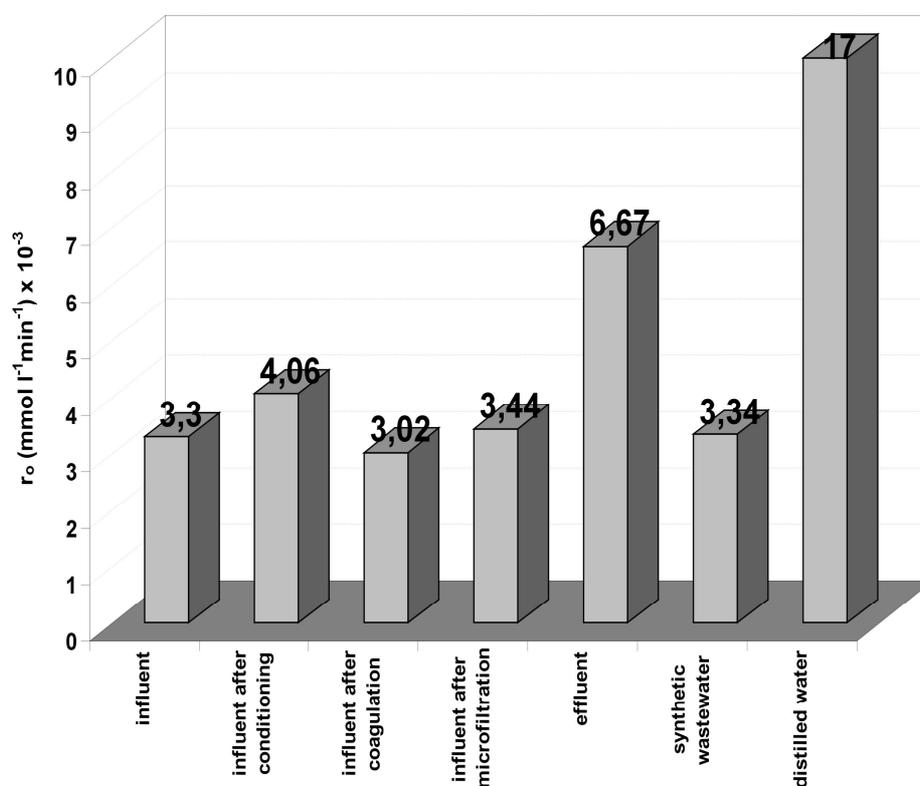


Fig. 3. The assessment of the initial reactions rate ( $r_0$ ) of SNs photodegradation in spiced real wastewater, before and after pretreatment, in synthetic wastewater and in distilled water with SNs (for the column corresponding to the  $r_0$  value for distilled water the scale is not preserved)

In order to decrease of the buffer capacity, wastewater samples were preliminary treated before the photocatalytic process. Then, SNs were added to treated wastewaters samples and samples were irradiated with TiO<sub>2</sub>/FeCl<sub>3</sub>/HCl at pH 2.98±0.5. The results obtained, namely the sum of  $r_0$  values, are showed in Figure 3.

According to expectations, the photodegradation rate of SNs was in each case

significantly lower in wastewater than in distilled water. Similar results were obtained using the model wastewater.

Microfiltration and coagulation are effective methods in the removal of suspended matter and colloids from the aquatic environment. It was observed that the investigated process efficiency did not change in influent samples after microfiltration and coagulation processes (Fig. 3). Probably it means that small amounts of suspended matter and colloids have no influence on the photodegradation process of SNs. The effectiveness of the elimination of substances forming non ideal solutions during coagulation and microfiltration was low. After these processes the concentration of dissolved organic substances in samples did not decrease considerably. Therefore, the photodegradation rate of SNs is decreased by organic, dissolved in water compounds (e.g. sugars, low-molecular peptides, organic acids and mainly detergents). Due to their significant concentration in wastewater these compounds can compete with SNs for hydroxyl radicals and active centers of catalyst. Negative effect on the SNs photodegradation may also have some inorganic ions with the reduction properties that are presented in insufficient oxygenated wastewater. The concentration of these ions can be decreased using the biodegradation and oxygenation processes proceeded during long-lasting conditioning (simultaneously with wastewater oxygenation) or their treatment in full scale WWTP. In wastewater samples that were previously conditioned, a slight increase in the photodegradation rate of SNs was observed. By this reason a significant higher photodegradation rate of SNs was in effluent obtained after full scale WWTP (Table 2) than in influent. After 60 min of irradiation of spiced effluent, the degradation degree of SDZ, SMX and STZ was 85.6, 76.9 and 92.7%, respectively whereas the degradation degree of SDZ, SMX and STZ in influent was 67.0, 62.5 and 83.9%, respectively. The observed phenomena can be the confirmation of the above-described thesis. The decrease in the concentration of dissolved organic compounds considerably affects on a decrease in the buffer capacity. In consequence, the amount of HCl used to adjust pH value to 3 is significantly lower in effluent than in influent (Table 2).

#### 4. CONCLUSIONS

Sulfonamides, including difficult biodegradable sulfa-drugs, can be removed from wastewater using the photodegradation process. The optimal catalytic system for the photodegradation of SNs in wastewater is the mixture containing  $\text{TiO}_2$  ( $0.5 \text{ g l}^{-1}$ ),  $\text{FeCl}_3$  ( $1 \text{ mmol l}^{-1}$ ) and HCl (in order to acidify the samples to pH 3). Under the used conditions the initial rate of the removal of SNs (spiced to municipal wastewater) is almost 15 times higher than for  $\text{TiO}_2$  alone.

In wastewater, the rate of SNs photodegradation can be also accelerated by their

pretreated in biological-mechanical processes. Preliminary filtration and coagulation did not effect on the course of investigated photocatalytic process.

## REFERENCES

- [1] KÜMMERER K. ed., *Pharmaceuticals in the environment. Sources, fate, effects and risks.* Heidelberg: Springer-Verlag 2001.
- [2] TERNES T.A. (project co-ordinator), JANEX-HABIBI M.L., KNACKER T., KREUZINGER N., SIEGRIST H., 2004, *Assesment of Technologies for the Removal of Pharmaceuticals and Personal Care Products in Sewage and Drinking Water Facilities to Improve the Indirect Potable Water Reuse.* Project POSEIDON, Contract No. EVK1-CT-2000-00047,
- [3] Eintrag von Arzneimitteln und deren Verhalten und Verbleib in der Umwelt Literaturstudie Fachbericht 2, Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen, Recklinghausen 2007.
- [4] Environmentally Classified Pharmaceuticals 2009, Stockholm County Council, [http://www.janusinfo.org/imcms/servlet/GetDoc?meta\\_id=10205](http://www.janusinfo.org/imcms/servlet/GetDoc?meta_id=10205)
- [5] SUKUL P., SPITTELER M., 2006, *Sulfonamides in the environment as veterinary drugs*, Environ. Contam. Toxicol., 187, 67-101.
- [6] KÜMMERER K., 2009, *Antibiotics in the aquatic environment – A review – Part I*, Chemosphere, 75, 417-434.
- [7] KOT-WASIK A., DĘBSKA A., NAMIEŚNIK J., *Przemiany, stężenia i oznaczanie pozostałości środków farmaceutycznych w środowisku*: Nowe horyzonty i wyzwania w analityce i monitoringu środowiskowym (34), Gdańsk: CEEAM 2003.
- [8] Knowledge and Need Assessment on Pharmaceutical Products in Environmental Waters, 2007, Project acronym: KNAPPE, Proposal N° 036864.
- [9] SARMAH A.K., MEYER M.T., BOXALL A.B.A., 2006, *A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (Vas) in the environment*, Chemosphere, 65, 725–759.
- [10] KEMPER N., 2008, *Veterinary antibiotics in the aquatic and terrestrial environment*, Ecol. Ind., 8, 1–13.
- [11] BATT A.L., KIM S., AGA D.S., 2007, *Comparison of the occurrence of antibiotics in four full-scale wastewater treatment plants with varying designs and operations*, Chemosphere, 68, 428-435.
- [12] TURKDOGAN F.I., YETILMEZSOY K., 2009, *Appraisal of potential environmental risks associated with human antibiotic consumption in Turkey*, J. Hazard. Mater., 166, 297–308.
- [13] KLAVARIOTI M., MANTZAVINOS D., KASSINOS D., 2009, *Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes*. Environ. Int. 35, 402–417.
- [14] BELTRAN F.J., AGUINACO A., GARCIA-ARAYA J.F., OROPESA A., 2009, *Ozone and photocatalytic processes to remove the antibiotic sulfamethoxazole from water*, Water Res., 43, 1359-1369.
- [15] KANIOU S., PITARAKIS K., BARLAGIANNI I., POULIOS I., 2005, *Photocatalytic oxidation of sulfamethazine*, Chemosphere, 60, 372–380.
- [16] HU L., FLANDERS P.M., MILLER P.L., STRATHMANN T.J., 2007, *Oxidation of Sulfamethoxazole and Related Antimicrobial Agents by TiO<sub>2</sub> Photocatalysis.*, Water Res., 41, 2612 – 2626.

- [17] CALZA P., MEDANA C., M. PAZZI, BAIOCCHI C., PELIZZETTI E., 2004, *Photocatalytic transformation of sulphonamides on titanium dioxide*, App. Catal. B-Environ., 53, 63-69.
- [18] ABELLAN M.N., GIMENEZ J., ESPLUGAS S., 2009, *Photocatalytic degradation of antibiotics: The case of sulfamethoxazole and trimethoprim*, Catal. Today 144, 131-136.
- [19] BARAN W., ADAMEK E., SOBCZAK A., SOCHACKA J., 2009, *The comparison of photocatalytic activity of Fe-salts, TiO<sub>2</sub> and TiO<sub>2</sub>/FeCl<sub>3</sub> during the sulfanilamide degradation process*. Catal. Comm., 10, 811-814.
- [20] BARAN W., ADAMEK E., SOBCZAK A., MAKOWSKI A., 2009, *Photocatalytic degradation of sulfa drugs with TiO<sub>2</sub>, Fe salts and TiO<sub>2</sub>/FeCl<sub>3</sub> in aquatic environment—Kinetics and degradation pathway*, Appl. Catal. B: Environ., 90, 516-525.
- [21] BARAN W., SOCHACKA J., WARDAS W., 2006, *Toxicity and biodegradability of sulfonamides and products of their photocatalytic degradation in aqueous solutions*, Chemosphere, 65, 1295-1299.
- [22] ADAMEK E., BARAN W., SOBCZAK A., MAKOWSKI A., 2009, *The photocatalytic decoloration of wastewater containing azo-dyes*. – Pol. J. Environ. Stud., 18-2B, 80-82.
- [23] WU F., DENG N., 2000, *Photochemistry of hydrolytic iron (III) species and photoinduced degradation of organic compounds*. A minireview, Chemosphere 40, 389-394.
- [24] CATASTINI C., SARAKHA M., MAILHOT G., BOLTE M., 2002, *Iron (III) aquacomplexes as effective photocatalysts for the degradation of pesticides in homogeneous aqueous solutions*, Sci. Total Environ., 298, 219-228.
- [25] ANDREOZZI R., CANTERINO M., MAROTTA R., 2006, *Fe(III) homogeneous photocatalysis for the removal of 1,2-dichlorobenzene in aqueous solution by means UV lamp and solar light*, Water Res., 40, 3785 – 3792.
- [26] MESTANKOVA H., MAILHOT G., JIRKOVSKY J., KRYSA J., BOLTE M., 2005, *Mechanistic approach of the combined (iron–TiO<sub>2</sub>) photocatalytic system for the degradation of pollutants in aqueous solution: an attempt of rationalisation*, Appl. Catal. B Environ., 57, 257-265.
- [27] BOREEN A.L., ARNOLD W.A., MC NEILL K., 2004, *Photochemical fate of sulfa drugs in the aquatic environment: sulfa drugs containing five-membered heterocyclic groups*, Environ. Sci. Technol., 38, 3933-3940.
- [28] BOREEN A.L., ARNOLD W.A., MC NEILL K., 2005, *Triplet-sensitized photodegradation of sulfa-drugs containing six-membered heterocyclic groups: Identification of an SO<sub>2</sub> extrusion photoproduct*, Environ. Sci. Technol., 39, 3630-3638.
- [29] ISO 9887:1992(E) Water quality - Evaluation of the aerobic biodegradability of organic compounds in an aqueous medium -Semi-continuous activated sludge method (SCAS)
- [30] HATCHARD C., PARKER C., 1956, *A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer*, Proc. Roy. Soc. A 235, 518-36.
- [31] BARAN W., MAKOWSKI A., WARDAS W., 2005, *The separation of catalyst after photocatalytic reaction conducted in the presence of TiO<sub>2</sub>/FeCl<sub>3</sub>/UV*, Chemosphere 59, 853-859.
- [32] FUJISHIMA A., ZANG X., TRYK D.A., 2008, *TiO<sub>2</sub> photocatalysis and related surface phenomena*, Surf. Sci. Rep., 63, 515-582.