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USE OF A TiO₂/FeCl₃ MIXTURE IN ENVIRONMENTAL CLEANING TECHNOLOGY

ZASTOSOWANIE MIESZANINY TiO₂/FeCl₃ W TECHNOLOGII OCZYSZCZANIA ŚRODOWISKA

Abstract: One of the methods allowing the use of solar energy being a renewable, alternative form of energy is the environmental cleaning technology. It was stated that many types of pollutants, regardless of their toxicity and resistance to biodegradation, can be effectively degraded in photocatalytic processes initiated by sunlight. Among many different heterogeneous photocatalysts examined, titania (TiO₂) is one of the commonly used in these processes. Unfortunately, in practice the main problem connected with the use of photocatalytic processes is their low quantum yield. In our opinion, the addition of Fe(III) salts to the reaction mixture will be a simple and inexpensive method that increases this yield. It was confirmed in studies on the photocatalytic degradation of many organic compounds, differing in chemical structure and properties. The goal of our study was to compare the results of photocatalytic degradation carried out in the presence of TiO₂ or Fe(III) salts as well in the presence of a mixture TiO₂ with Fe(III) salts. It was found that the ability of organic substrates to form the coordination complexes with Fe(III) ions and their adsorption onto TiO₂ surface has the greatest effect on the course of photocatalytic reaction and its efficiency. Based on the literature data and own studies we propose a probable mechanism of process carried out in the presence of TiO₂/Fe(III) mixture.

Keywords: photocatalysis, TiO₂, environmental cleaning technology

Introduction

One of the methods allowing the use of solar energy is the environmental cleaning technology. It was stated that many types of pollutants, regardless of their toxicity and resistance to biodegradation, can be effectively degraded in photocatalytic processes initiated by sunlight [1-5]. Among many different heterogeneous photocatalysts examined, titania (TiO₂) is one of the commonly used in these processes. Unfortunately, in practice the main problem connected with the use of photocatalytic processes is their low quantum yield and the lack of photocatalytic activity at a wavelength (λ) < 400 nm [1-5].

The subject of TiO₂ activity is widely discussed in scientific journals [1-9]. One of the investigated methods involves extending useful radiation range to visible light. It can be achieved by TiO₂ structure modification by doping with non-metals (like nitrogen, sulfur, fluorine, boron, carbon), platinoids and lanthanides. However, such methods not always are effective and it might increase the cost of catalyst production [1, 8].

In order to sensitize of TiO₂ doping to visible light, Fe³⁺ ions can be used [5, 10-14]. These ions and their partly hydrolysis products may be adsorbed on TiO₂ surface [15, 16]. In our opinion, the addition of Fe³⁺ salts to the reaction mixture containing commercial photocatalyst TiO₂-P25 will be a simple and inexpensive method that increases

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yield of reaction. The addition of Fe^{3+} salts to TiO_2 increases the efficiency of anionic compounds degradation during UVA illumination [10-12, 15-18]. Such effect may be explained by various reasons. There is possible the intensification of sorption process of substrate [16, 17] or the photochemical synergy of TiO_2 and $\text{Fe}(\text{OH})^{2+}$ [11]. Additionally, Fe^{3+} ions can take part in light initiated red-ox processes or extending useful radiation range [13-15].

The goal of our study was to compare the results of photocatalytic degradation carried out in the presence of TiO_2 or Fe(III) salts as well in the presence of a mixture TiO_2 with Fe(III) salts.

Materials and methods

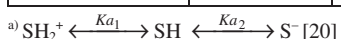
Reagents

As model reagents sulfanilamide and its derivatives were used. The characteristics of the investigated sulfonamides are presented in Table 1.

Table 1

Characteristics of the investigated sulfonamides

Sulfonamides	CAS number	Abbr. in text	pKa ₁ ^a	pKa ₂ ^a	Mobile phase
Sulfanilamide	63-74-1	SAD	2.4	10.1	AcCN (5%), buffer (K_2HPO_4) pH=8.2
Sulfacetamide	144-80-9	SCT	1.8	5.4	as above
Sulfathiazole	72-14-0	STZ	2.36	7.23	as above
Sulfisoxazole	127-69-5	SSZ	1.5	5.0	as above
Sulfamethoxazole	723-46-6	SMX	1.60	5.81	as above
Sulfadiazine	68-35-9	SDZ	2.00	6.48	as above
Sulfamerazine	127-79-7	SMR	2.1	6.9	as above
Sulfamethazine	57-68-1	SDM	2.3	7.4	AcCN (10%), buffer (K_2HPO_4) pH=8.2
Sulfapyridine	144-83-2	SPY	2.7	8.4	as above
Sulfadimethoxine	122-11-2	SDT	2.9	6.1	as above



All sulfonamides used throughout this study were of analytical grade and were manufactured by Sigma. Just before experiments, 0.1 mmol of each sulfonamide were added to 1 dm³ of distilled water and samples were intensively mixed. Titanium(IV) dioxide (TiO_2 -P25) obtained from Evonic Degussa GmbH and iron(III) chloride (FeCl_3) purchased from POCH were used as photocatalysts.

Irradiation

Before irradiation, a solid TiO_2 (500 mg dm⁻³) and/or 1 cm³ of FeCl_3 stock solution (0.1 mol dm⁻³) was added to 100 cm³ samples containing sulfonamides (Table 1). The pH of the irradiated samples was adjusted with concentrated HCl or NaOH solutions (< 1 cm³). Next, mixtures were homogenized in dark for 30 min by means of magnetic stirrers. In all experiments, open glass crystallizers (volume: 500 cm³, exposed surface: 102 cm²) containing the samples were irradiated by UVA lamps (Table 2). The intensity of radiation

(I) was measured by Quantum-photo radiometer Delta OHM DO9721. During the irradiation, mixtures were magnetically stirred and were in free contact with the air. The temperature of samples was $21 \pm 1^\circ\text{C}$.

Table 2

The characteristics of radiation sources

Radiation sources	Abbr., in text	Manufacturer	The I value at the selected λ [W m^{-2}]		
			< 315 nm ^a	315-400 nm	400-1050 nm
4 fluorescent lamps (Actinic BL L40W/10)	UVA lamps	Philips	< 0,02 ^a	13.6	6.0

^a) based on manufacturer's data

Analytical methodology

After the appropriate irradiation time the samples were centrifuged (30 min, 4000 RPM). Before and after irradiation, the concentration of sulfonamides in mixtures was determined using HPLC method (column Supelcosil Suplex pKB-100 LC-18, 5 mm, 250 mm x 4.6 mm, detector Waters TAD 486, $\lambda = 254$ nm, the characteristics of mobile phases are in Table 1).

Results and discussion

The assessment of photocatalytic degradation dynamics during UVA irradiation

Before the beginning of photocatalytic experiments it was found that in the observed time interval the sulfonamides concentration in samples practically did not decrease as a result of different physicochemical and biochemical processes *eg* hydrolysis, photolysis or biodegradation.

The dynamics of photocatalytic degradation of all investigated sulfonamides (0.1 mmol dm^{-3}) during UVA irradiation of samples in the presence of TiO₂ (0.5 g dm^{-3}) or/and FeCl₃ (1.0 mmol dm^{-3}) were also studied. The photocatalytic reactions carried out in the presence of FeCl₃ run only in narrow range of pH ~ 3 [11, 17, 18]. Therefore, if necessary, pH of samples was corrected to 3.00 ± 0.05 , the samples containing as catalyst TiO₂ only, were irradiated at natural pH and also at pH = 3.

Figure 1 shows the dynamics of this process during UVA irradiation of samples containing the investigated catalysts, using SAD as an example. The plot of function $\ln C_0/C_i = f(t)$ is shown in the upper right corner of Figure 1.

It was stated that during irradiation of samples with TiO₂/FeCl₃ the photocatalytic reaction had been inhibited at $C_i/C_0 < 0.15$. The similar effect was observed for all investigated sulfonamides. It was probably caused by the reduction of Fe³⁺ to Fe²⁺ [12, 13, 18, 19]. All experimental results and pH of irradiated samples are presented in Table 3. The photodegradation rate constant (k) was calculated based on the linear function $\ln(C/C_0) = f(t)$.

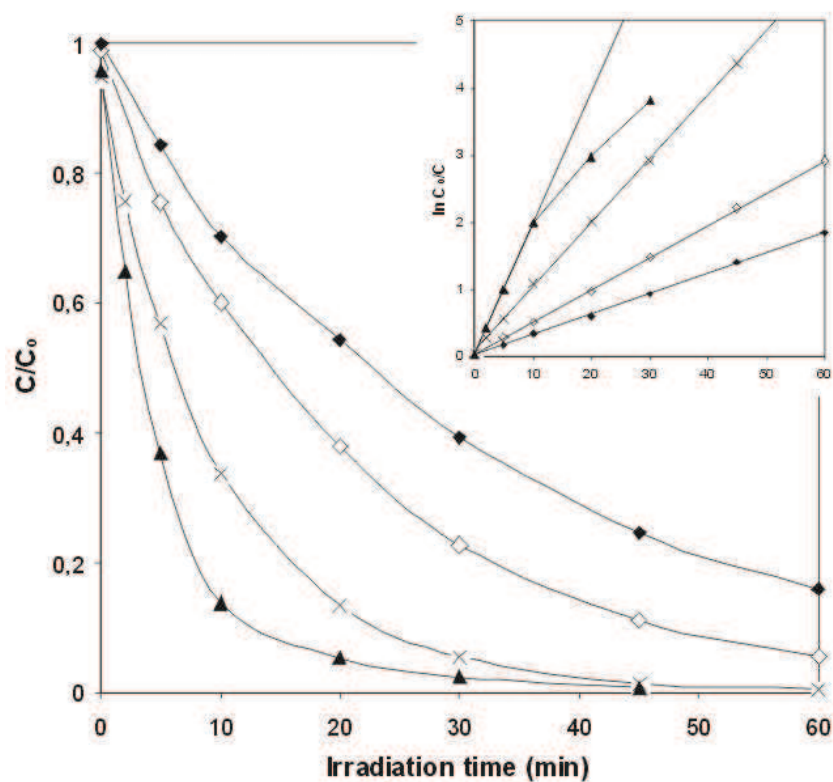


Fig. 1. Degradation of SAD ($C_0 = 0.1 \text{ mmol dm}^{-3}$) during UVa irradiation in the presence of: \diamond - TiO_2 (pH 6), \blacklozenge - TiO_2 (pH 3), \times - FeCl_3 (pH 3) and \blacktriangle - $\text{TiO}_2/\text{FeCl}_3$ (pH 3)

Table 3

The results of experiments

Sulfonamide	Removal ^a [%]	k [min^{-1}]			
	Without catalyst	TiO_2 (pH 4-8)	TiO_2 (pH-3)	FeCl_3 (pH-3)	$\text{TiO}_2/\text{FeCl}_3$ (pH-3)
SAD	3.0±1.2	0.048±0.000	0.031±0.000	0.095±0.002	0.197±0.004
SCT	0.0±3.2	0.044±0.001	0.028±0.001	0.074±0.004	0.159±0.008
STZ	0.1±4.5	0.048±0.002	0.051±0.001	0.095±0.002	0.228±0.018
SSZ	5.6±3.3	0.034±0.001	0.035±0.001	0.073±0.003	1.27±0.13
SMX	5.1±3.0	0.033±0.001	0.034±0.001	0.090±0.003	0.121±0.010
SDZ	0.0±1.8	0.032±0.001	0.019±0.001	0.038±0.001	0.146±0.011
SMR	9.5±3.8	0.039±0.001	0.036±0.001	0.068±0.000	0.188±0.009
SDM	3.6±1.5	0.055±0.003	0.052±0.002	0.086±0.002	0.217±0.010
SPY	4.8±1.5	0.050±0.003	0.036±0.002	0.069±0.002	0.141±0.020
SDT	2.4±1.0	0.036±0.001	0.030±0.001	0.062±0.003	0.150±0.013

^{a)} after 120 min of stirring

It was found that all investigated sulfonamides underwent photocatalytic degradation. The highest activity among the investigated catalysts had TiO₂/FeCl₃. Particularly high rate of degradation was observed for SSZ. Under the experimental conditions, just after 150 s of irradiation, about 98% of SSZ was decomposed (data not shown in the text). For comparison, in the same conditions (after 150 s of irradiation and the presence of TiO₂/FeCl₃) remaining sulfonamides were decomposed in the range from 26 (SMX) to 51% (STZ). It was stated that the above described degradation of SSZ in the presence of TiO₂/FeCl₃ was not caused by photolysis, biodegradation, hydrolysis and stable binding to the components of the catalytic system. A photoactive complex compound of SSZ with Fe also did not form. Unfortunately, we can not explain this anomaly.

The mechanism of photocatalytic process carried out in the presence of TiO₂/FeCl₃

Under the investigated conditions, there was no relationship between the rate of photocatalytic degradation of sulfonamides and their rate of acid hydrolysis, photolysis and the presence of chloride ions. Except SMX and SSZ, the k value for the reactions carried out in the presence of TiO₂/FeCl₃ was from 1.3 to 2.5 times higher than would result from the algebraic sum of k values for reactions carried out separately in the presence of TiO₂ (at pH 3) and FeCl₃ (Table 3). The similar effect was described by Mestankova et al [13, 20].

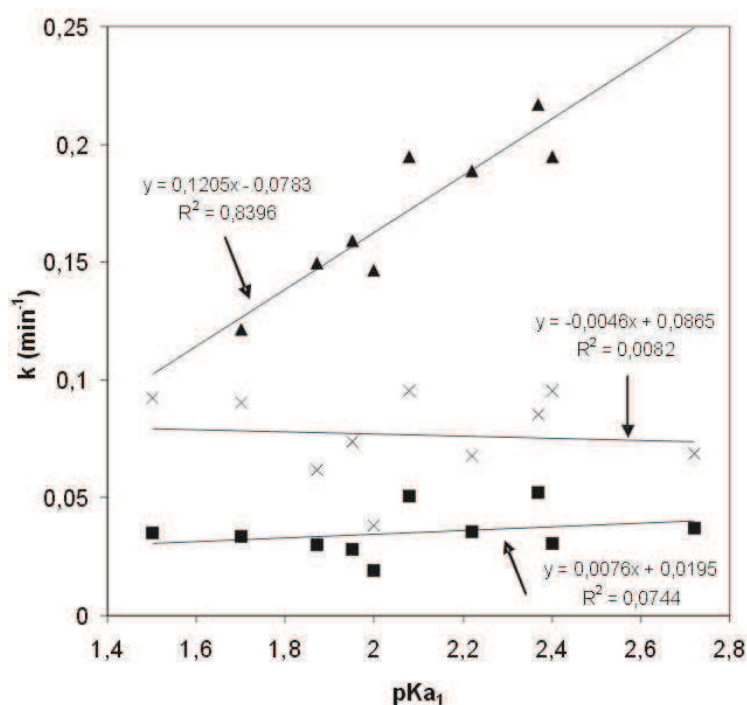


Fig. 2. Effect of the pKa of sulfonamides on the rate of photocatalytic degradation during UVA irradiation in the presence of ■ - TiO₂, × - FeCl₃ and ▲ - TiO₂/FeCl₃ (this figure does not show the results for the degradation of SSZ and SPY in the presence of TiO₂/FeCl₃)

In our opinion, it might be caused by the intensification of sulfonamide sorption on the TiO_2 surface after addition of Fe^{3+} salts to the sample. In darkness, the decrease of sulfonamides concentration was slightly higher in samples with FeCl_3 and $\text{TiO}_2/\text{FeCl}_3$ than in the presence of TiO_2 . According to Nahar et al [15], the hydrolysis products of Fe^{3+} ions are adsorbed onto TiO_2 surface. Thus, the compound can be formed as follows:



Both in the anatase as well as in rutile structure each titanium atom is surrounded by six oxygen atoms (negative charges). Therefore, it is possible to form a chemical bond between oxygen atom and the positively charged substrate. In solution at pH 3, sulfonamides occur mainly as neutral molecules (SH) and cations (SH_2^+). Figure 2 shows the relationships between the concentration of the cationic form of sulfonamide and the k value for reactions carried out in the presence of TiO_2 , FeCl_3 and $\text{TiO}_2/\text{FeCl}_3$, at pH 3.

It was found that in the case of processes carried out with $\text{TiO}_2/\text{FeCl}_3$ the concentration of SH_2^+ ions was directly proportional to the k value (with the exception of SSZ and SPY). There was no correlation in samples containing TiO_2 and FeCl_3 . Additionally, in most cases a decrease in the pH of samples containing only TiO_2 as catalyst caused a decrease in the photocatalytic reaction rate. These facts indicate that one of the factors affecting the rate of photocatalytic reaction is the simultaneous presence of Fe^{3+} ions and the cationic form of substrate. Thus, it is possible that the essential for the photocatalytic reaction rate in the presence of $\text{TiO}_2/\text{FeCl}_3$ can be the process shown in Figure 3.

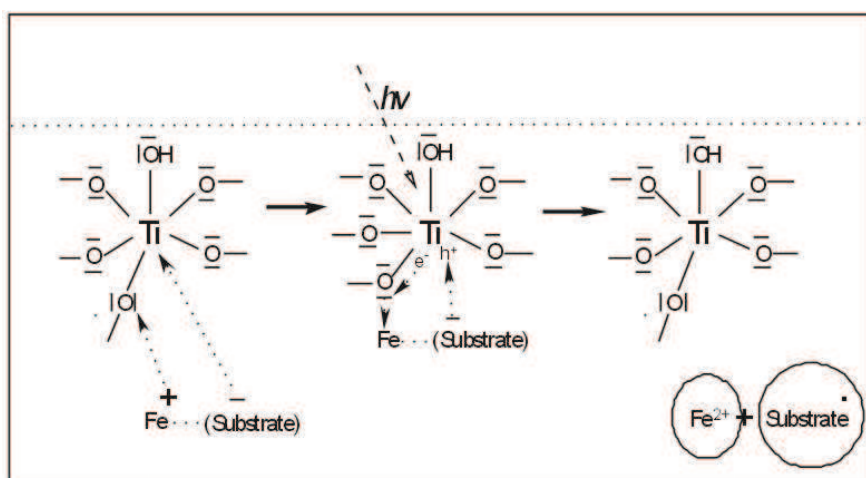


Fig. 3. The mechanism of photocatalytic process carried out in the presence of $\text{TiO}_2/\text{FeCl}_3$

Conclusions

The addition of FeCl_3 to the commercial catalyst TiO_2 -P25 significantly increases their photocatalytic activity for UVA irradiation. In the case of sulfonamides, an increase in this activity is directly proportional to the concentration of cationic form the substrate. Assuming the use of sunlight which about 5% of the energy corresponds to a light of

wavelength < 400 nm, the application of TiO₂/FeCl₃ mixture may be more reasonable than the use of TiO₂ doped with non-metals.

Acknowledgements

This work was supported by Medical University of Silesia in Katowice (Poland), contract No. KNW-1-056/P/1/0.

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ZASTOSOWANIE MIESZANINY $\text{TiO}_2/\text{FeCl}_3$ W TECHNOLOGII OCZYSZCZANIA ŚRODOWISKA

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Abstrakt: Jedną z metod zagospodarowania energii słonecznej jest jej wykorzystanie w technologiach oczyszczania środowiska. W inicjowanych światłem słonecznym procesach fotokatalitycznych mogą być skutecznie degradowane zanieczyszczenia, niezależnie od swojej toksyczności i odporności na biodegradację. Fotokatalizatorem w takich procesach najczęściej jest TiO_2 . Niestety problemem tych procesów jest ich niska wydajność kwantowa. Prostą i tanią metodą jej podwyższenia jest dodatek soli Fe(III) . Fakt ten potwierdzono w badaniach nad fotokatalityczną degradacją wielu substratów zróżnicowanych pod względem chemicznym. Celem naszej pracy było porównanie rezultatów degradacji fotokatalitycznej prowadzonej w obecności TiO_2 , soli Fe(III) i w obecności mieszaniny $\text{TiO}_2/\text{sól Fe(III)}$ oraz ustalenie mechanizmu procesu fotokatalitycznego prowadzonego w obecności $\text{TiO}_2/\text{sól Fe(III)}$. Stwierdzono, że na przebieg reakcji i jej efektywność największy wpływ ma zdolność organicznego substratu do tworzenia związku koordynacyjnego z Fe(III) i jego sorpcji na powierzchni TiO_2 . Na podstawie danych literaturowych i badań własnych ustalono mechanizm początkowego etapu tej reakcji.

Słowa kluczowe: fotokataliza, TiO_2 , technologie oczyszczania środowiska