

Advanced photooxidation of surfactants in wastewater

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Introduction

Surfactants are commonly used in the households as detergents, or care products; their specific features make them become useful also in various industries: in pesticides, pharmaceuticals, textile and others. All of these have resulted in their common presence in the wastewater. According to various studies and different tests, it has been confirmed that non-ionic surfactants (at lethal concentrations: 0.0025 to 300 mg/dm³) are more toxic than others (anionic: 0.3 to 200 mg/dm³) [1]. Some of surfactants, however, can be successfully used for soil-washing or soil-flushing pump-and-treat technologies in the surfactant-enhanced remediation, where TX enhances the solubilization of hydrophobic contaminants through micellar solubilization in soil [2]. For the studies Triton X-100 (TX) as one of the representatives of widely industrial scale used non-ionic surfactants of alkylphenyl polyoxyethylene type was chosen. Alkylphenyl compounds are suspected to be the endocrine disrupters in aquatic organisms [3].

There are several conventional methods used for the removal of surfactants from wastewater, but they are not satisfactory enough for the hardly biodegradable pollutants. It has also been observed that the treatment of surfactants usually requires periods of long acclimation and it typically results in a quite incomplete degradation [1]. Advanced Oxidation Processes (AOP) [4,5], promising techniques because of their capability to mineralize completely recalcitrant water, air or soil contaminants into CO₂, H₂O and small amount of simple inorganic compounds, have received much attention recently. Heterogeneous photocatalysis, being one of AOP, is an efficient and economic method that can be used in the decomposition of hazardous pollutants, because it is able to mineralize almost all organic compounds only by means of atmospheric oxygen at the ambient conditions of temperature and pressure [6]. It was observed [7÷8] that the heterogeneous photocatalysis can be applied for the surfactants removal from the wastewater successfully.

TiO₂, among other widely tested semiconductors, seems to be the most suitable for both fundamental research and practical applications, as it is chemically and biologically inert, photostable, non-toxic, affordable, cheap and has high oxidative power [4]. The detailed mechanism of photocatalysis over TiO₂ surface is well known and involves the generation of high energy electron-hole pairs and their reactions with organic molecules adsorbed on the surface or oxygen yielding the formation of •OH radicals. •OH radicals are also formed via the reaction of the photo-generated holes with hydroxyl ions and water molecules adsorbed on the surface of TiO₂ [2, 9]. The radicals react non-selectively and quickly with the organic molecules leading to their mineralization.

In the studies concerning the photocatalytic removal of contaminants from water there are often applied suspended TiO₂ photocatalysts. However, the recycling and recovery of nanoparticles are quite troublesome and uneconomical, which becomes the main

disadvantage of using the suspended systems. Therefore, many efforts are being made to compose the immobilized TiO₂ e.g. over Al₂O₃ foams or TiO₂ hollow spheres and construct reactors with an immobilized active phase [10÷11].

It has been observed that due to the pre-adsorption of reactants on the TiO₂ surface during a photocatalytic reaction, the process of electron transfer is more efficient [12]. The supportive porous catalysts with enlarged surface area have been chosen, since, apart from easier disposal, they ensure a high density of active centres for photocatalytic reactions and an enhanced light harvesting because of light reflection and scattering by the pores [6]. Therefore, Al₂O₃, the support widely used and tested in the catalysis, has been adopted.

Transition metal ion doping has been suggested to increase the response to solar spectrum over 380 nm, and to develop the photocatalytic activity by introducing the defects into TiO₂ lattice and reducing e⁻/h⁺ pair recombination. However, the loss of photocatalytic activity can be observed, which is suggested to be caused either by an increase of the photogenerated e⁻/h⁺ recombination rate [11÷12]. Therefore, it can be implied that the results of doping depend on the type of dopant, its amount and the treated compound. What is more, the photocatalytic processes and their efficiency can also be enhanced by means of adding the auxiliary electron acceptors, such as H₂O₂ and O₃ [9].

In these studies the photocatalytic oxidation of model wastewater was investigated. TX and the mixture of surfactants, as commercially available wash-up liquid (containing 5-15% anionic, <5% non-ionic and <5% amphoteric surfactants and many additives), were used. The main aim of these studies was the determination of the catalytic activity of Cu or Zn modified TiO₂/Al₂O₃ photocatalysts in the removal of the pollutants from wastewater. The effectiveness was measured in the following configurations: TiO₂/UV/O₂ and TiO₂/UV/O₂/H₂O₂. The aim of the research was also to investigate the role of catalysts preparation method: Classical Impregnation Method (CIM) [13] and Double Impregnation Method (DIM) [14] on the photocatalytic activity of studied catalysts. In DIM there are two stages: the first one is the impregnation of inorganic support with complexing agent, namely disodium salt of the ethylenediaminetetraacetic acid (EDTA) solution and then, after drying, the impregnation with the solution containing metal ions. Thus, the inorganic support is therefore preliminarily modified by EDTA. The application of EDTA permits to prepare well dispersed metal catalysts with a relatively high metal loading [15]. As it was observed earlier [16] from the FT-IR/PAS spectra of EDTA adsorbed on alumina and titania-alumina under the same conditions, the p*H*_{pzc} of the TiO₂/Al₂O₃ support (3.57) has a strong influence on the adsorptive properties and surface species formed. The adsorption of disodium salt of EDTA (p*H*_{pzc}=4.71), although impeded, because -OH and -O⁻ groups dominate on the support surface (p*H*>p*H*_{pzc}), however, occurs. The adsorption

of disodium salt of EDTA can be described by different types of interactions (via hydrogen bonds or via electrostatic interactions) depending on the pH of impregnating solution that has an influence on the hydroxyl group distribution on the support surface [17].

Experimental

Preparation of the photocatalysts

All the chemicals were analytical grade and used without further purification. The modified TiO_2 catalysts supported by $\gamma\text{-Al}_2\text{O}_3$ (INS Pulawy, Poland) were chosen for the studies. The support, being in a form of beads with the diameter ca. 3 mm and BET surface area of $150 \text{ m}^2/\text{g}$, was treated in the proper solution of TiCl_4 (Sigma-Aldrich) dissolved in the aqueous solution of concentrated hydrochloric acid for 10 minutes at the room temperature. After the impregnation of the support, the sample was dried at 388K for 2 hours and calcinated at 873K for 3 hours. The application of TiCl_4 is connected with the presence of the Cl^- on the surface of the catalysts, though the catalysts were washed with the water until the reaction of Cl^- with AgNO_3 was not observed.

CIM was carried out as follows: the obtained $\text{TiO}_2/\text{Al}_2\text{O}_3$ support was impregnated with 5 wt.% aqueous solution of nitrates: $\text{Zn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ (POCh, Gliwice, Poland) (samples CIM-Zn and CIM-Cu respectively). The amount of salt was calculated on the basis of the pure metal. The process of impregnation lasted 9 minutes. For DIM, the titania-alumina support was initially impregnated with 0.1M aqueous solution of EDTA (POCh Gliwice, Poland) at 343K for 0.5 h. In the second step, the support with the adsorbed EDTA was impregnated with 5 wt. % solution of Cu or Zn for 9 minutes (samples DIM-Cu and DIM-Zn respectively). After they were dry, all the precursors under study were calcinated at 873K for 3 hours.

Photoreactor and photocatalytic studies

The experiments concerning the photocatalytic degradation of organics in the wastewater were conducted in a band reactor of our own construction [18]. The reactor (Fig. 1.) has a form of two tubes placed above the UV lamp (254 nm, 50 Hz) with the light intensity of $1.56 \cdot 2.09 \text{ mW}/\text{cm}^2$, equipped with the Radiometer VLX254 (Vilber Lourmat, 254 nm) that was used to measure the emitted by the applied lamp UV. The employed light source emitted light of more than 95% within the UV light wavelength. The bands, being the main mixing agents, ensure the counter-current contact of the reagents. A mixture of oxygen ($3 \text{ dm}^3/\text{h}$) and nitrogen ($37 \text{ dm}^3/\text{h}$) was introduced into the reactor. Oxygen plays a key role in the TiO_2 photocatalysis, as it is found to be the rate-limiting step [9].

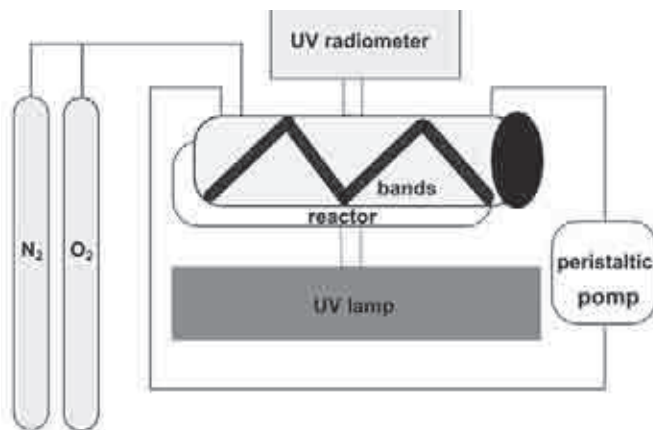


Fig. 1. The scheme of the band reactor

Triton X-100 (POCh Gliwice, Poland) and a commercially available wash-up liquid ("Ludwik", Inco Veritas, Poland) were chosen to be

the model contaminants. The solutions were prepared so as to have the COD value of ca. $3000 \text{ mg O}_2/\text{dm}^3$, which is the concentration of $22.6 \cdot 10^{-4} \text{ mol}/\text{dm}^3$ for TX. The wash-up liquid contained: 5-15% anionic, <5% non-ionic and <5% amphoteric surfactants and many others (e.g. oxyethylene fatty alcohols, amine oxides, EDTA, acetic acid, polyethylene glycol, 2-bromo-2-nitropropane-1,3-diol and inorganic additions). A sample of wastewater was pumped in the reactor with the volumetric flow of $1.3 \text{ dm}^3/\text{h}$ and 20g of the catalyst (e.g. ca. $8 \text{ g}/\text{dm}^3$) were placed inside. Moreover, H_2O_2 (0.01 vol.%) was used as an additional oxidizing agent. After 115 minutes, e.g. one complete run through the reactor, the sample was taken out and analysed for COD (Chemical Oxygen Demand) by means of a bichromate method [19].

Catalysts examination

The total surface areas of the catalysts were determined on the basis of nitrogen adsorption at liquid nitrogen temperature using the BET method in a volumetric apparatus ensuring a vacuum of at least $2 \cdot 10^{-6} \text{ kPa}$ (AUTOSORB-1CMS, Quantachrome Instruments, USA). Due to the X-ray diffraction (XRD), the phase composition diagram of the catalysts was determined (HZG-4, Carl Zeiss Jena). While Raman spectroscopy allowed to show the crystallographic orientation of a sample (inVia Reflex, Renishaw, UK), the UV-Vis spectroscopy was applied to characterize the absorbance spectra of the photocatalysts. The sample morphology was observed in the scanning electron microscope (Quanta 3D FEG), equipped with an energy dispersive X-ray detector (EDX), which was used for the determination of the surface elemental composition. The physicochemical properties of the studied catalysts are presented in Table I. The photocatalytic activity of the catalysts was estimated for TX and the commercially available wash-up liquid during the photooxidation in the band reactor.

Results and Discussion

TiO_2 (AEROXIDE® TiO_2 P25, Evonik Degussa GmbH formerly Degussa P25), being widely tested [20] and commercially available, is used as a standard catalyst in various studies, but the application of powder photocatalysts creates great technological problems in recycling, management and disposal. The powdered catalysts are inconvenient to study in the band reactor, as it is a flow type device. In order to avoid these problems, the supported catalysts were used. The results obtained using suspended and immersed supported TiO_2 photocatalysts are though very difficult to compare directly.

Photocatalysts characterization results

Physicochemical properties

All studied catalysts preparation methods enables to introduce a similar amount of dopant – 2.5-2.8wt.% independently from the type of impregnation (Tab. I). Double Impregnation Method used for the preparation of modified $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts did not result in the enlarged dopant content in comparison to CIM. But the distribution of dopant is slightly different in CIM and DIM produced material. In case of using more complicated Double Impregnation Method, however it does not produce catalysts with the better ability for the removal of surfactants from wastewater that will be described further.

From the adsorption-desorption isotherms with the H_2 -type hysteresis loop of studied catalysts (not shown) it was conformed that studied photocatalysts are mesoporous materials. Observed increase in the adsorption branch of the isotherms at a high relative pressure ($P/P_0 > 0.5$) is attributed to the uniform pore size distribution [21]. The mean pore diameter is similar for all studied

photocatalysts (10-11 nm), is in the range typical for mesopores. A slight increase of their diameter in case of CIM produced photocatalysts may indicate that EDTA used during DIM modifies the adsorptive properties of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ and Cu or Zn may be more dispersed.

Table 1

Physicochemical properties of studied photocatalysts

Catalyst	Ti content (wt.%)	Dopant content (wt.%)	Total surface area S_{BET} (m ² /g)	Mean pore size (nm)	Total pore volume (cm ³ /g)
Al_2O_3	-	-	150.66	8.43	0.336
$\text{TiO}_2/\text{Al}_2\text{O}_3$	2.69	-	149.80	9.62	0.377
CIM-Cu	2.62	3.13	128.47	11.07	0.367
DIM-Cu	2.70	3.01	129.34	10.88	0.369
CIM-Zn	2.34	2.75	124.53	11.15	0.360
DIM-Zn	2.83	2.71	130.31	10.07	0.337

SEM and SEM-EDX results

The surface morphology was determined using SEM and SEM-EDX. The roughness of the surface of $\text{TiO}_2/\text{Al}_2\text{O}_3$ beads (Fig. 2a,b) is large enough to ensure the better contact of the pollutants and the photocatalysts surface. The results obtained for modifications by Zn and Cu are similar, though there were presented Zn modified photocatalysts.

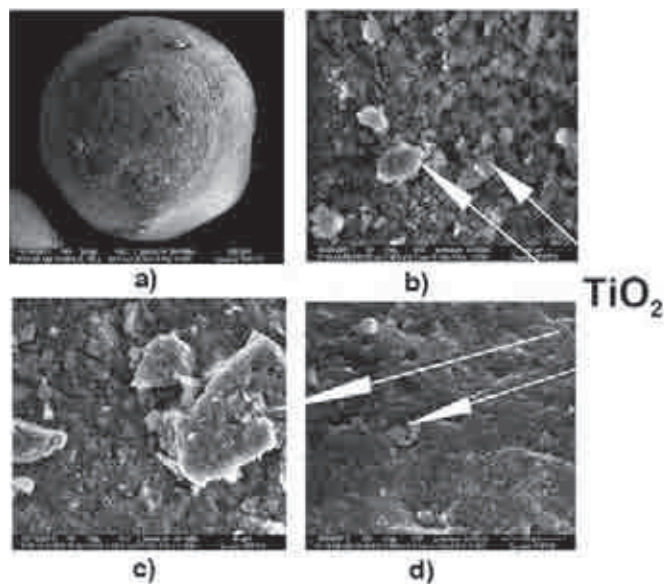


Fig. 2. SEM images of studied photocatalysts: a) bead of $\text{TiO}_2/\text{Al}_2\text{O}_3$, b) surface of $\text{TiO}_2/\text{Al}_2\text{O}_3$, c) CIM-Zn surface, d) DIM-Zn surface. The arrows indicate TiO_2

In the SEM micrographs presented in Figures 2b-d are observed bright areas. The surface composition of these points in all studied photocatalysts indicates that some larger crystals have been created with at least 43wt.% Ti content, in comparison to dark areas constituted of 2-7wt.% Ti (Table 2). TiO_2 tends to agglomerate over the surface of Al_2O_3 beads. SEM micrographs reveal that the TiO_2 crystals are spherical or oval in shape and the photocatalysts contained several

voids and pores. The dark areas in the SEM micrographs are connected with the presence of Al_2O_3 and constituted of Al, ca. 45-55wt.% and O- 35-40wt.%.

Table 2

Surface composition according to SEM-EDX studies

catalysts	element	Surface composition according to SEM-EDX studies (wt.%)	
		bright region	dark region
$\text{TiO}_2/\text{Al}_2\text{O}_3$	O	27.83	39.06
	Al	9.84	55.79
	Ti	59.92	2.33
CIM-Zn	O	22.92	36.05
	Al	12.28	52.10
	Ti	61.12	4.51
	Zn	1.37	2.90
DIM-Zn	O	30.49	38.72
	Al	16.63	52.59
	Ti	49.39	4.15
	Zn	1.57	2.53

The modification of previously prepared $\text{TiO}_2/\text{Al}_2\text{O}_3$ has resulted in uniform distribution of dopants. They are present in the same areas of the surface of all studied photocatalysts. It was observed that their amount in bright and dark areas is remarkably different. They are observed mainly in dark areas with the concentration even twofold increased in comparison to the content in bright areas, what may suggest that their adsorption occurred easier on Al_2O_3 than TiO_2 .

The application of DIM did change the surface structure that was the mostly observed for Zn- $\text{TiO}_2/\text{Al}_2\text{O}_3$. One of the factors that is visible in SEM image (Fig. 2c,d) is lower roughness. Another factor is that the amount of Ti on the surface of Zn modified photocatalyst changed rapidly – from initial 59wt.% to 49wt.%. It results probably from the creation of some clusters and Ti is incorporated into the lower layers of the surface. Zn and Cu are still present over Al_2O_3 surface. TiO_2 larger crystals are also observed. The comparison of the surface composition of Zn- $\text{TiO}_2/\text{Al}_2\text{O}_3$ suggests that more efficient in photooxidation should be CIM prepared photocatalyst – it posses higher Ti and Zn content; that assumption was confirmed during catalytic tests.

XRD results

The greatest signal of $2\theta=66.89$ in the XRD spectra (Fig. 3) is obtained from the Al_2O_3 support (JCPD 01-1303). All XRD spectra of studied photocatalysts looks similarly, which may indicate the metal dispersion, or hiding the signal by the support. In the XRD spectra are present the peaks at 2θ of about 25.2, 37.9, 48.3, 53.8, 62.7 and 68.9 that according to JCPD 21-1272 are indicating for the presence of anatase structure (planes 1 0 1, 1 0 3, 2 0 0, 1 0 5, 2 1 3 and 1 1 6 respectively).

The analysis of the XRD spectra revealed that according to the JCPD base, there are observed some peaks indicating that Cu is present as CuO, Zn as ZnO. Some mixed alumina-titania forms are also observed.

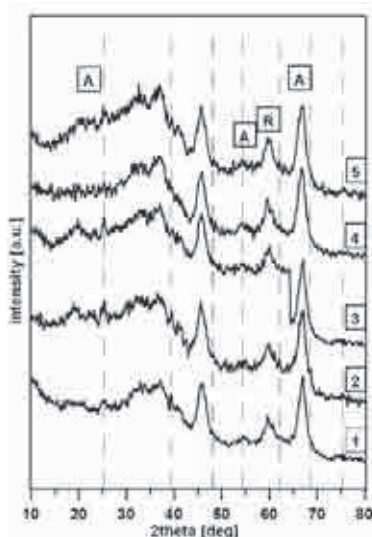


Fig. 3. XRD patterns of the studied support and catalysts: A, broken line – anatase, R- rutile, 1 – $\text{TiO}_2/\text{Al}_2\text{O}_3$, 2 – CIM-Cu, 3 – DIM-Cu, 4-CIM-Zn, 5 – DIM-Zn

Raman spectroscopy results

All studied catalysts were characterised by Raman spectroscopy and the spectra are shown in Figure 4. All spectra look similarly. Raman modes can be assigned to the Raman spectra of the anatase single crystal (main modes shows in Figure 4 by broken lines): 639 cm^{-1} (E_g), 519 cm^{-1} (B_{1g}), 513 cm^{-1} (A_{1g}), 399 cm^{-1} (B_{1g}), 197 cm^{-1} (E_g) and $\sim 144\text{ cm}^{-1}$ (E_g). The 449 cm^{-1} A_{1g} and 610 cm^{-1} E_g Raman modes for TiO_2 decreased during further impregnation and calcination. A slight changes in the peak position, linewidth and shape of the E_g Raman mode in anatase TiO_2 (e.g. towards 150 cm^{-1} , 192 cm^{-1} , 651 cm^{-1}) may have resulted from phonon confinement, strain, non-homogeneity of the size distribution, defects or nonstoichiometry [22].

The characteristic modes for CuO or ZnO (388 cm^{-1} , 430 cm^{-1} , 461 cm^{-1} , 498 cm^{-1}) are not clearly seen in the picture. According to the studies and strong signal obtained from anatase in the Raman spectra of all studied catalysts (Fig. 4) indicates that Zn or Cu are incorporated into the structure of some alumina or alumina-titania forms. They are probably hidden and superimposed in the spectra though the deconvolution of the peaks was necessary.

The curve-fitting analysis was performed using Peak Fit programme (Version 4.12). In the Raman spectra of studied photocatalysts the deconvolution revealed the presence of hidden and superimposed peaks: CIM-Zn and CIM-Cu at 449 cm^{-1} , 597 cm^{-1} , 680 cm^{-1} , in DIM produced photocatalysts at 196 cm^{-1} and 386 cm^{-1} .

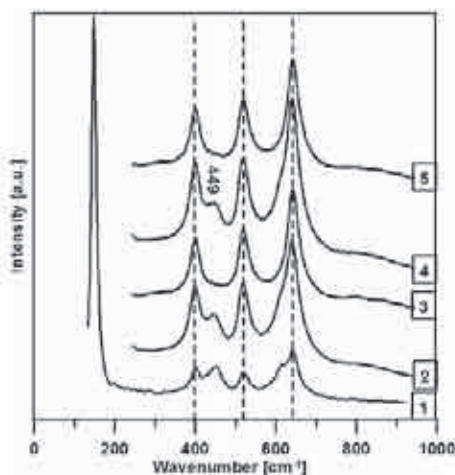


Fig. 4. Raman spectra of studied photocatalysts: broken line – anatase characteristic modes, 1 – $\text{TiO}_2/\text{Al}_2\text{O}_3$, 2 – CIM-Cu, 3 – DIM-Cu, 4-CIM-Zn, 5 – DIM-Zn

The Raman studies results have confirmed the data obtained by SEM/EDX. The surface of all photocatalysts looks similarly. There are observed some agglomerates of TiO_2 , dopants are introduced and adsorbed over Al_2O_3 creating some mixed alumina-dopant oxides.

UV-visible spectroscopy results

Figure 5 presents UV-Vis absorbance of studied catalysts. It can be clearly observed that the absorption band of $\text{TiO}_2/\text{Al}_2\text{O}_3$ and $\text{Zn-TiO}_2/\text{Al}_2\text{O}_3$ is mainly located in the UV light region with wavelength of 200–400 nm. The modification of $\text{TiO}_2/\text{Al}_2\text{O}_3$ with Zn by DIM decreased the intensity of the maximum absorption in the UV region.

The increased response to the visible light region for studied catalysts was obtained for Cu modified $\text{TiO}_2/\text{Al}_2\text{O}_3$. It can be seen that the UV-Vis absorbance for Cu modified catalysts was shifted to longer wavelengths (the red shift) compared with unmodified one. The photocatalyst are activated by the irradiation with light at 420nm and above 650nm.

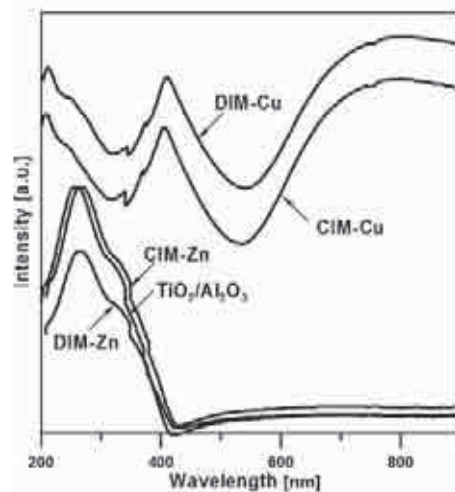


Fig. 5. UV-Vis spectra of studied catalysts

However, the visible light response of the Cu modified photocatalysts did not pose any significant effect on their photocatalytic activity during the removal of studied because the employed light source emitted light of more than 95% within the UV light wavelength.

Catalytic activity

The activity of the photocatalysts has been tested in the removal of TX and wash-up liquid from water. c/c_0 has been used to calculate the conversion, where c_0 was the initial COD of the surfactant, and c was COD of the compounds under study that did not react at a steady state.

All studied catalysts enabled a significant removal of COD of waste water containing TX and wash-up liquid at least by 80% (Fig. 6 a,b). The photooxidation of TX over all examined catalysts was efficient – it was observed at least 90% COD reduction. The best results were obtained using $\text{TiO}_2/\text{Al}_2\text{O}_3$. Modification of that photocatalyst hindered photooxidation of studied pollutant – the addition of Zn affected TX removal slightly and the results obtained over CIM-Zn were almost similar to those observed over $\text{TiO}_2/\text{Al}_2\text{O}_3$. This may suggest that the photoremoval of TX proceeds mainly over TiO_2 . $\text{Cu-TiO}_2/\text{Al}_2\text{O}_3$ showed the same activity independently from its preparation method. Its activity, however, is strongly connected with the amount of a dopant by which Cu effectively inhibits the recombination of photoinduced charge carriers. The observed decrease in the removal of TX can be attributed to the excess of Cu when compared with TiO_2 . It has been stated [23] that too high Cu values in the photocatalysts result in the more excessive oxygen vacancies, and thus Cu species become the recombination centers of photoinduced e^-/h^+ . Cu covering the TiO_2 surface can be also noticed.

The synergistic effect of ZnO and TiO₂ semiconductors has not been observed during the removal of COD of waste water containing TX. It can be, however, noticed during the removal of more complicated compositions and compounds e.g. wash-up liquid (Fig. 6b). CIM-Zn caused better removal of wash-up liquid than the same photocatalyst prepared by DIM what may suggest that different sites participate in the process or may indicate that TiO₂ has oxidized the non-ionic surfactants and the dopants have facilitated photooxidation of the other wash-up liquid components, even inorganic. That may be in agreement with the literature data [24]. It was observed only a slightly enhanced photoremoval of methyl orange over ZnO-TiO₂. However, about 5-8% of the deepened photooxidation using modified photocatalysts has not been economically justified.

The similar results of the photooxidation over Cu-TiO₂/Al₂O₃ prepared both by CIM and by DIM, although generally worse than over TiO₂/Al₂O₃, indicate that, in case of this photocatalyst and UV irradiation, the type of preparation method used is insignificant. The obtained data, however, do not exclude its higher activity in Vis.

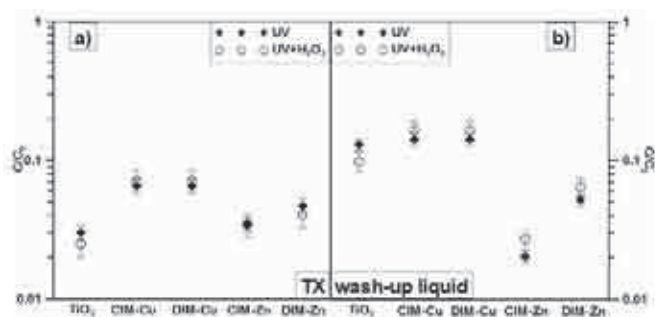


Fig. 6. The effect of H₂O₂ addition during pollutants removal from wastewater using modified TiO₂/Al₂O₃ catalysts: UV – UV irradiation, UV+H₂O₂ – H₂O₂ addition during UV irradiation a) TX, b) wash-up liquid

The effect of photocatalytic oxidation can be improved using the addition of external oxidants, e.g. H₂O₂, O₃ but the effect is not obvious and depends on many factors [9]. H₂O₂ is one of the cheapest oxidants with high oxidative power, soluble in water and thermally stable. It is easy to use, the only final products formed during oxidation are O₂ and H₂O. In the presence of UV irradiation at 254 nm, H₂O₂ photolysis into 2 ·OH has been observed because of H₂O₂ weak absorption of UV. However, the addition of too high H₂O₂ concentration hinders the process, since the excess of H₂O₂ captures the radicals and created HO₂· possesses lower oxidative power. It may be stated that irradiation favours the radical reactions but H₂O₂ initiates the chain reactions that run after the irradiation is finished [25].

The studied effect of H₂O₂ addition has varied depending on the type of the pollutant used, or the photocatalyst (Fig. 6a,b). Generally, the positive effect of H₂O₂ addition on the COD during the photooxidation of TX in wastewater was not observed. It did not cause any significant changes in the water quality, however some observations may be made – insignificant increase of the efficiency of photooxidation was determined using TiO₂/Al₂O₃ or DIM-Zn; insignificant decrease was observed over Cu-TiO₂/Al₂O₃.

In case of wash-up liquid removal, H₂O₂ also slightly decreased efficiency of the COD reduction over all modified photocatalysts; a small increase was observed only over TiO₂/Al₂O₃. Not observed visible effect of H₂O₂ may be attributed to the fact that H₂O₂ caused the decomposition of more complex pollutants or the matrix elements that are not easy oxidized by dichromate.

As the removal of TX and wash-up liquid was studied in prolonged time, some significant changes have been observed mainly during the first two hours of treatment (Fig. 7 a,b). The results obtained over

all photocatalysts have been similar. The desorption of impurities (previously adsorbed surfactant) from the catalysts surface may slightly affect the effectiveness of the studied reaction – after four or six hours its effectiveness has decreased a bit. All the effects indicated however that the changes of the concentration in timespan only in the range of about 5-10% caused that it is economically unjustified to conduct the treatment for more than 2 hours.

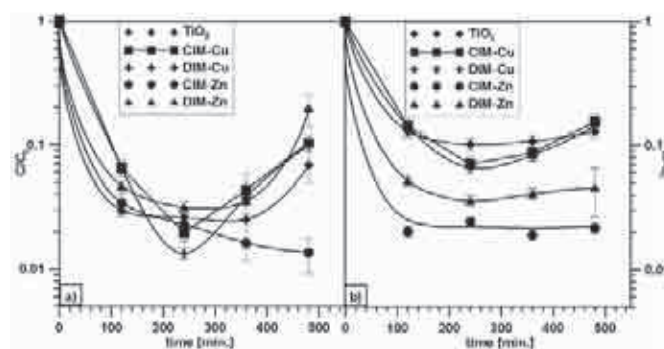


Fig. 7. Removal as a function of time a) TX, b) wash-up liquid

The reaction rates expressed as $dc/dt \cdot m_{cat}$, where c is concentration, t time and m_{cat} catalyst's mass, were the highest during the first two hours of the treatment and then they decreased from value of $1.15 \cdot 10^{-6}$ mol/g_{cat}·h (wash-up liquid removal over CIM-Zn after 2 hrs. treatment) to $9.65 \cdot 10^{-7}$ mol/g_{cat}·h (TX removal over TiO₂/Al₂O₃ after 8 hrs. treatment). The reaction rates decrease can be attributed to the strong adsorption of organics [9]. Moreover, the UV light intensity in the studied range (1.55-2.01 mW/cm²) has enhanced the photooxidation at 1.6 to 1.8 mW/cm² (not shown). The decrease of light intensity below 1.6 mW/cm² may also contribute to the loss of the activity in the COD removal after 6 or 8 hours of treatment (especially for TiO₂/Al₂O₃).

The observed decrease of the photocatalytic activity using the transition metal doped TiO₂ may be attributed to the increase of the photogenerated e⁻/h⁺ recombination rate [12]. Therefore, it can be implied that the results of doping catalysts depend on the type of a dopant, its amount and the treated compound.

Conclusions

- According to the obtained results it may be concluded that:
- for the removal from water of non-ionic surfactants of the alkylphenyl polyoxyethylene type, e.g. Triton X-100, TiO₂/Al₂O₃ as the photocatalyst can be applied successfully
 - TiO₂ tends to agglomerate on the surface of Al₂O₃ beads; the modification of the photocatalyst by Zn or Cu is connected with the adsorption of dopants over Al₂O₃
 - more complicated Double Impregnation Method turned to be economically and environmentally useless to obtain highly efficient photocatalysts Cu-TiO₂/Al₂O₃ and Zn-TiO₂/Al₂O₃
 - the effect of the treatment with UV irradiation over Cu modified TiO₂/Al₂O₃ is independent from the catalysts impregnation method
 - the addition of H₂O₂ does not cause any significant changes in COD of wastewater during treatment using studied TiO₂/Al₂O₃ catalysts
 - it is economically unjustified to conduct the treatment for more than 2 hours
 - the most time stable activity showed CIM-Zn.

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Translation into English by the Author

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International Conference on Advanced Complex Inorganic Nanomaterials 15 – 19 July 2013 Namur, Belgium, Europe

Following the great success of ACIN2011 and spurred on by the enthusiasm of the participants at ACIN2011, the organising committee would like to extend a cordial invitation to all researchers with an interest in advanced complex inorganic nanomaterials, to participate in the second International Conference on Advanced Complex Inorganic Nanomaterials (ACIN 2013) that will be held in Belgium from 15th to 19th July 2013.

ACIN 2013 is a four day scientific meeting jointly organised by the University of Namur (FUNDP) and the Université Catholique de Louvain (UCL).

The aim of this meeting is to offer an update of recent innovations in both fundamental and applied aspects and to highlight the latest advances and progress in the field of inorganic nanomaterials (inorganics, ceramics, hybrids and bio-inspired materials). We encourage researchers to submit an abstract of their most recent work related to all fields of Inorganic Nanomaterials such as:

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Nanomaterials, functional porous materials, coordination networks, bio-inspired nanomaterials, hybrid nanomaterials and living materials: Nanostructures, nanoparticles, nanotubes, ceramics, membranes, films, self-assembly, supramolecular systems, co-ordination polymers, zeolites, MOFs, mesoporous materials, hierarchically structured materials, carbons, natural materials, bioinspired and biomimetic materials, biomineralisation and biotemplating, bio-integrated materials, biocomposites, organometallics, green materials for construction, inorganic switches etc.

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