Surfactants removal from water and wastewater using Co modified TiO$_2$/Al$_2$O$_3$ photocatalysts[*]

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The photocatalytic oxidation of Triton X-100, its oxidation products: polyethylene glycol, phenol and also commercially available wash-up liquid in water in the band reactor of our construction with supported TiO$_2$ catalysts was studied. As a photocatalyst Co-TiO$_2$/Al$_2$O$_3$ was used. The main aim of these studies was the determination of catalytic activity of Co-TiO$_2$/Al$_2$O$_3$ in pollutants removal from water and the effect of O$_2$, H$_2$O$_2$ or UV addition on the photooxidation. It was found that the H$_2$O$_2$ addition has a detrimental influence on aerated wastewater containing surfactants, and UV has an increasing effect on process. 2 hours treatment of water is enough to obtain a significant COD reduction of all studied pollutants.

1. INTRODUCTION

Commonly used in production and households surfactants are introduced into water as pollutants. Beside surfactants bath composition contains a lot of auxiliaries having different effect on environment. Most detergents composition is non toxic. Beside surfactants the most toxic are anionic and non-ionic. According to various studies and different tests used it was confirmed that non-ionic surfactants (at lethal concentrations: 0.0025 to 300 mg/dm^3) are more toxic

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than others (anionic: 0.3 to 200 mg/dm^3). It was also observed that surfactants' treatment usually requires long acclimation periods and typically results in rather incomplete degradation [1].

Traditional oxygen processes in biological treatment are not enough sufficient in the removal of industrial wastewater' pollutants because chemicals present in wastes are toxic for activated sludge and biological membrane of bed. Biological methods are useful only for per-treatment of some types of wastewater, because beyond non-biodegradable compounds they consist of the substances yielding to enzymatic decomposition. These processes, however, are long-lasting and cause the BOD reduction but do not change the other water factors e.g. COD, TOC [2].

The solution for water remediation could be a photocatalysis with semiconductors – one of Advanced Oxidation Processes. It does not require any special conditions for the reaction: only air and UV rays presence and it enables the total destruction of pollutants into CO_2 and water or their transformation into less toxic products [2-7]. For the removal of surfactants heterogeneous photocatalysis can be successfully applied [8, 9].

Many factors exert the influence on photodegradation: type of semiconductor, its surface, light intensity, solvent, temperature, pH and substances present in solution. Catalysis is applied into the decomposition of organic compounds containing halogens, nitrogen and sulfur e.g. polychlorinated biphenyls, pesticides, dioxins, alcohols, aldehydes, ketones, carboxylic acids, ethers, amines, thioethers, merkaptans [10-11].

As the photocatalyst of mineralization of all organics TiO_2 is chosen, but typically used in form of powder causes a lot of problems with separation after the process completed. In all photocatalytic processes are used two main types of reactors:

- with catalyst immobilized on stationary elements: e.g. nylon fiber net or reactor walls
- with catalyst dispersed in reactor [12]. The first manner is connected with the replacement of the parts of apparatus when the catalyst is changed what is not only time-consuming but also expensive. Therefore the great attention is paid to the reactors having suspended catalysts. For the photocatalytic oxidation were used reactors in form of tubes, ring and spiral reactors, made out of glass, quartz or plexiglass. The lamp is placed inside, at the top, aside or at the bottom [7].

The key for the process is a photocatalyst with designed physicochemical properties. Beside widely tested semiconductors TiO_2 seems to be the most suitable for both fundamental research and practical applications. TiO_2 is chemically and biologically inert, photo-stable, non-toxic, affordable, cheap and has high oxidative power [13-14]. The detailed mechanism of photocatalysis is very complicated and varies for different pollutants [15]. One of the primary

factors affecting the photocatalysis is the double aptitude of the photocatalyst to simultaneously adsorb reactants and to absorb efficient photons. It was observed that pre-adsorption of reactants on the surface of TiO_2 during a photocatalytic reaction leads to a more efficient electron transfer process [16]. Supported porous photocatalysts, beside easier disposal ensure a high density of active centers for photocatalytic reactions and an enhanced light harvesting because of light reflection and scattering by the pores [5]. That was the main reason to type supported catalysts with enlarged surface area. Al_2O_3 is widely used and tested support in catalysis. The strong adsorption of organics can however decrease the reaction rates [14].

For the preparation of highly active catalysts different methods can be applied. Double impregnation method (DIM) introduced at the Faculty of Chemistry at Maria Curie-Sklodowska University in Lublin, Poland is one of them [17]. DIM is very useful to obtain highly dispersed catalysts. In DIM there are two stages: the first one is the impregnation of inorganic support with disodium salt of the ethylenediamminetetraacetic 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 [18].

2. MATERIAL AND METHODS

Photocatalyst preparation. All chemicals were analytical grade and were used without further purification. For the studies were typed modified TiO_2 catalysts supported over γ–Al_2O_3 (INS Pulawy, Poland). A support in a form of beads with the diameter ca. 3-5 mm and BET surface area of 150 m^2/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 room temperature. After the impregnation of the support the sample was dried at 388K for 2 hrs and calcinated at 873K for 3 hrs. The application of $TiCl_4$ is connected with the presence of the Cl^- on the catalysts surface, though catalysts were washed with the water till the reaction of Cl^- with $AgNO_3$ was not observed.

The titania-alumina support was initially impregnated with 0.1M aqueous solution of EDTA (POCh Gliwice) at 70°C for 0.5 h. In the second step, the support with the adsorbed EDTA was impregnated with 5 wt. % aqueous solution of cobalt nitrate (POCh, Gliwice) (the amount of salt was calculated on the basis of the pure metal) for 1, 2, 4, 8 or 16 respectively (samples Co1, Co2, Co4, Co8 and Co16, respectively). After impregnation and drying all studied precursors were calcined at 600˚C for 3 hrs [19].

The catalysts were examined to determine the total surface area from nitrogen adsorption at liquid nitrogen temperature by the BET method in a volumetric apparatus ensuring a vacuum of at least $2*10^{-6}$ kPa. The phase composition of catalysts was determined by means of X-ray diffraction (XRD) according to peak Kα. Catalyst characterization XRF (X-ray fluorescence) was also applied. All the experiments mentioned were conducted in Analytical Laboratory of Faculty of Chemistry UMCS in Lublin. Temperature-programmed reduction (TPR conducted in AMI–1 Altamira Instruments Inc. – USA) was also used for catalysts characterization.

Photocatalytic studies. The experiments of photocatalytic degradation of organics in wastewater were conducted in band reactor of our construction (Figure 1.) [20]. Reactor was designed from organic glass transparent and resistant to UV light. Two tubes were placed below the UV lamp (254 nm, 50 Hz). Intensity of UV light was measured by Radiometer VLX254 (Vilber Lourmat, 254 nm). In the reactor the bands were the main mixing system and enabled the counter-current contact of reagents. Into the reactor at room temperature the mixture of oxygen ($3dm^3/h$) and nitrogen ($37dm^3/h$) was introduced because the aeration is usually used to prevent or hinder the charge carriers' recombination [7].

As the model contaminants were used solutions of Triton X-100 and its oxidation products e.g. polyethylene glycol and phenol (POCH Gliwice, Poland) and also commercially available wash-up liquid ("Ludwik", Inco Veritas, Poland). The solutions were prepared to have a COD value ca. 3000 mg O_2/dm^3 that is typical for real wastewater and simultaneously is exceeding the norms. As the oxidizing agents were typed oxygen (from air) and H_2O_2. The effectiveness was measured in the few configurations: $TiO_2/UV/O_2/H_2O_2$, $TiO_2/O_2/H_2O_2$, $TiO_2/UV/O_2$, TiO_2/O_2.

The sample was taken back after 115 minutes assuming that by the volumetric flow 1.3 dm^3/h, the whole sample would be pumped out. The system with single run or two hours time is very often used [5]. The next stage was the analysis of organic compound concentration using COD method with bichromate method [21] that is a standard water analysis.
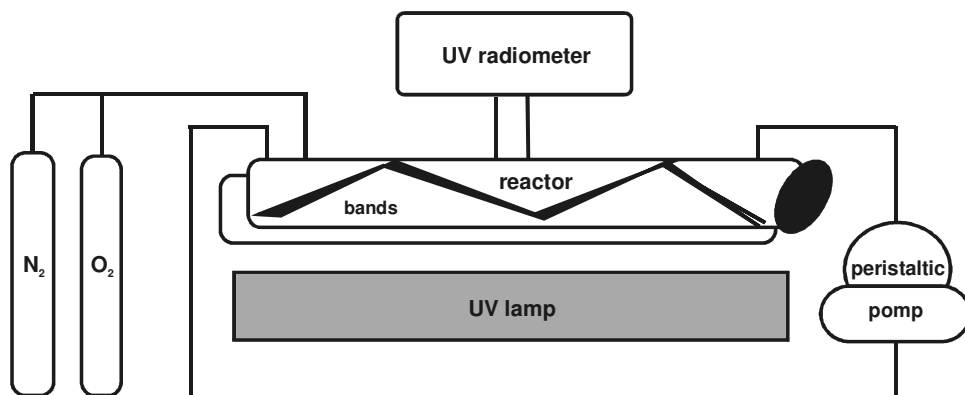
Fig. 1. Scheme of apparatus for photooxidation of organic compounds in water.

3. RESULTS AND DISCUSSION

Sakhtivel et al. [22] indicated that high effectiveness of Acid Brown 14 oxidation over TiO_2/Al_2O_3 is ascribed to the adsorption properties of support Al_2O_3. In order to prevent recombination or decrease the rate of recombination the factor close to catalysts surface can be applied. This incorporates the more effective adsorption places located close to catalysts surface. Generated in this way by oxidants ($^*OH$) h^+ can reach them before the intermediate products would yield to further reaction what takes place in the presence of strong adsorbents. That was the main reason to type supported TiO_2 photocatalysts.

Tab. 1. Physicochemical properties of $Co-TiO_2/Al_2O_3$ photocatalysts.

Photocatalyst	Ti content [%wt.]	Co content [%wt.]	total surface area [m^2/g_{cat}]
TiO_2/Al_2O_3	5.34	-	95.5
Co1	5.34	1.19	72.6
Co2	5.34	1.22	72.4
Co4	5.34	1.25	65.8
Co8	5.34	1.33	63.8
Co16	5.34	1.47	71.0

DIM technique does not enable to obtain from $Co(NO_3)_2$ catalysts having a significant differences in Co content (Table 1.). The Co loading was about 1.25%wt. Elongation of the second impregnation time till 16 minutes results in incorporation of 1.47%wt. Co in photocatalyst.

From XRD spectra it is shown that TiO_2 is present in a form of anatase (Figure 2, peaks by $2\Theta = 25.23$ and 55.11; JCPD (Joint Committee on Powder Diffraction Standard) 21-1272) with the crystallite size 4-7 nm. Co is present in form of Co_3O_4, what is confirmed by [23] when the substrate is $Co(NO_3)_2$. The XRD spectra looks similarly what may indicate the dispersion of metal or hiding the signal by the support. The greatest signal by $2\Theta=66.89$ is obtained from the support Al_2O_3 (JCPD [01-1303]).
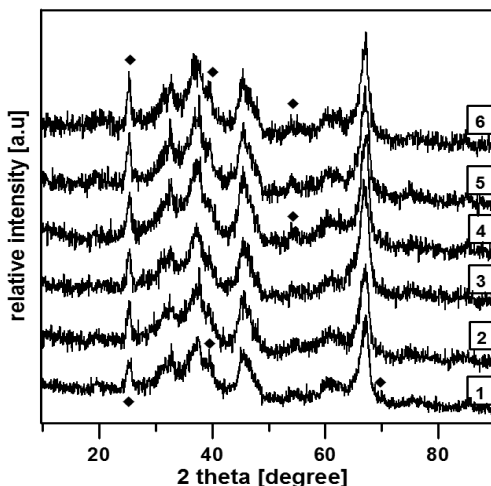

Fig. 2. XRD spectra of studied catalysts: 1 – TiO_2/Al_2O_3, 2 – Co1, 3 – Co2, 4 – Co4, 5 – Co8, 6 – Co16.

But the TPR studies indicates that low reducibility of catalyst is connected with presence of some mixed alumina-titania forms e.g. Al_2TiO_5, $CoTi_2O_5$ or $CoAl_2O_4$ (Figure 3) that were also present in XRD spectra.

Creation of hardly reductive alumina phases can result from the presence of $Al\equiv OH^-$ and $Al(OH)_4^-$, that are at the Al_2O_3 surface during impregnation in basic condition. These ions bind with Co [24] giving – $CoTi_2O_5$ or $CoAl_2O_4$.

Novel Me-anatase/Al_2O_3 catalysts are effective in oxidation of organic water pollutants – they enable significant at least 60% reduction of COD [18,19]. Our previous studies of alcohols, carbohydrates and HCHO oxidation over Co indicated that Co4 which has the medium content of Co, medium total surface area, is sensitive to the presence of UV, H_2O_2. The results were typical for Co catalysts or significantly different [19]. Though the determination of UV, H_2O_2 presence during surfactants removal over Co modified TiO_2/Al_2O_3 was taken into consideration.
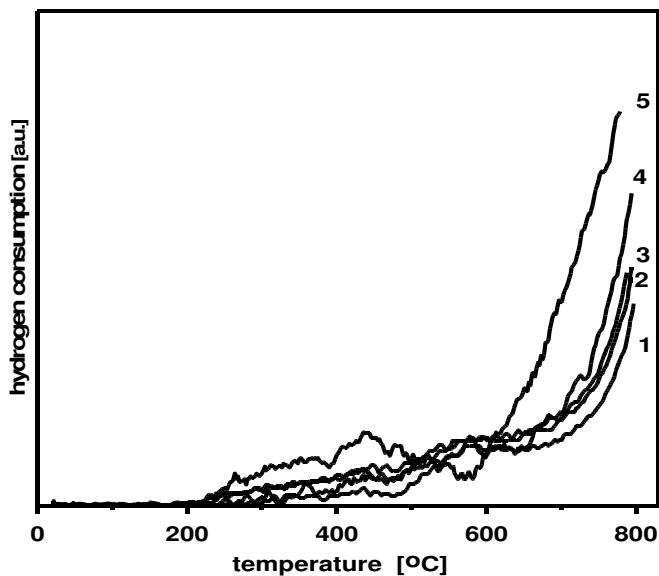
Fig. 3. TPR studies of Co catalysts: 1- Co1, 2- Co2, 3- Co4, 4-Co8, 5-Co16.

Photooxidation of wastewater. The biggest effect of UV was shown for small amount of Co in the TiO_2/Al_2O_3 photocatalyst for all studied pollutants (Figure 4). For phenol removal optional Co content was above 1.20%wt. Both for glycol, Triton X-100 and wash-up liquid photooxidation the best results were obtained over catalysts with lower Co content.

Generally Co addition to TiO_2/Al_2O_3 retarded treatment what indicates that photooxidation of studied pollutants proceeds mainly over TiO_2. Modification of TiO_2/Al_2O_3 with Co shifted the absorption spectrum of light toward longer wavelengths and the response for UV is smaller.

The effect of H_2O_2. The effect of photocatalytic oxidation can be improved using the addition of external oxidants, e.g. H_2O_2, O_3 but the effect is not obvious and depends on many factors. H_2O_2 is one of the cheapest oxidants with high oxidation power, soluble in water and thermally stable. In the presence of UV irradiation at 254 nm the photolysis of H_2O_2 into $2\ ^*OH$ is observed. The photolysis rate of H_2O_2 is dependent on the pH and increases in basic conditions. The photolysis rate of H_2O_2 is dependent on the pH and increases in basic conditions:

$$2H_2O_2 + 2^*OH \rightarrow H_2O + HO_2^* \tag{1}$$

$$2HO_2^* \rightarrow H_2O_2 + O_2 \tag{2}$$

However, too high H_2O_2 addition causes the process to hinder because the excess of H_2O_2 captures the radicals (3) [25]:

$$H_2O_2 + {}^*OH \rightarrow HO_2^* + H_2O \tag{3}$$

Hydrogen peroxide is an active electron scavenger preventing recombination of charge carriers and enhancing the creation of other radicals ${}^*OH$ and ${}^*O_2^-$ on the catalyst's surface, too.
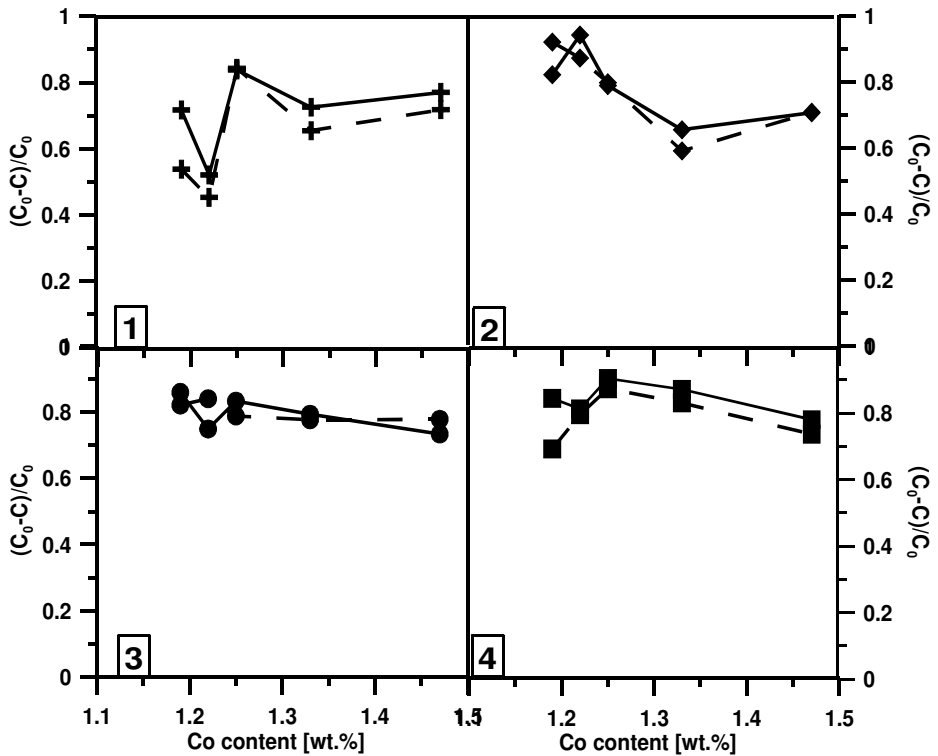

Fig. 4. Photocatalytic oxidation of wastes: 1 – phenol, 2 -polyethylene glycol, 3 – Triton X-100, 4 – wash-up liquid; broken line – aeration, solid line – UV irradiation.
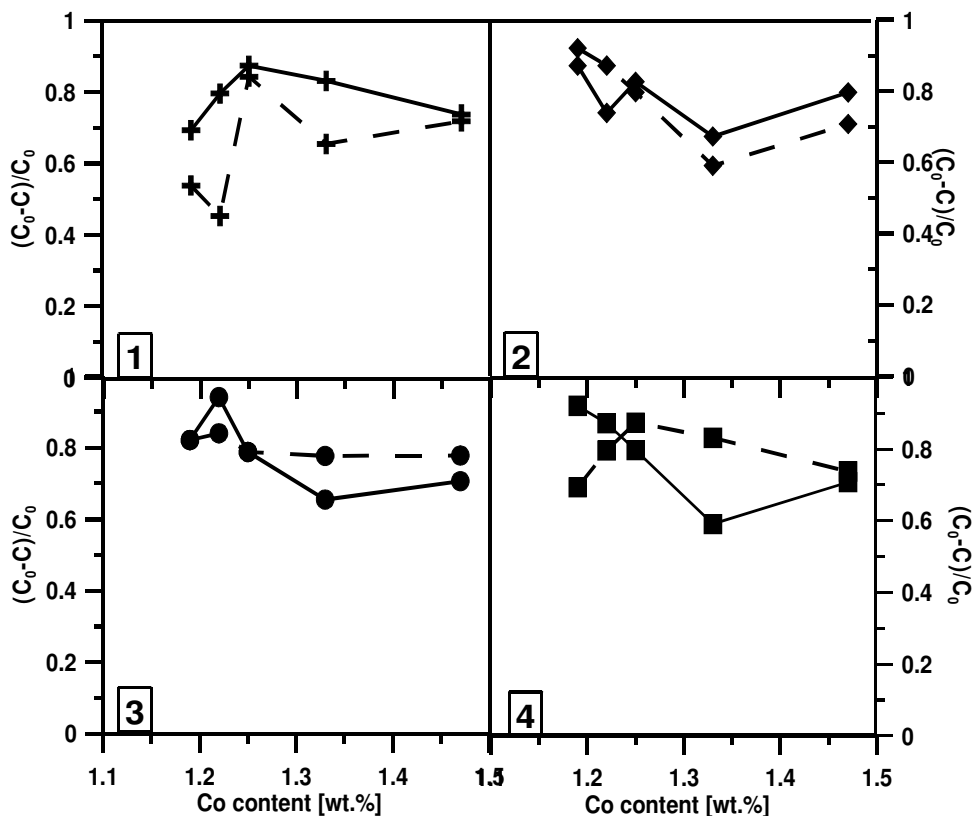
Fig. 5. The effect of H_2O_2: 1 – phenol, 2 -polyethylene glycol, 3 – Triton X-100, 4 – wash-up liquid; broken line – aeration, solid line – H_2O_2 addition.

The effect of H_2O_2 addition during photooxidation over $Co-TiO_2/Al_2O_3$ is not obvious and depends on the type of compounds (Figure 5.). The most visible effect is observed during phenol oxidation and small amount of Co in the photocatalyst – the oxidation is deepen by 30%. During phenol and glycol removal H_2O_2 addition enhances the oxidation. The positive effect of H_2O_2 addition is correlated with Co content – for higher values the effectiveness of removal is lower. Photooxidation of glycol and Triton X-100 is as effective as photooxidation with H_2O_2. It indicates that the H_2O_2 does not pay a significant role during photooxidation over $Co-TiO_2/Al_2O_3$ and may even, in case of photocatalysts with Co content above 1.25%wt., retard treatment.

Photocatalytic oxidation with H_2O_2 addition. The studies were conducted taking into account the effect of H_2O_2 during photooxidation of wastewaters.

Photooxidation of phenol and glycol seemed to be sensitive to H_2O_2 presence and it resulted in deepened removal (Figure 6). During Triton X-100 and wash-up liquid the enhanced photooxidation was observed only over $Co-TiO_2/Al_2O_3$ catalysts with lower Co content.
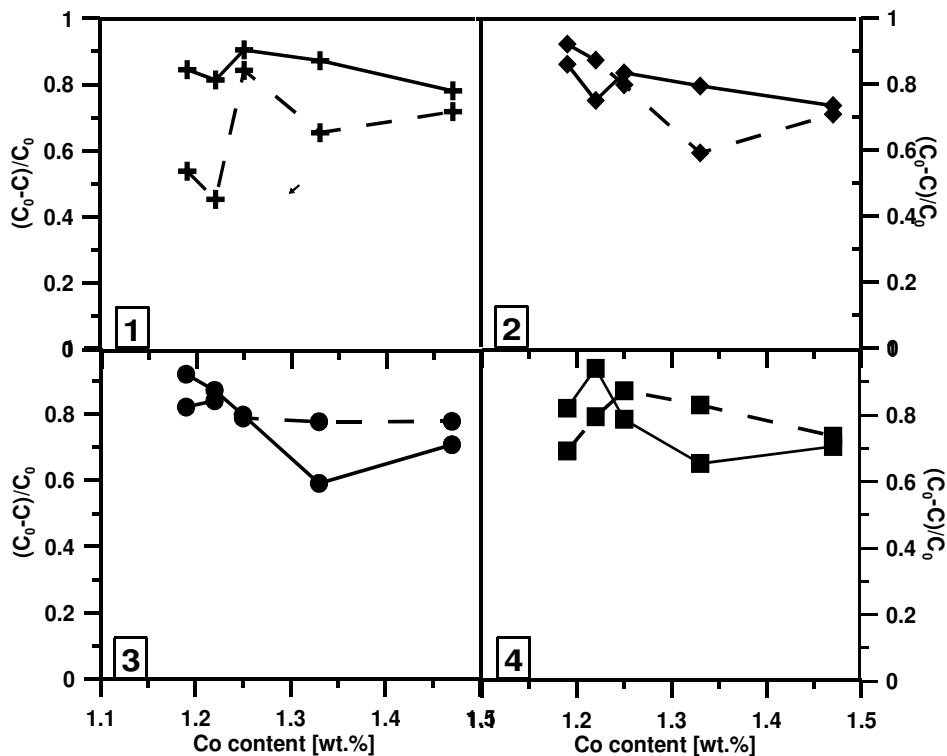

Fig. 6. Photo-catalytic oxidation of wastewater with H_2O_2: 1 – phenol, 2 -polyethylene glycol, 3 – Triton X-100, 4 – wash-up liquid; broken line – UV irradiation, solid line – H_2O_2 addition during UV irradiation.

Generally H_2O_2 influenced the photooxidation positively for all studied pollutants but by smaller Co content what indicates that process of photooxidation proceeds mainly over TiO_2. For photocatalysts with higher Co content the effectiveness slightly decreases. There is no need to use additionally any oxidizing agents such as H_2O_2 during Triton X-100 and wash-up liquid removal because it may even retard oxidation.

Photocatalytic oxidation in time. Catalysts' activity changes in time. The same tendency was presented for all studied photocatalysts. The most visible effect

was observed after 2 hours treatment of water (Figure 7): there was only about 20% of initial COD value left for glycol and Triton X-100 and 10% for wash-up liquid. The photooxidation of phenol proceeds with the lowest effectiveness – about 50%.
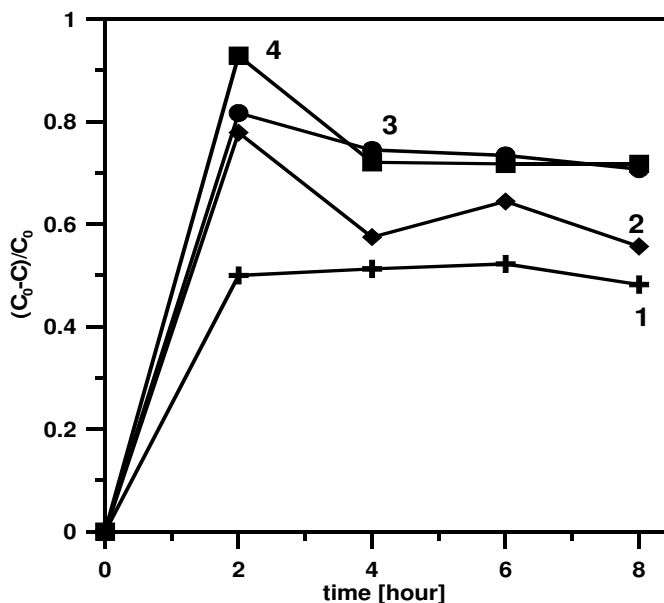

Fig. 7. COD changes in time during photooxidation over Co2: 1 – phenol , 2 – polyethylene glycol, 3 – Triton X-100, 4 – wash-up liquid.

Observed decrease in removal during prolonged time may be connected with the desorption of pollutants and their oxidation by-products from the photocatalyst's surface. It indicates that it is not economically justified to conduct treatment for more than 2 hours.

4. CONCLUSIONS

According to obtained results of photocatalytic oxidation of phenol, polyethylene glycol, Triton X-100 and wash-up liquid it can be concluded:
– the greater effect on oxidation of simple organic compound has the addition of O_2,
– the most efficient method for removal of surfactants is photocatalytic oxidation with H_2O_2,
– H_2O_2 has a positive effect on aerated wastewater containing phenol and polyethylene glycol, a detrimental one - for Triton X-100 and wash-up liquid

removal, but the results are not justified economically
- H_2O_2 does not pay a significant role during photooxidation over Co-TiO_2/Al_2O_3 and may even, in case of photocatalysts with Co content above 1.25%wt., retard treatment.
- Co addition to TiO_2/Al_2O_3 retarded treatment what indicates that photooxidation of studied pollutants proceeds mainly over TiO_2,
- 2 hour treatment of water is enough to obtain a significant COD reduction of all studied pollutants, it is not economically justified to conduct treatment any longer.

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