

Decomposition of Detergents Present in Car-Wash Sewage by Titania Photo-Assisted Oxidation

J. Perkowski^{1*}, S. Bzdon¹, A. Bulska², W. K. Józwiak²

¹Institute of Applied Radiation Chemistry, Wróblewskiego 15, 93-590 Łódź, Poland

²Institute of General and Ecological Chemistry, Technical University of Lodz, Żeromskiego 116, 90-924 Łódź, Poland

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Abstract

Advanced oxidation process (AOP) has been shown to be effective in water and air decontamination. Ultraviolet-oxidation has been evaluated for most contaminants. In this work UV/TiO₂/O₂ version of AOP method was used to decompose surfactants and, applied in car washing installations, commercial products. The influence of such parameters like the amount of TiO₂ catalyst's dose, the acidity of aqueous solution and the type of applied UV lamp were examined. Additionally, in order to evaluate the effects associated with photocatalysis, studies of the contributions like adsorption of surfactants on catalysts and photooxidation were undertaken. Photocatalytic oxidation of Cleentex aqueous solution was investigated, using TiO₂ and 10% – TiO₂/SiO₂ as catalysts. The most efficient process appeared to occur in weakly basic solution pH = 8.9 with TiO₂ catalyst dose about 1.5 g dm⁻³. The photo-efficiency of UV lamps should be verified in order to avoid the excessive losses of light power. All detergents showed a high affinity for photocatalytic decomposition and final degree of COD reduction was in the range 35-60 %, depending on detergent composition. The degree of TOC reduction was slightly lower.

Keywords: advanced oxidation processes, photocatalysis, photooxidation, adsorption on TiO₂

Introduction

The Industrial Revolution brought about a vehement enhancement of production, which caused a tremendous increase of solid, liquid and gaseous waste materials, resulting in increased contamination of the environment.

Surfactants belonging to those compounds, which have a great impact on water pollution, are commonly used in domestic households and many branches of industry. In recent years a considerable increase in surfactant usage and significant enhancement of surfactant concentration in sewage water have been observed in chemistry, pharmacology, textile and metallurgy branches, reaching even several hundreds of mg per liter. Surfactants being the common contamination of sewage belong to the

chemical compounds which are hardly removable during classical, physical-chemical and biological methods. Oxidation combined with the usage of photo-catalysts is one of the most efficient processes. The preliminarily cleaned wastewater can be deeply purified by fast, efficient and economically accepted biological process.

Car washing installations producing detergent-rich sewage are usually located together with petrol stations. Some of them are placed far away from urban area and are facing serious problems of sewage utilization. A characteristic feature of sewage production is its periodic character and the fact that an entire amount of wastewater is produced usually during summer days. Thus, the TiO₂-assisted photochemical oxidation process seems to be a desirable solution for sewage purification. This approach belongs to the modern chemical technology methods of sewage and water purification known as AOP

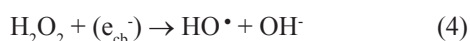
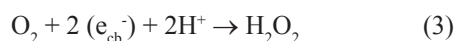
*Corresponding author; e-mail: japerepi@mitr.p.lodz.pl

– advanced oxidation processes [1-3]. Their common feature is an engagement of strong oxidation radicals HO[•] evolved in different ways. Historically, the first application of TiO₂-assisted UV photo-catalysis was combined with water decomposition on titania electrodes and was reported in 1972 by Fujishima and Honda [4]. TiO₂ assisted decomposition of biphenyl and chlorine-biphenyl in sewage was reported in 1976 by Carey [5]. Now the ultraviolet photo-catalytic oxidation process is applied frequently in the effective decomposition of many toxic compounds present in sewage [6-8].

During exposure of the TiO₂ surface with radiation of minimum energy 3.2 eV photon (hν) can transfer an electron (e_{cb}⁻) from the valence band of crystal into the conduction band, leaving an electron hole (h_{vb}⁺). This energy is equivalent to photons with wavelength 388 nm. The activation of TiO₂ takes place in the range of radiation 300-388 nm. Both the whole valence bands and electrons of the conduction band can recombine in a crystal network, resulting in fluorescence and heat evolution effects and they can migrate on catalyst surface, where they can be involved in redox reactions with adsorbed water molecules, hydroxyl groups, oxygen atoms and molecules of organic compounds. The hydroxyl groups are produced as a result of oxidation between hole (h_{vb}⁻) and H₂O molecule or [•]OH group.



Electron can react with adsorbed O₂(aq) generating O₂⁻, which additionally can give H₂O₂ and HO[•]:



In lower pH range hydrogen atoms and molecules can arise [9-11].

The adsorption of compounds on metal oxide surface (TiO₂, SiO₂) is strongly influenced by charge generation during dissociation of surface chemical groups or interaction with H⁺ and OH⁻ ions from the solution. For TiO₂ the mechanism is as follows:



The surface of TiO₂ catalyst is charged positively at low pH as a result of protonation, whereas the catalyst surface acquires negative charges at high pH in the course of deprotonation reaction.

The properties of catalysts and mechanism of photo-oxidation were deeply investigated in many review papers and monographs [12-19]. In this work titania was verified as photo-catalyst in the process of oxidation of different

surfactants in aqueous solution. This process is treated as a model system, which can be applied in car-washing devices.

Experimental Procedure

Objects

The applied objects were aqueous solutions of commercial detergents made by Organica (Poland) and used in domestic car washing procedures. The applied concentrations of solution were prepared according to the producer's indications required in the course of car washing procedure:

Surfactants such as Cleentex, car shampoo and car shampoo with wax are commercial products, whereas Sulforokanol L – 327 and Sulfapol 35 are compounds used in production of the above-mentioned commercial products:

1. Cleentex – (Organica Car SA, Łódź) contains ethoxyl alcohols C 9-11, quaternary ammonium salt, alkyl glycols, EDTA disodium salt, sodium metasilicate and other components according to the producer specification (density 1.085 g·cm⁻³) [20]. An aqueous solution with detergent concentration of about 12.5 g·dm⁻³ was used.
2. Sulforokanol L-327 – (Rokita – Brzeg Dolny) contains sulfated ethoxyl fat alcohols [21]. Detergent concentration was about 10 g·dm⁻³.
3. Sulfapol 35 – (Organica Car SA, Łódź) contains sodium alkylbenzenesulfonic salt (density 1.01 – 1.05 g cm⁻³) [20]. Detergent concentration about was 10 g·dm⁻³.
4. Car washing shampoo – (Organica Car- Łódź) contains nonionic and anionic surfactants, - ethoxyl fat alcohols, Sulfarokanol, diethyl coconut acid amid, derivative of betaine, EDTA disodium salt and other components according to the producer specification (density 1.001 – 1.006 g cm⁻³) [20]. Detergent concentrations of about 12.5 g·dm⁻³ and 25 g·dm⁻³ were used.
5. Car washing shampoo with wax – (Organica Car SA, Łódź) contains oksyetylen(3)sulfatedalcohol sodium salt C₁₂ – C₁₄, ethers of polyethoxyl fat alcohols. Detergent concentration was about 12.5 g·dm⁻³.
6. Mixture of Cleentex (12.5 g·dm⁻³) and car washing shampoo (12.5 g·dm⁻³).
7. Mixture of Car washing shampoo (12.5 g·dm⁻³) and car washing shampoo with wax (12.5 g·dm⁻³).

The above products were tested by the Polish Agency of Hygiene and basic data referring to product constituents and physical and chemical properties were delivered.

Surface area measurements were carried out using BET (liquid N₂) method. TiO₂ catalysts were based on TiO₂ P25 produced by Degussa with phase composition, anataz 20% and rutile 80%. Silica support was obtained by sol-gel method used as a starting material

– tertetoxysilicon(IV). Titania supported on silica – 10% $\text{TiO}_2/\text{SiO}_2$ catalyst was prepared by TiO_2 deposition on silica, suspended in hexane solution of titanium isopropanol, as a result of hydrolysis in argon atmosphere and left for 48 hours at room temperature. Then solvent was removed in a vacuum and the catalyst was dried at 120°C (4 h) and finally calcinated at 400°C (3h) in oxygen stream. Silica (0.1 – 0.2 mm fraction) with surface area $430 \text{ m}^2\cdot\text{g}^{-1}$, manufactured by Machery Nagle Co., was applied.

Apparatus and Procedure

Photo-oxidation and photo-catalytic processes were run in a photo-reactor (Heraus) consisting of a glass vessel – volume of 1000 cm^3 equipped in UV lamp 150 W (type TQ 150 Heraus) or 8 W (COBR Polam – Warsaw) placed in a Quartz lining and magnetic rotor. Oxygen was delivered to the solution via a special tube and constant volume rate was kept $10 \text{ dm}^3 \text{ h}^{-1}$. Temperature of reaction was usually about 20°C . The amount of catalyst was added to the solution before the experiment (only in case of photo – catalytic experiments). Time of reaction was 5-8 h. Adsorption processes were run in the same reactor covered by aluminum foil to avoid unwanted photolitic effects (without UV lamp).

In order to estimate the efficiency of photons produced by applied lamps, the procedure of chemical actinometer was performed. The emission spectra were obtained by using a Hewlett Packard model HP 8542 spectrophotometer. The chemical ferric-oxalic actinometer was applied and resultant Fe^{2+} ions formed color complex with 1.10 fenantrolin, whose concentration was measured at wavelength 510 nm [22,23]. In this way the intensity of photons emitted per unit time was evaluated for both 8 and 150 W lamps. For lamp 8 W emitting light in the range 254-578 nm (about 45% of light in UV range, about 38.9% light emission at 254 nm) the amount of absorbed light by aqueous solvent was estimated as $1.249\cdot 10^{20}$ photons $\text{min}^{-1}\cdot\text{dm}^{-3}$, which corresponds to energy consumption

equal to $4.532\cdot 10^{20} \text{ eV min}^{-1}\cdot\text{dm}^{-3}$ or $72.5 \text{ J min}^{-1}\cdot\text{dm}^{-3}$. For lamp 150 W emitting light in the range 254-578 nm (about 21% in UV range, 2.3% light emission at 256 nm) the intensity of light absorption was $1.91\cdot 10^{21}$ photon $\text{min}^{-1}\cdot\text{dm}^{-3}$ which is equivalent to energy uptake $5.81\cdot 10^{21} \text{ eV min}^{-1}\cdot\text{dm}^{-3}$ or $931 \text{ J min}^{-1}\cdot\text{dm}^{-3}$. In the range 250-350 nm the efficiency of photon emission were $5.73\cdot 10^{19}$ and $50.5\cdot 10^{19}$ photons $\text{min}^{-1}\cdot\text{dm}^{-3}$ for 8 i 150 W lamps, respectively. The yields at 254 nm are similar $4.85\cdot 10^{19}$ and $5.62\cdot 10^{19}$ photon $\text{min}^{-1}\cdot\text{dm}^{-3}$, respectively. The ratio of electric power for both lamps, reflecting the ratio of emitted photons was 18.75 in the entire range of light radiation but about 9 in ultraviolet range.

Analytical Methods

The oxidation of surfactants was carried out in the system with photo-catalyst as a suspension. The reaction run was monitored by spectrophotometric, polarographic, measurements of total organic carbon TOC (5000 Shimadzu), chemical and biochemical oxygen demand (COD and BOD) methods. Process optimization was performed taking into account the following parameters: concentration and type of surfactant, the amount of surfactant, the mass of photo-catalyst, pH of solution, radiation intensity, time of reaction and the possibility of re-usage of catalyst, co-operate action of O_3 , H_2O_2 and UV. All analytical procedures were made according to Polish Legislative Norms.

Results

Three steps of TiO_2 -assisted photo-catalytical processes can be anticipated: the adsorption of chemical compound on catalyst surface, the oxidation of adsorbed compound on catalyst surface and simultaneously the oxidation of compounds in aqueous solution. Usually the last process of oxidation can be treated as photo-oxidation because additionally the solution is strongly saturated with

Table 1. Initial data for aqueous solutions of detergents and their mixtures.

Detergent	Concentration	COD	BOD ₅	pH	TOC	BOD ₅ /COD
Units	g dm^{-3}	$\text{mgO}_2 \text{ dm}^{-3}$	$\text{mgO}_2 \text{ dm}^{-3}$		mg dm^{-3}	
Cleantex	12.5	345	160	10.9	111	0.464
Sulforokanol L-327	10	550	150	7.2	165	0.273
Sulfapol 35	10	685	208	7.2	224	0.304
Car shampoo	25	928	420	7.1	244	0.453
Car shampoo with wax	12.5	542	226	7.7	248	0.417
Cleantex + Car shampoo (1:1)	12.5 + 12.5	665	380	10.1	219	0.572
Car shamp. + Car shamp. with wax (1:1)	12.5 + 12.5	543	180	7.8	258	0.331

oxygen gas. In order to get deeper insight into the mechanism of compound decomposition in aqueous solution the adsorption of surfactants and their photodecomposition on titania surface should be estimated.

Adsorption Process

The adsorption of surfactants on catalyst surface was performed in a dark environment during 8 h in room temperature using suspension of TiO_2 1.5 g dm^{-3} without oxygen saturation. COD measurements were made every one-hour and the results are presented in Figure 1 for Sulfapal 35, Sulforokanol L-327 and car shampoo with wax solutions. Rather surprisingly unexpected curves were found during adsorption on titania for aqueous solution of car shampoo and car shampoo with wax, depicted in Fig. 2.

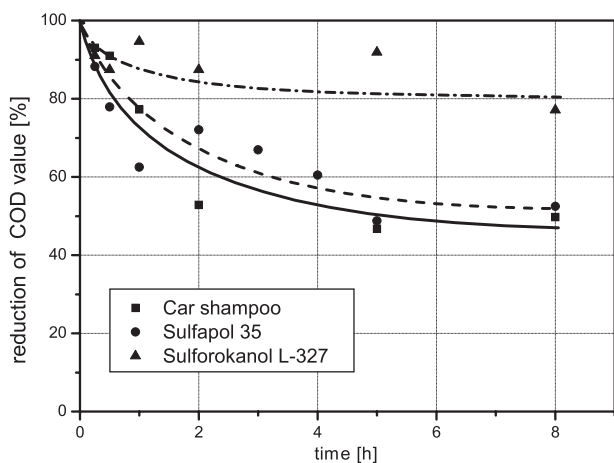


Fig.1. COD changes of aqueous solutions of Sulfapal 35, Sulforokanol L-327 and Car shampoo with wax during adsorption (8 h) on titania (1.5 g dm^{-3}) in a dark environment.

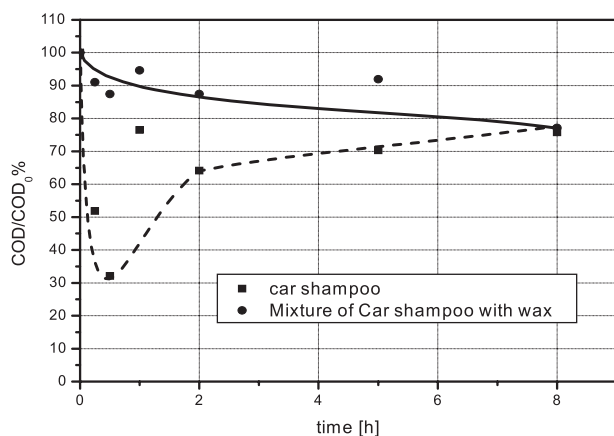


Fig.2. COD changes of solutions: car shampoo and mixture of car shampoo with wax taking place during adsorption (8 h) on titania (1.5 g dm^{-3}) in a dark environment.

The adsorption process was also carried out on silica surface. The applied SiO_2 consisted of powder grains in the range 100-200 mesh and surface area was $420 \text{ m}^2 \text{ g}^{-1}$. The typical examples of COD changes during the adsorption of Sulforokanol L-327 and Cleentex on silica are illustrated in Figure 3. Silica was used as a reference system because TiO_2/SiO_2 (titania supported on silica) photo-catalyst was also used.

Photo-Oxidation Process

Ultraviolet photo-oxidation process (without TiO_2 as a catalyst) was used for aqueous solution of different detergents and their mixtures. Two UV lamps were applied: the low pressure 8 W and the medium pressure 150 W. The following degrees of COD and TOC values reduction were obtained after a 5-hour photo-oxidation process: for Sulforo-

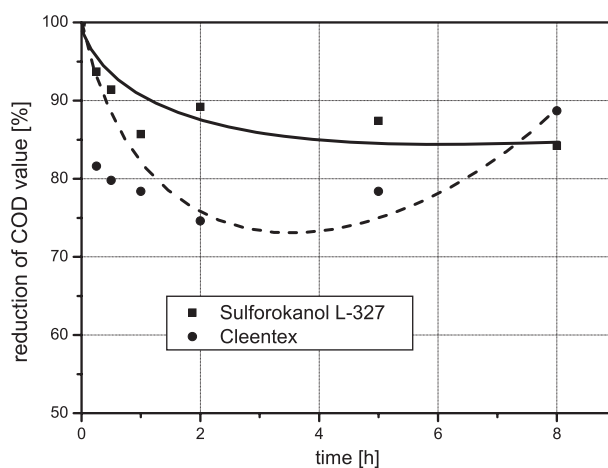


Fig.3. COD changes of solutions: Sulforokanol L-327 and Cleentex taking place during adsorption (8 h) on silica (1.5 g dm^{-3}) in a dark environment.

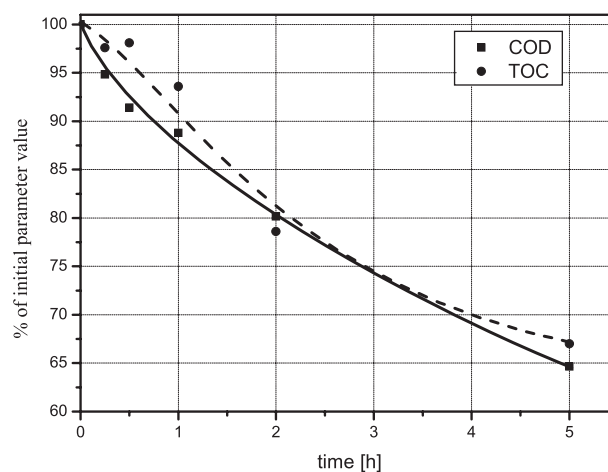


Fig. 4. The final changes of COD, TOC obtained during photo-oxidation (lamp 8 W) of Sulforokanol L – 327 in water solution in 5 h.

kanol L-327 above 30% COD and 32% TOC, Sulfapol 35 – 25% COD and 5% TOC and for mixture of Cleentex and car washing shampoo above 30% COD and 18% TOC. The above values were found for UV lamp 8 W (Fig. 4).

Photo-Catalytic Oxidation on TiO_2

The optimization of measurements referring to the influence of TiO_2 dose and pH on the efficiency of UV photodecomposition process of Cleentex solution (12.5 g dm^{-3}) is presented in Figs. 5 and 6, respectively.

The Influence of TiO_2 Dose

Four different TiO_2 suspensions were applied 0.5; 1.0; 1.5 and 2.0 gram per 1 dm^3 of 12.5 g dm^{-3} Cleentex aqueous solution. The use of higher TiO_2 content was rather undesirable taking into account the efficiency of UV photo-catalyst and the economical point of view. The influence of TiO_2 dose on the main parameters of the 5 hours UV photo-oxidation of Cleentex solution: COD, BOD and TOC values is presented in Fig. 5. Rather small ef-

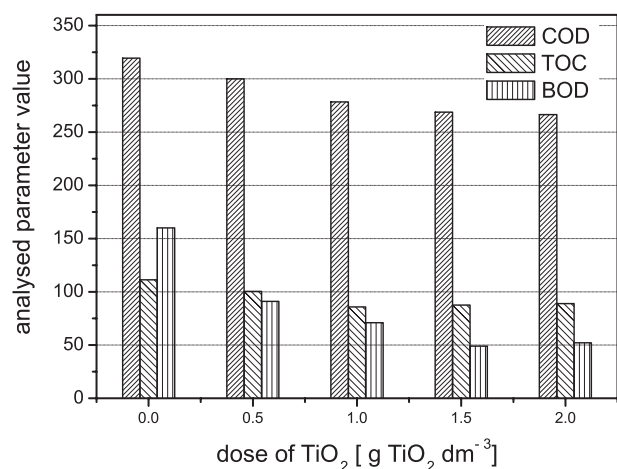


Fig. 5. The final changes of COD, TOC and BOD_5 obtained during photo-oxidation of Cleentex water solution for different applied doses of TiO_2 (lamp 150 W, pH = 10.9, 5 h).

fects are observed, especially for higher loading of TiO_2 (1.5 and 2.0)

The Influence of pH

The influence of pH on the efficiency of UV photodecomposition process of Cleentex solution (12.5 g dm^{-3}) is presented in Fig. 6. In all cases a 5-hour run was performed. The measurements were carried out applying light radiation originating from the medium pressure UV lamp 150 W. The values COD and TOC were modified by subtraction of the estimated values obtained during UV photocatalytic oxidation of solution with applied pH buffer. The initial pH value of Cleentex solution was 9.86. The desirable pH values were obtained in the following way:

pH = 2.51 – addition of 45 cm^3 $0,1 \text{ mol dm}^{-3}$ HCl

pH = 5.20 – applying $\text{NaCH}_3\text{COO} + \text{CH}_3\text{COOH}$ buffer

pH = 8.90 – applying glycine – NaOH buffer

pH = 12.05 – addition of 20 cm^3 $0,1 \text{ mol dm}^{-3}$ NaOH

Photo-catalytic oxidation of applied buffers glycine – NaOH and $\text{NaCH}_3\text{COO} + \text{CH}_3\text{COOH}$ (without surfactants) were examined in the same conditions. The changes of measured parameters are in Table 2.

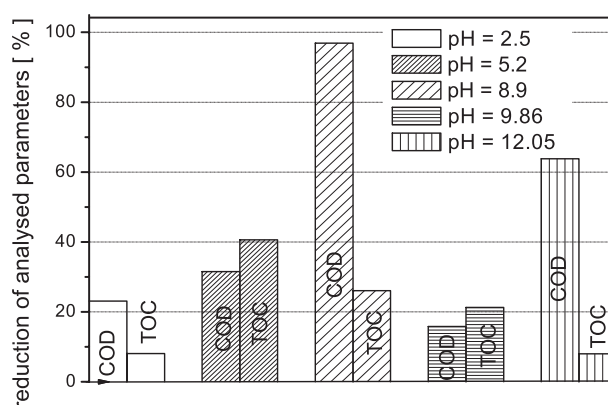


Fig. 6. The influence of pH on final changes of COD and TOC obtained during TiO_2 assisted photo-oxidation of Cleentex water solution (lamp 150 W, 5 h).

Table 2. The changes of parameters measured after 5 h photo – catalytic oxidation of buffers.

Parameters [units]	glycine – NaOH buffer	$\text{NaCH}_3\text{COO} + \text{CH}_3\text{COOH}$ buffer
COD_0 [$\text{mg O}_2 \text{ dm}^{-3}$]	1840	11410
COD_5 [$\text{mg O}_2 \text{ dm}^{-3}$]	970	11290
TOC_0 [mg dm^{-3}]	1064	5027
TOC_5 [mg dm^{-3}]	968	4747
pH_0	8.95	5.20
pH_5	8.15	5.24

The main problem of these measurements results from the interaction between different compounds present in aqueous solutions. The independence of decomposition for given compound is disputable. Thus, the lack of promotion and inhibition effects was assumed.

The Influence of UV Radiation Intensity

The influence of UV radiation intensity on the efficiency of TiO_2 assisted photodecomposition of the example solution – mixture of Cleentex and car shampoo is illustrated in Fig. 7. The comparison of photolysis efficiency was made by applying two UV lamps 8 and 150 W. Three parameters were recorded: COD, BOD_5 and TOC after 5 h reaction time. About 19% and 47% decrease of COD value were found for 8 and 150 W lamps, respectively. The diminishments of TOC values were smaller by

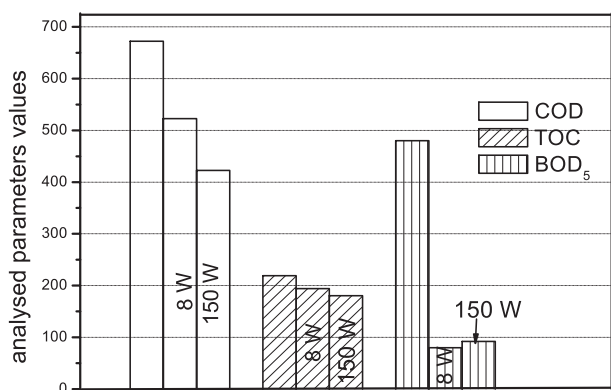


Fig. 7. The influence of lamp radiation power (8, 150 W) on final changes of COD, TOC and BOD_5 values obtained during TiO_2 -assisted photo-oxidation of Cleentex and car shampoo water solution (pH = 10.1; time of reaction 8 h).

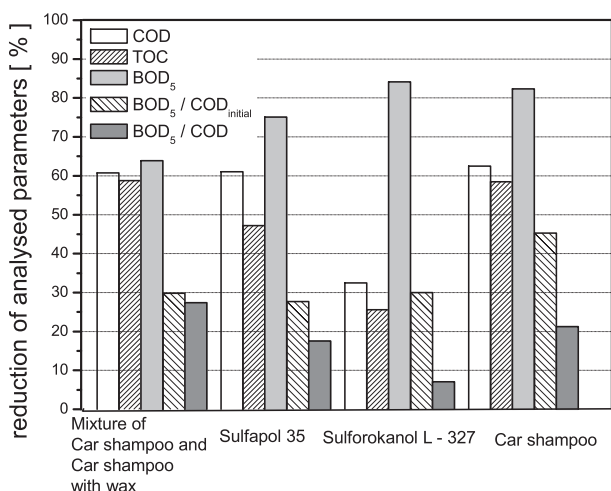


Fig. 8. The final decrease of COD, TOC and BOD_5 values and their ratios COD, TOC and $\text{BOD}_5/\text{COD}_{\text{init}}$ obtained during TiO_2 photo-oxidation of surfactant-water solution (pH not modified, time of reaction 5 h).

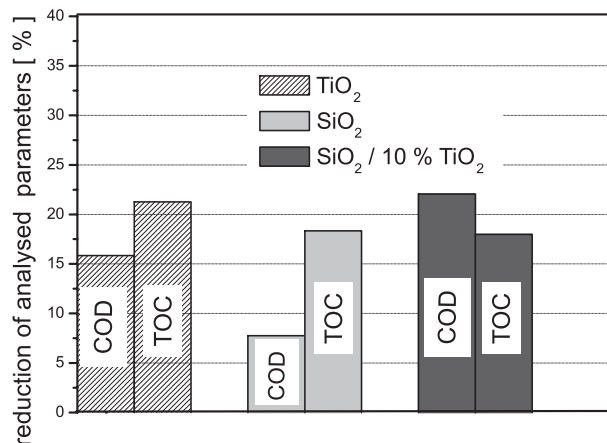


Fig. 9. The influence of kind catalyst (TiO_2 , 10% $\text{TiO}_2/\text{SiO}_2$, SiO_2) on final changes of COD and TOC obtained during photo-oxidation of Cleentex water solution (lamp 150 W, time of reaction 5 h).

about 12 and 18%, respectively. The decrease of BOD_5 values was about 80% in both cases.

Photo-Catalytic Oxidation of Detergents

Titania assisted ($1.5 \text{ g TiO}_2 \text{ dm}^{-3}$) photo-catalytic oxidation of detergents (Sulforokanol L-327, Sulfapol-35, car shampoo, car shampoo with wax and their mixture) is illustrated in Fig. 8 as COD, BOD_5 , BOD_5/COD and TOC values obtained after 5 hours of reaction time. BOD values were estimated, obtained after 5 hours of reaction time. BOD values were estimated, both at the beginning (BOD_{init}) and after 5 h (BOD_5) and the ratio $\text{BOD}_5/\text{BOD}_{\text{init}}$ was calculated what can be used as a measure of biological affinity for decomposition of surfactant.

The influence of catalyst types (TiO_2 , 10% $\text{TiO}_2/\text{SiO}_2$, SiO_2) on final changes of COD and TOC values estimated after 5 h photo-oxidation of Cleentex water solution is presented in Fig. 9. The load of photo catalyst was 1.5 g dm^{-3} and applied 150 W ultraviolet lamp. The obtained results both for 10% $\text{TiO}_2/\text{SiO}_2$ catalyst ($320 \text{ m}^2\text{g}^{-1}$) and TiO_2 alone ($49 \text{ m}^2\text{g}^{-1}$) were 22 and 18%, respectively. Time-dependent COD curve for silica ($420 \text{ m}^2/\text{g}$) shows a minimum after 2 h of about 21% and further increase to about 10% after 5 h.

Discussion

The measurements of surfactant adsorption on titania surface described above play an important role in TiO_2 assisted photo-catalytic oxidation of these detergents. The adsorption process is strongly dependent on the type of surfactant compounds. The commercial detergents like Sulfapol 35, Sulforokanol L-327 and car shampoo with wax adsorb on catalyst surface in a classical manner and the adsorption equilibrium was established after 5-6 hours. When the amount of TiO_2 was $1.5 \text{ g}\cdot\text{dm}^{-3}$ the highest ad-

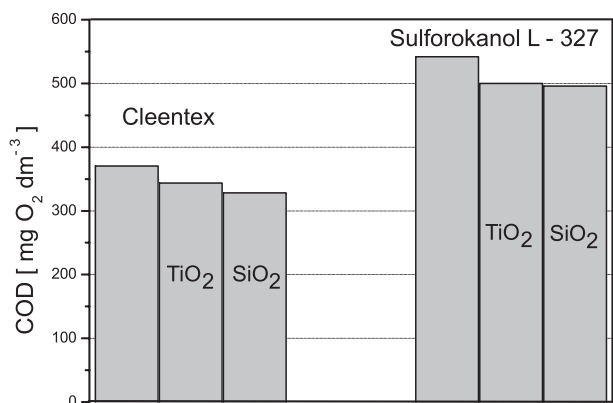


Fig. 10. The comparison of COD values after 5 h adsorption in dark environment for Cleentex and Sulforokanol L – 327 solutions on TiO₂, 10%TiO₂/SiO₂ and SiO₂ catalysts (1.5 g dm⁻³).

sorption was found for the solutions of Sufapol-35 and car shampoo with wax and corresponding decrease of COD value was about 50%. Adsorption of Sulforokanol L-327 was considerably smaller and COD decrease was about 20%. The profound deviations of time-dependent adsorption curves were found for car washing shampoo. Because this commercial product is a mixture of many different chemical compounds, their affinity toward titania surface differs considerably and at the beginning COD value significantly drops down to about 30% of initial value reaching a minimum of 0.5 h. The longer adsorption time considerably restores COD value of solution that seem to indicate the replacement process on TiO₂ surface. Probably the adsorbed long molecules are replaced by much shorter ones, which would explain the experimental findings. This co-adsorption and replacement phenomena on silica is similar to that observed for titania. The final effect observed after 5 h for Surfakanol was 11% and Cleentex about 12% and the minimum occurred after 2h. The comparison of adsorption effects for solutions of Cleentex and Sulforokanol L-327 detergents is presented in Fig. 10.

The above experiments show that photo-oxidation of detergents occurs with good efficiency. The analogical conclusion was drawn earlier from the investigations carried out with nonionic detergent Triton X-114 dissolved in water [24]. Similar behavior was observed during photodecomposition of surfactants present in dye and washing sewage [25]. Rather small decreases of COD values of model solutions and sewage confirmed the fast first stage of detergent decomposition but the total degrees of oxidation were much smaller than 100%, indicating only partial decomposition of organic compounds. For Sulforokanol and Cleentex solutions the decrease of COD values was in the range 20-30% after 5 h decomposition of solution exposed for light radiation of 8 W lamp. Such results confirm the affinity of these commercial detergents for photo-oxidation. The degree of solution mineralization expressed as COD parameter change in the range of a few tens of percent, which confirms the stability of the compounds being the end products of de-

tergent photodecomposition. Those organic compounds can result from reactions between the intermediate complexes and several additives present in commercial detergent composition.

In the course of photo-catalyst experiments efficiency, the optimum 1.5 g dm⁻³ loading of TiO₂ in aqueous suspension of catalyst powder and detergent solution was established. The COD and TOC parameters are not influenced very much by titania content in a photo-catalytic system but too large load of catalyst leads to the decrease of suspension transparency, which determines the concentration of radicals in decomposed solution.

The solution acidity strongly affects photo-catalytic efficiency. In the case of Cleentex solution the best results were obtained for pH value in a weakly basic range and for pH=8.9, COD value reduction was about 97%, whereas TOC value only diminished about 26%. The largest decrease of TOC value (about 41%) was measured for weakly acidic solution, pH=5.2. For starting aqueous solution of Cleentex with pH=9.86 the change of both COD and TOC values was about 20% and strongly depends on acidity. The considerable changes of solution acidity can strongly affect the mutual interaction between buffer additives and the ingredients of commercial detergents. Additionally, the considerable change of hydrogen ions concentration may influence the accuracy of measurements, especially when the COD and TOC values do not change very much.

The final results of TiO₂-assisted photodecomposition of aqueous solution of detergent appeared different after a 5 h process. The reduction of COD values was in the range 30-61% depending on the kind of commercial detergent and the process conditions. In general the reduction of TOC parameter was in the same range from 25 up to 58%. Not very useful was the reduction of BOD₅ parameters being in the range of 64 up to 84% because such a considerable decrease indicates rather low affinity of biological degradation.

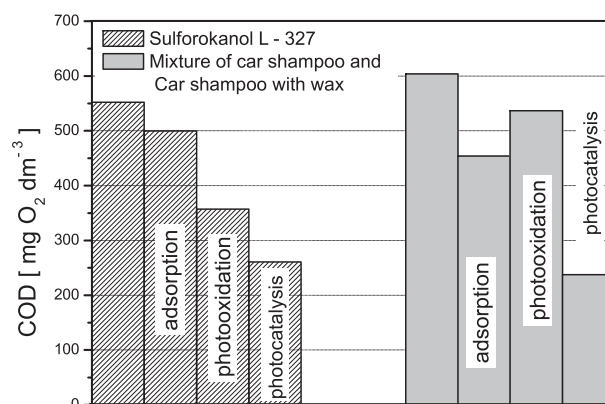


Fig. 11. The comparison of adsorption, UV photo-oxidation (without TiO₂) and UV photo-catalytic oxidation on TiO₂ (1.5 g dm⁻³), expressed as COD values obtained after 5 h process for water solution of Sulforokanol and mixture of car shampoo and car shampoo with wax (lamp 8 W, time of reaction 5 h).

The evaluation of percentage contribution of adsorption, photo-oxidation and TiO₂-assisted photo-oxidation into the total decomposition process is presented in Fig. 10 for Sulfarokanol and the mixture of two shampoos with and without wax. The comparison is illustrated by adequate changes of COD values. Rather clear differences can emerge from these results. The final decomposition is similar for both detergent solvents, although the contribution of adsorption and COD change in TiO₂ photo-catalytic process for Sulfarokanol L-327 are lower. The presented COD results can be ambiguously representative describing the complicated process of TiO₂-assisted photodecomposition of commercial detergents. Photo-oxidation does not take place in exactly the same conditions as during catalytic photo-oxidation. Although the amount of absorbed radiation can be slightly different but most light radiation is dispersed on titania grains in TiO₂-UV oxidation. And the adsorbed molecules of detergent undergo oxidation on catalyst surface or they can desorb into liquid phase. Despite this obvious limitation the photo-catalytical process is dominant in detergent decontamination.

The considerable increase of UV lamp light radiation power from 8 to 150 W does not reflect desirable increase of photo-catalytic yield of oxidation process. On the bases of actinometrical measurements the calculated increase of electric power about 19 times leads only to about 13 times higher efficiency of light emission. The increase of photo-oxidation yield is even about 2.5 times lower referring to COD values and 2 times lower for TOC values. The powerful UV lamp loses considerable part of light emission energy in a rather unprofitable way.

The attempt to use TiO₂ deposited on silica as photo-catalyst support gave promising results of detergent oxidation. The use of a photo-catalyst consisting of 10% TiO₂/SiO₂ resulted in about 22% decrease of COD value whereas TiO₂ alone was about 16%. For comparison, the use of silica alone resulted in the reduction of COD value about 7% and this effect is attributed only to adsorption and UV oxidation (without TiO₂). The diminishment of TOC values was in the same range (18-21%) as COD values. Titania supported on silica photo-catalyst 10% TiO₂/SiO₂ has much higher surface area 320 m²·g⁻¹ in comparison with TiO₂ alone 49 m²·g⁻¹. Thus, it is possible to obtain high surface efficient photo-catalyst using only 10% of TiO₂. The removal of solid suspension is much easier in the case of silica-supported TiO₂ in comparison with TiO₂ requiring spin-drying. Much simpler technical solution would be needed in future practical application.

Conclusions

Titania assisted UV photo-catalytical oxidation is one of the alternative ways of detergent decomposition. At this stage of knowledge it is not possible to make the

objective economical analysis and the optimal version of chemical treatment of sewage produced by a car washing procedure. The main advantage of UV catalytic process is the lack of necessity in using strong oxidants like ozone or hydrogen peroxide and the possibility of catalyst activation by sun radiation. In this way the problem of reaction activation by expensive UV radiation would be solved. The construction of suitable photo reactor combined with sun batteries would make possible sewage decontamination with the use of sun radiation. The scale of installation and its efficiency would be proportional with the amount of produced sewage, usually during summer days.

The lack of hydroxyl group selectivity allows for the conclusion that effectiveness of the proposed method would not be limited by the kind of applied detergents. The changes of decomposition yield would be re-compensated by the time of process. The decontamination end parameters would make it possible to combine this process with household sewage and the final purifying in local, unmanned sewage purification set.

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