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 TiO$_2$-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.
– advanced oxidation processes [1-3]. Their common feature is an engagement of strong oxidation radicals $\text{HO}^\cdot$ evolved in different ways. Historically, the first application of TiO$_2$-assisted UV photo-catalysis was combined with water decomposition on titania electrodes and was reported in 1972 by Fujishima and Honda [4]. TiO$_2$-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 TiO$_2$ surface with radiation of minimum energy 3.2 eV photon (hv) can transfer an electron ($e^\cdot$) from the valence band of crystal into the conduction band, leaving an electron hole ($h^\cdot$). This energy is equivalent to photons with wavelength 388 nm. The activation of TiO$_2$ 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 ($h^\cdot$) and H$_2$O molecule or ‘OH’ group.

$$h^\cdot + H_2O \rightarrow H^+ + HO^\cdot \quad (1)$$
$$h^\cdot + OH^- \rightarrow HO^\cdot \quad (2)$$

Electron can react with adsorbed O$_2$(aq) generating O$_2^\cdot$, which additionally can give H$_2$O$_2$ and HO$^\cdot$:

$$O_2 + 2(e^\cdot) + 2H^+ \rightarrow H_2O_2 \quad (3)$$
$$H_2O_2 + (e^\cdot) \rightarrow HO^\cdot + OH^- \quad (4)$$

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

The adsorption of compounds on metal oxide surface (TiO$_2$, SiO$_2$) is strongly influenced by charge generation during dissociation of surface chemical groups or interaction with H$^+$ and OH$^-$ ions from the solution. For TiO$_2$ the mechanism is as follows:

$$H^+ + TiOH \leftrightarrow TiOH^+_2 \text{ at low pH} \quad (5)$$
$$TiOH \leftrightarrow TiO^+ + H^+ \text{ at high pH} \quad (6)$$

The surface of TiO$_2$ 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 ethoxy 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 ethoxy fat alcohols [21]. Detergent concentration was about 10 g·dm$^{-3}$.

3. Sulfapol 35 – (Organica Car SA, Łódź) contains sodium alkilbenzenesulfonic 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, ethoxy fat alcohols, Sulforokanol, 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 oksyethylen(3)sulfatedalcohol sodium salt C$_{12}$ – C$_{14}$, 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 N$_2$) method. TiO$_2$ catalysts were based on TiO$_2$ P25 produced by Degussa with phase composition, anatase 20% and rutile 80%. Silica support was obtained by sol-gel method used as a starting material.
tert toxysilicon(IV). Titania supported on silica – 10% TiO₂/SiO₂ catalyst was prepared by TiO₂ deposition on silica, suspended in hexane solution of titanium isopropyl alcohol, 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 (3 h) in oxygen stream. Silica (0.1 – 0.2 mm fraction) with surface area 430 m² 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 cm³ 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 dm³ 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 using a Hewlett Packard model Hp 8542 spectrophotometer. The chemical ferric-oxalic actinometer was applied and resultant Fe²⁺ 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 1.249·10⁻¹⁹ photons min⁻¹ dm⁻³, which corresponds to energy consumption equal to 4.532·10⁻²⁰ eV min⁻¹ dm⁻³ or 72.5 J min⁻¹ 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 1.91·10⁻¹⁴ photon min⁻¹ dm⁻³ which is equivalent to energy uptake 5.81·10⁻¹⁸ eV min⁻¹ dm⁻³ or 931 J min⁻¹ dm⁻³. In the range 250-350 nm the efficiency of photon emission were 5.73·10⁻⁹ and 50.5·10⁻⁹ photons min⁻¹ dm⁻³ for 8 i 150 W lamps, respectively. The yields at 254 nm are similar 4.85·10⁻⁹ and 5.62·10⁻⁹ photon min⁻¹ 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 O₃, H₂O₂ and UV. All analytical procedures were made according to Polish Legislative Norms.

Results

Three steps of TiO₂-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.

<table>
<thead>
<tr>
<th>Detergent</th>
<th>Concentration</th>
<th>COD</th>
<th>BOD₇₅</th>
<th>pH</th>
<th>TOC</th>
<th>BOD₇₅/COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Units</td>
<td>g dm⁻³</td>
<td>mgO₂ dm⁻³</td>
<td>mgO₂ dm⁻³</td>
<td></td>
<td>mg dm⁻³</td>
<td></td>
</tr>
<tr>
<td>Cleentex</td>
<td>12.5</td>
<td>345</td>
<td>160</td>
<td>10.9</td>
<td>111</td>
<td>0.464</td>
</tr>
<tr>
<td>Sulforokanol L-327</td>
<td>10</td>
<td>550</td>
<td>150</td>
<td>7.2</td>
<td>165</td>
<td>0.273</td>
</tr>
<tr>
<td>Sulfapol 35</td>
<td>10</td>
<td>685</td>
<td>208</td>
<td>7.2</td>
<td>224</td>
<td>0.304</td>
</tr>
<tr>
<td>Car shampoo</td>
<td>25</td>
<td>928</td>
<td>420</td>
<td>7.1</td>
<td>244</td>
<td>0.453</td>
</tr>
<tr>
<td>Car shampoo with wax</td>
<td>12.5</td>
<td>542</td>
<td>226</td>
<td>7.7</td>
<td>248</td>
<td>0.417</td>
</tr>
<tr>
<td>Cleentex + Car shampoo</td>
<td>12.5 + 12.5</td>
<td>665</td>
<td>380</td>
<td>10.1</td>
<td>219</td>
<td>0.572</td>
</tr>
<tr>
<td>Car shampoo + Car champ. with wax (1:1)</td>
<td>12.5 + 12.5</td>
<td>543</td>
<td>180</td>
<td>7.8</td>
<td>258</td>
<td>0.331</td>
</tr>
</tbody>
</table>
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 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.

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 m$^2$ 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-
kanol L-327 above 30% COD and 32% TOC, Sulfarol 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 TiO₂**

The optimalization of measurements referring to the influence of TiO₂ 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 TiO₂ Dose**

Four different TiO₂ suspensions were applied 0.5; 1.0; 1.5 and 2.0 gram per 1 dm³ of 12.5 g dm⁻³ Cleentex aqueous solution. The use of higher TiO₂ content was rather undesirable taking into account the efficiency of UV photo-catalyst and the economical point of view. The influence of TiO₂ 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 effects are observed, especially for higher loading of TiO₂ (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 cm³ 0.1 mol dm⁻³ HCl
- pH = 5.20 – applying NaCH₃COO + CH₃COOH buffer
- pH = 8.90 – applying glycin – NaOH buffer
- pH = 12.05 – addition of 20 cm³ 0.1 mol dm⁻³ NaOH

Photo-catalytic oxidation of applied buffers glycin – NaOH and NaCH₃COO + CH₃COOH (without surfactants) were examined in the same conditions. The changes of measured parameters are in Table 2.

![Fig. 5. The final changes of COD, TOC and BOD obtained during photo-oxidation of Cleentex water solution for different applied doses of TiO₂ (lamp 150 W, pH = 10.9, 5 h).](image)

![Fig. 6. The influence of pH on final changes of COD and TOC obtained during TiO₂ assisted photo-oxidation of Cleentex water solution (lamp 150 W, 5 h).](image)

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

<table>
<thead>
<tr>
<th>Parameters [units]</th>
<th>glicyn – NaOH buffer</th>
<th>NaCH₃COO + CH₃COOH buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD₁ [ mg O₂ dm⁻³ ]</td>
<td>1840</td>
<td>11410</td>
</tr>
<tr>
<td>COD₂ [ mg O₂ dm⁻³ ]</td>
<td>970</td>
<td>11290</td>
</tr>
<tr>
<td>TOC₁ [ mg dm⁻³ ]</td>
<td>1064</td>
<td>5027</td>
</tr>
<tr>
<td>TOC₂ [ mg dm⁻³ ]</td>
<td>968</td>
<td>4747</td>
</tr>
<tr>
<td>pH₀</td>
<td>8.95</td>
<td>5.20</td>
</tr>
<tr>
<td>pH₅</td>
<td>8.15</td>
<td>5.24</td>
</tr>
</tbody>
</table>
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 pro-
motion and inhibition effects was assumed.

The Influence of UV Radiation Intensity

The influence of UV radiation intensity on the effi-
ciency of TiO\textsubscript{2} assisted photodecomposition of the ex-
ample solution – mixture of Cleentex and car shampoo
is illustrated in Fig. 7. The comparison of photolysis effi-
ciency was made by applying two UV lamps 8 and 150 W.
Three parameters were recorded: COD, BOD, and TOC
after 5 h reaction time. About 19% and 47% decrease of
COD value were found for 8 and 150 W lamps, respec-
tively. The diminishments of TOC values were smaller by
about 12 and 18%, respectively. The decrease of BOD\textsubscript{5}
values was about 80% in both cases.

Photo-Catalytic Oxidation of Detergents

Titania assisted (1.5 g TiO\textsubscript{2} dm\textsuperscript{-3}) photo-catalytic ox-
diation of detergents (Sulforokanol L-327, Sulfapol-35,
car shampoo, car shampoo with wax and their mixture)
is illustrated in Fig. 8 as COD, BOD\textsubscript{5}, BOD\textsubscript{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\textsubscript{init}) and after 5 h (BOD\textsubscript{5}) and the ratio BOD\textsubscript{5}/BOD\textsubscript{init}
was calculated what can be used as a measure of biologi-
cal affinity for decomposition of surfactant.

The influence of catalyst types (TiO\textsubscript{2}, 10\%TiO\textsubscript{2}/SiO\textsubscript{2},
SiO\textsubscript{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\textsuperscript{-3} and applied 150 W ultraviolet lamp. The obtained
results both for 10\% TiO\textsubscript{2}/SiO\textsubscript{2} catalyst (320 m\textsuperscript{2}/g) and
TiO\textsubscript{2} alone (49 m\textsuperscript{2}/g) were 22 and 18%, respectively.
Time-dependent COD curve for silica (420 m\textsuperscript{2}/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\textsubscript{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 absorb on catalyst surface in a classical manner and
the adsorption equilibrium was established after 5-6 hours.
When the amount of TiO\textsubscript{2} was 1.5 g·dm\textsuperscript{-3} the highest ad-
Adsorption 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 TiO$_2$ 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 Surfarokanol 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 Surfarokanol 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 detergent 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 TiO$_2$ 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 Cleenex 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 Cleenex 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 TiO$_2$-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 BOD$_5$ parameters being in the range of 64 up to 84% because such a considerable decrease indicates rather low affinity of biological degradation.
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 decomposition. 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 diminish-ment 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.

Acknowledgements

This work was supported by KBN grant 7T09B10321

References


