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Application of Photocatalytic Oxidation in the Presence of TiO_2 in Small Sewage Treatment Plants

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Abstract: In many small rest centers, bungalows, including those located at the seaside, there are various facilities which during the holiday season generate highly concentrated sewage. An example may be car washes at gas stations, small sandwich bars, and camping sites. One of the possibilities of solving the problem of treating sewage generated in such places are small treatment plants which can operate periodically and are characterized by low running costs. This possibility is offered by a photocatalytic oxidation in the presence of titanium dioxide as a preliminary treatment process and the next biological treatment in a so-called household sewage treatment plant. In particular, it is suitable for strongly insulated areas. The stage of chemical oxidation was a subject of our research and was performed using model solutions of surfactants and commercially available car shampoos. Promising results of their degradation were obtained.

Keywords: Photocatalytic oxidation, titanium dioxide, sewage, surfactants

INTRODUCTION

In many small recreation centers situated, among others, at the seaside, various types of services which generate strongly concentrated sewage are provided during the holiday season. An example is car washes located at

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petrol stations, fast-food restaurants, and camping sites. Practically, all sewage is generated during the daytime in summer. Due to location and seasonal work, in most cases sewage produced there is not treated properly. Besides typical municipal pollutants, various types of surfactants are the main sewage component.

In general, surfactants do not belong to the compounds that are directly harmful for man and organisms living in water. Their negative impact is that they cause the solution of hardly water-soluble or insoluble toxic substances in water. By a decrease of the surface tension of water they induce foaming, which deteriorates the conditions of oxygen diffusion and decreases its concentration in water. This has a negative impact on the self-purification ability of water reservoirs and the development of biological life.

One of possible solutions to the problem of sewage treatment in these places are small treatment plants adjusted to periodic work at low operating costs. This possibility is provided by the application of a pretreatment method, i.e. a photocatalytic oxidation in the presence of titanium dioxide, and next, the biological treatment in the so-called household sewage treatment plants. The proposed solution needs practically no operating costs. It is particularly suitable to work in strongly insulated regions.

The photocatalytic process of oxidation in the presence of titanium dioxide belongs to the group of modern technologies of chemical sewage purification, and water treatment called an advanced oxidation process – AOP (13). Their common feature is to take advantage of the strong oxidizing properties of $HO^{\bullet}$ hydroxyl radicals produced in different ways. In a water solution, in the presence of oxygen, the $HO^{\bullet}$ radicals participate in non-selective chain reactions of oxidation.

Historically, the first application of photocatalysis with the use of TiO_2 referred to studies carried out by Fujishima and Honda on the decomposition of water on titanium dioxide electrodes (3). In 1976 Carey et al. published results of the photocatalytic decomposition of biphenyl and chlorobiphenyl in the presence of TiO_2 (1). A detailed description of the photocatalytic oxidation with the use of titanium dioxide can be found in many monographs (2, 6, 9, 10). Now, the photocatalytic oxidation gains importance in environmental protection because it enables efficient decomposition of many toxic compounds contained in sewage such as pesticides, freons, dyestuffs, phenol, and other pollutants and sewage (2, 4, 6, 9–11, 13, 14). Water solutions of various types of surfactants, both ionic and non-ionic, are also investigated extensively (5, 7, 8, 12).

The aim of our research was to verify the applicability of photocatalytic oxidation in the presence of titanium dioxide to decompose commercial preparations containing various types of surfactants and their mixtures. The results obtained in a laboratory system will be the starting point for constructing a flow system with a new type of a photochemical reactor, to further optimize the process by using modified TiO_2 and to check the possibility of integrating the photochemical process with biological treatment.

METHODS

The object of this research were solutions of detergents used most frequently in car wash facilities. The applied surfactant concentrations resulted from manufacturer's recommendations and solubility during washing.

The following solutions were used in the experiments: car shampoo at the concentration 0.25% vol.s; Cleentex at the concentration 0.125% vol. and a mixture of the surfactants; Cleentex at the concentration 0.0625% vol. and car shampoo at the concentration 0.125% vol.

Cleentex, a preparation for car washing, contains fourth-order ammonium compounds, alkyl-glycols, surfactants, sodium silicate, and other components according to the producer's documentation.

The car shampoo contains Sulfarokanol, diethylamide of coconut acid, betaine derivatives, sodium chloride, EDTA, and other components as listed by the producer. (Table 1).

Reactions were carried out in a Heraus photoreactor composed of a glass vessel 1000 cm^3 in volume equipped with a UV lamp placed in a water-thermostated quartz casing. The reactor was equipped additionally with a pipe with a microporous plate supplying oxygen to the solution. The flat bottom of the reactor enabled the use of a magnetic stirrer. 800 cm^3 of the tested solution was put in the reactor and a determined amount of TiO_2 was added. In all experiments the oxygen flow rate was 10 dm^3/h. The reaction temperature kept by the flow of cooling water in the UV lamp was about 20 C. The process was carried out for 5 to 8 hours.

The following determinations were made: pH, chemical oxygen demand—COD, biochemical oxygen demand—BOD_5 and dilute organic carbon – DOC. The DOC analysis was made using 7 cm^3 samples taken during the reaction. The sample size for the COD analysis was 25 cm^3. BOD_5 was determined only in the solution after completing the process. The solution prior to analysis was centrifuged (6500 rpm) and filtered to separate TiO_2. In all experiments titanium dioxide P-25 (Degussa) was used. All analyses were made based on Polish Standards, and the total amount of carbon was determined using a Shimadzu TOC-5000 Analyzer.

Table 1. Input data of detergent solutions and mixtures used in the experiment

Detergent	Concentration (% vol.)	COD (mgO_2/dm^3)	BOD_5 (mgO_2/dm^3)	pH	DOC (mg/dm^3)	BOD/COD
Cleentex	0.125	345	160	10.9	111	0.464
Car shampoo	0.25	928	420	7.12	244	0.453
Cleentex + car shampoo	0.125+0.25	665	380	10.1	219	0.572

RESULTS AND DISCUSSION

In studies on optimization of the photocatalytic oxidation, the effect of such parameters as TiO_2 photocatalyst doses, reaction time, pH of the solution, and lighting intensity was considered.

The Effect of the Reaction Time

The oxidation of Cleentex and a car shampoo was tested for up to 5 hours and their mixtures for up to 8 hours. Changes in COD and DOC of the solutions and BOD and pH after completing the reaction, were analyzed. The trials were made for a medium pressure 150 W lamp at the temperature 20 C. Fig. 1 shows the obtained results.

The experiments indicate clearly a very differentiated dependence of the decomposition degree on the detergent type and composition. The most degradable appeared to be the car shampoo solution. After 5 hours of the reaction, the COD was reduced by 62%, and a decrease of DOC was slightly lower, about 59%. Cleentex proved to be less degradable; DOC was reduced by about 21%, while COD by only 16%. The mixture of both the substances had average degradation yields. During all experiments a significant

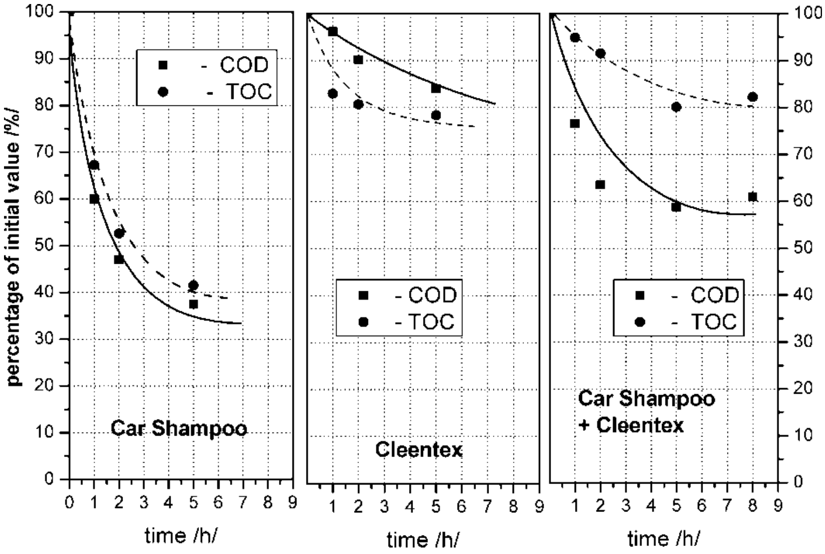

Figure 1. The effect of reaction time on COD and DOC reduction in car shampoo, Cleentex and their mixture during photocatalytic oxidation. The TiO_2 dose 1.5 g/dm^3, temperature 20°C, medium-pressure 150 W lamp. Input data of detergent solutions and mixtures used in the experiment are in Table 1.

reduction of BOD_5 and acidification of the solutions were observed. For instance, for Cleentex, the BOD_5 reduction was 70% and pH of the solution changed from 10.9 to 4.9.

The Effect of the Titanium Dioxide Dose

The results of studies on the optimization of photocatalyst doses are presented with reference to Cleentex, taking into account that it was hardly degradable. The experiments were carried out using a medium-pressure 150 W lamp characterized by a significant contribution of visible light in the emission spectrum. Four TiO_2 doses were applied, namely 0.5, 1.0, 1.5, and 2.0 gram per 1 dm^3 of the solution. The use of bigger photocatalyst doses was not recommended mainly for economic reasons and because of the degree of photocatalyst utilization when the process was carried out in a slurry.

Only a slight effect of the photocatalyst dose on the oxidation yield was observed, mainly in the case of small doses (0.5 and 1.0). Practically, a further increase of the amount of photocatalyst does not improve the yield of the Cleentex degradation. An optimum dose in the reaction conditions was $1.5\ g/dm^3$. This result is in agreement with literature data, where the optimum TiO_2 doses for the reaction carried out in a slurry, range from 1.5 to $3.5\ g/dm^3$, depending on the photoreactor structure as well as the type and concentration of the oxidized compound (Figure 2).

The Effect of pH of the Solution

Taking as an example the solution of Cleentex at the concentration of 0.125% vol., the effect of pH of the medium on the photocatalytic degradation was investigated. Experiments were made with the use of the 150 W lamp. The COD and DOC reduction was attained by subtracting the value obtained in the photocatalytic oxidation of the applied buffer from that achieved in the photooxidation of surfactants (at a given pH).

The following pH values of the initial solution were used:

pH = 2.51 by adding the solution of 0.1 mol/dm^3 HCl
pH = 5.20 by using an acetate buffer
pH = 8.90 by using a glycine–NaOH buffer
pH = 10.9 by using in the experiments a natural solution without any additives
pH = 12.05 by adding a solution of 0.1 mol/dm^3 NaOH

The main difficulty in studies on the effect of pH on the decomposition of various compounds is the selection of adequate buffers and lack of interactions between compounds present in the solution. Naturally, it is assumed that all

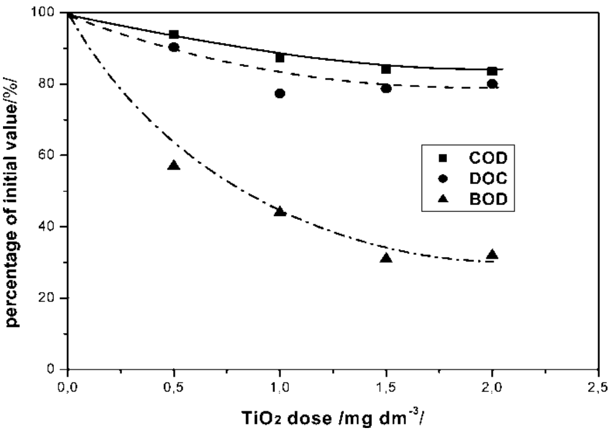

Figure 2. Changes of COD, DOC and BOD_5 in the Cleentex solution induced by photocatalytic oxidation at different TiO_2 doses. Reaction time 5 hours, medium-pressure 150W lamp, initial natural pH 10.9, temperature 20°C. Input data of detergent solutions and mixtures used in the experiment are in Table 1.

factors in oxidation processes are independent, i.e. there are no inhibiting or promoting effects. In all five cases, the reaction was observed for 5 hours. During the reaction, in all cases the solution was acidified. The highest acidification was reported in the case of the natural Cleentex solution. Figure 3 shows a comparison of results.

Photocatalytic oxidation of Cleentex is most efficient in weak alkaline and strongly basic solutions. The COD reduction is very high reaching 96% at pH 8.9 and 64% at 12.05. The DOC reduction is much lower, which thereby provides an evidence of low mineralization of the solution. In acid solutions, Cleentex is poorly degraded. The COD reduction is 20 to 30%. In the case of a solution with natural pH equal to 10.9, we also observe a small yield of Cleentex degradation. Lack of pH stabilization (no other buffer was used) results in the solution getting acidified quickly to 4.9. So, the reaction takes place practically in the acid solution and hence the COD reduction is so low. The process of degradation should be carried out in neutral or weak alkaline solutions.

The Effect of Light Intensity

The photo-oxidation process was tested using two lamps: a 8 W UV low-pressure lamp and 150 W medium-pressure lamp.

The 8 W medium-pressure lamp emits light in the range of 254-578 nm at the yield $1.249 \cdot 10^{20}$ quantum/min dm^3 which corresponds to the absorbed energy equal to $4.532 \cdot 10^{20}$ eV/min dm^3, i.e. 72.5 J/min dm^3

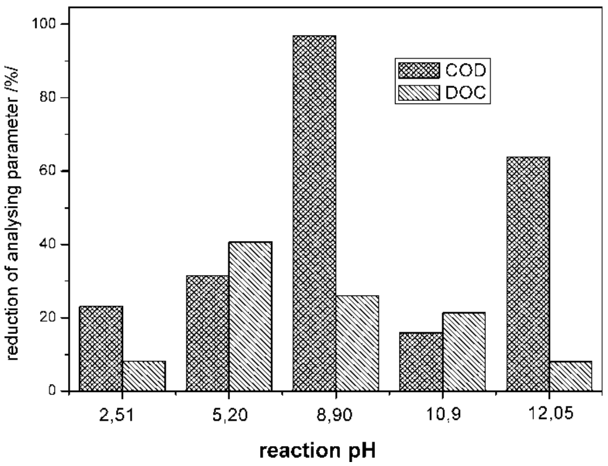

Figure 3. The effect of pH of the solution on COD and DOC changes in Cleentex solution induced by the photocatalytic oxidation. Reaction time 5 hours, TiO_2 dose–1.5 g/dm^3, 150 W lamp, temperature 20°C. Input data of detergent solutions and mixtures used in the experiment are in Table 1.

(1.21 W/dm^3). The number of quantum of length below 310 nm is 41.2%, while of that below 400 nm reaches 52.6%. A maximum emission occurs at 254 nm.

In the case of the 150 W medium-pressure lamp emitting light at the wavelength 254 to 578 nm, the amount of absorbed light was $2.38 \cdot 10^{21}$ quantum/min dm^3 which corresponded to absorbed energy equal to $7.27 \cdot 10^{21}$ eV/min dm^3, i.e. 1163 J/min dm^3, or in other words 19.39 W/dm^3. The number of quantum with length below 310 nm is 10.8%, while that below 400 nm amounts to 36.7%. A maximum emission is at 366 nm.

Taking the Cleentex and car shampoo mixture as an example, the photocatalytic oxidation in the presence of TiO_2 induced by the light emitted by 8 W and 150 W lamps is compared. Figure 4 shows the reduction of COD, DOC, and BOD_5. As can be observed, after 5 hours of the reaction, a 19% COD reduction was obtained in the case of the 8 W lamp and 47% for the 150 W lamp. A decrease of DOC was smaller reaching 12 and 18%, respectively. The reduction of BOD_5 did not differ significantly in both cases and was ca. 80%.

Light intensity significantly affects the yield of photocatalytic oxidation. However, quantitatively, this effect is very different, much higher for the solutions of car shampoo and its mixture with Cleentex and smaller in the case of Cleentex solutions. This is visible mainly in relation to changes of COD and DOC of the solution. The reduction of BOD_5 does not depend on it so strongly. Much higher increase of the UV lamp power does not provide expected results of the process yield growth. A possible explanation

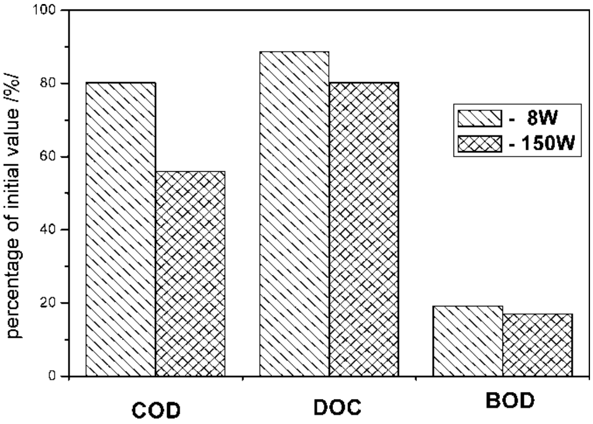

Figure 4. Comparison of changes in COD, DOC, and BOD_5 of the Cleentex solution induced by the photocatalytic oxidation with the use of two different light sources: 8W and 150W lamps. Reaction time – 5 hours, TiO_2 dose – 1.5 g/dm^3, temperature 20°C. Input data of detergent solutions and mixtures used in the experiment are in Table 1.

is that with higher light intensities higher recombination rates (photogenerated electrons/holes) take place. From actinometric measurements it follows that when electric power is increased by 18.75 times, the amount of emitted light grows only by 12.3 times. An increase of the yield of oxidation process is much lower being only a dozen percent, so at high-power UV lamps major part of light is not used for the initiation of a degradation reaction.

Type of the Catalyst

Within this research project a possibility of multiple use of the catalyst was checked by using it three times. The yield of photocatalytic oxidation lasting for 5 hours with the use of the 150 W lamp was investigated taking as an example the car shampoo. With each and every reaction the shampoo was filtered off, but not eluted, and then it was reused. A significant decrease of the photocatalytic oxidation was observed at the third use of TiO_2. The reduction of COD of the solution was lower by 18.16% than in the case when the catalyst was used for the first time.

A possibility of using titanium dioxide deposited on silica in the amount of 10% - $SiO_2/10\%TiO_2$ was also checked. A subject of experiments was the Cleentex solution. Comparing the yield of degradation in 5 hours a slight increase of the COD reduction (22%) was observed as compared to the use of pure titanium dioxide. The DOC reduction on both catalysts was similar reaching around 18%. This follows undoubtedly from a significant extension of the photocatalyst surface. For this catalyst the specific surface is 320 g/m^2, and for pure TiO_2 – 49 g/m^2, while for SiO_2 – 420 g/m^2.

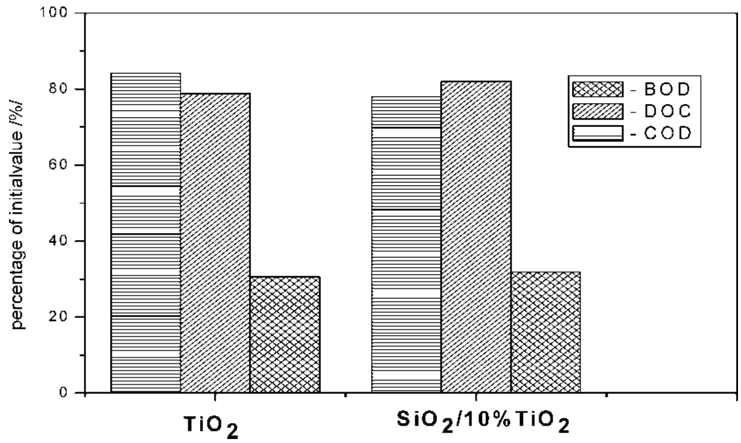

Figure 5. Comparison of changes in COD, DOC, and BOD_5 of the Cleentex solution induced by the photocatalytic oxidation with the use of two different catalysts: pure titanium dioxide – TiO_2 and titanium dioxide deposited in the amount of 10% on silica – $SiO_2/10\%TiO_2$. The reaction time – 5 hours, catalyst amount – 1.5 g/dm^3, temperature 20 C, 150W lamp. Input data of detergent solutions and mixtures used in the experiment are in Table 1.

The obtained result is very promising because despite a slight increase of the surfactant reduction, the application of the catalyst consisting of 10% TiO_2 deposited on silica enables a significant simplification of the process technology and a decrease of titanium dioxide doses (Figure 5).

CONCLUSIONS

The most susceptible to photocatalytic degradation with the use of TiO_2 appeared to be the solution of car shampoo. The solution of Cleentex was photocatalytically oxidized at a much slower rate. It was interesting to note that the reduction of DOC higher by 6%. The mineralization of the Cleentex solution at low reaction degrees was faster than the decrease of oxidisability of the solution. Hence, at the initial stage first of all simple compounds are oxidized which has an effect on the reduction of DOC. As can be expected, the reduction of indices for the car shampoo and Cleentex mixture was average as compared to the values obtained for both the components. During the photocatalytic oxidation with the use of TiO_2 a decrease of biodegradability was observed. This is a negative effect from the point of view of biological treatment of surfactants.

The reaction medium appeared to be an important factor in the process of photocatalytic oxidation. The highest degree of COD reduction was attained in a weak basic medium. In all cases of the photocatalytic degradation of surfactants a decrease of pH value was reported. This means that in the process low-molecular carboxyl acids are formed.

A multiple application of TiO_2 in the photocatalytic oxidation of surfactants is not recommended. Already at the third use of TiO_2 a significant decrease of the photocatalyst activity is observed. Although the use of a catalyst in the form of titanium dioxide deposited on silica gives slightly better results of detergent degradation, it enables a significant simplification of technology of the process carried out in a slurry and great savings of TiO_2.

Further studies are necessary to carry out reactions in flow photoreactors in which solar energy can be used. During the process, the pH of the solution should be corrected to slightly basic which will make it possible to increase remarkably the efficiency of oxidation processes. It is also necessary to check the possibility of biological treatment of the oxidized sewage, particularly after mixing it with municipal sewage. It seems that a very important factor will be an adequate selection of the degree of photochemical sewage degradation prior to biological treatment.

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