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PREPARATION AND CHARACTERIZATION OF TITANIA COATING USED AS A PHOTOACTIVE REFILL IN THE PROCESS OF WATER PURIFICATION

The aim of the present work was to characterize the photoactive refill used in the process of photocatalytic decomposition of organic dye (Acid Red 18) in water. Titanium dioxide was immobilized on the base material as a thin layer from the alcoholic suspension followed by thermal stabilization. The prepared coating exhibited high stability in repeated cycles of water treatment. The photoactive refill was characterized not only by the activity tests but also by XRD, FTIR and UV/Vis - DRS. The amount of titanium dioxide immobilized on a glass fabric support was determined as well. The reactor with photoactive refill solves the problem of the replacement of the reactor or its parts when the photocatalyst activity decreases.

1. INTRODUCTION

The development in the field of chemical water purification stimulates an improvement in the oxidative degradation processes applying catalytic and photochemical methods. They are known as advanced oxidation processes (AOPs). AOPs are able to deal with the problem of organic pollutant destruction in aqueous systems [1]–[10]. Advanced oxidation processes are based on in situ generation of highly reactive species, mainly $HO^{\bullet}$, by using solar, chemical or other forms of energy. These strongly oxidizing agents allow destruction of a wide range of organic chemical substrates with no selectivity. Of the various AOPs employed in water treatment, heterogeneous semiconductor photocatalysis is an emerging technology with key advantages such as operation under ambient conditions and a possible use of solar irradiation. Titanium dioxide has essentially proved itself to be the best material for environmental protection because of its many desirable properties. TiO_2 is a cheap, readily available material capable of oxidizing a wide range of organic pollutants to harmless compounds.

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The photocatalytic processes can be carried out with the catalyst either suspended in the solution or immobilized. These configurations have both advantages and disadvantages. Photocatalytic reactors with the suspended catalyst allow the photocatalyst and the dissolved impurities to come into much closer contact compared with that in the reactors with the immobilized catalyst. The advantage of water suspension is that a big surface area of a photocatalyst is suitable for a photocatalytic reaction. However, in this case the photocatalyst should be separated from the reaction mixture after the process is completed. Removal of the catalyst from the reaction mixture is an additional step in the process that increases its costs. Different researchers have tried to minimize these problems by immobilizing TiO_2 on various solid supports or on the reactor walls, which eliminates arduous step of separation [11]–[18]. Immobilization of the photocatalyst on the reactor walls or on its other parts shows its disadvantages when the activity of the catalyst decreases and it has to be replaced. Thus, the better solution is to immobilize the photocatalyst on the replaceable elements that can easily be removed and placed again in the reactor. Such supports have the other advantages of providing a good contact of the treated medium with the photocatalyst surface and also of allowing deeper light penetration into the reactor. A flexible textiles seemed to be an adequate support for the photoactive titania coatings. However, textiles as organic materials can undergo the photocatalytic degradation themselves.

The aim of the present work was to characterize the photoactive refill prepared by immobilizing titanium dioxide on the base material as a thin layer made of alcoholic suspension followed by thermal stabilization. A glass fabric was applied as the support for the titania coating.

2. MATERIALS AND METHODS

The anatase form of titanium dioxide produced by Chemical Factory “Police” (Poland) was used as a photocatalyst. The support for titania photoactive coating was a glass fabric. The photoactive coating was prepared as follows: a piece of glass fabric with dimensions of about 19 cm × 24 cm was immersed in the ethanolic suspension of TiO_2 (5% by weight) for 30 seconds followed by drying for 1 hour at the temperature of 105 °C. After cooling, the fabric was reimmersed in the ethanolic suspension of TiO_2, dried and then placed in the furnace at the temperature of 150 °C for 24 hours. The glass fabric with coating was a photoactive refill placed in the reactor where water purification took place.

Acid Red 18 (AR18) produced by Chemical Factory “Boruta-Kolor” (Poland) was used as a model organic compound. AR18 belongs to the group of azodyes with a light fastness equal to 4 (8-grade ISO Blue Wool Scale). The chemical structure of AR18 is presented in figure 1. The process of photocatalytic oxidation of AR18 was conducted using a laboratory installation (figure 2) whose main component was the flow reactor (Trojan Technologies, Canada) with a photoactive refill. The mercury lamp emitting UV radiation in the range of 250–800 nm, with high maximum at 254, 436 and 546 nm, was placed inside the reactor, in its center. The photoactive refill was also placed inside the reactor in such a way as to stick the inner walls of the reactor. The excess of the immobilized photocatalyst was rinsed with the water flowing through the reactor before photocatalysis, so only a thin layer of the photocatalyst remained on the fabric.

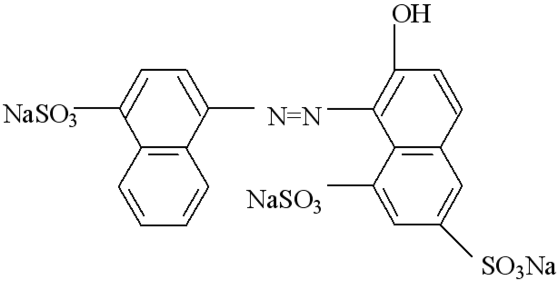

Fig. 1. Chemical structure of Acid Red 18

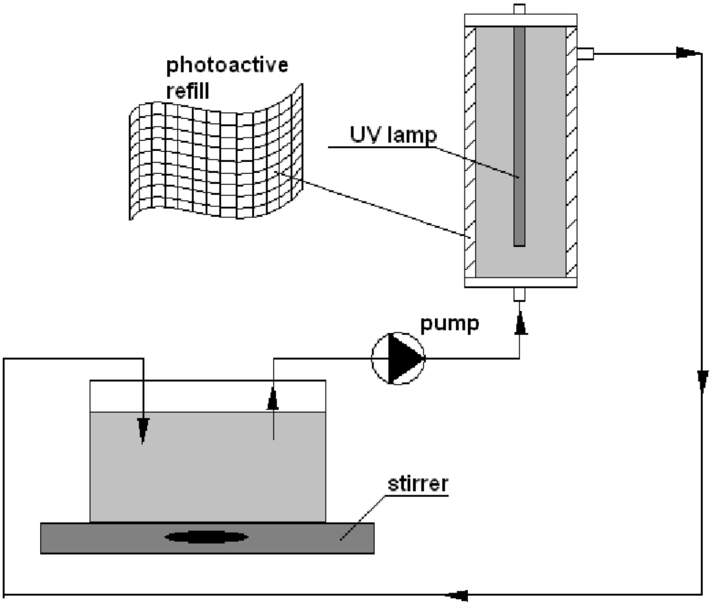

Fig. 2. Scheme of installation for photocatalytic oxidation of AR18

The photoacatalytic decomposition of a model organic compound, monoazo dye Acid Red 18, was carried out in order to determine the photocatalytic activity of titania photoactive coating. The solution of AR18 was pumped to the reactor by peristaltic pump from the container and then circulated through the reactor with the flow rate of 36 dm^3/h until the solution became colorless. The solution of dye circulated in the reactor for 15 minutes without illumination to reach the adsorption equilibrium. The adsorption of dye onto photocatalyst surface was poor, even less than 1% (by weight).

The changes of dye concentration in the solution were determined by absorbance measurement at the maximum absorption wavelength of 507 nm (Jasco V-530 spectrometer, Japan).

3. RESULTS AND DISSCUSION

3.1. CHARACTERISTICS OF PHOTOACTIVE REFILL

XRD, FTIR, UV-Vis/DRS and flatband potential measurements were carried out in order to identify any possible change in the properties of titanium dioxide during the thermal treatment used for the preparation of the photoactive refill. Thermal treatment can influence the phase composition, crystalline structure, surface properties and bandgap energy of photocatalytic materials. These properties are important since they determine the catalyst photoactivity.

3.1.1. XRD

The phase composition of photocatalyst and crystallite size were determined by XRD method using X'Pert PRO diffractometer with CuKα (35kW, 30mA) lamp irradiation. The diffraction patterns were collected in the range of 10–80° 2Θ. A particular reflex was assigned to adequate phase by comparing their position with the standards (Join Committee on Powder Diffraction Standards cards). The crystallite size was determined according to the Scherrer equation:

$$D = \frac{\lambda}{\beta \cos \theta},$$

where:

D – crystallite size,
λ – radiation wavelength ($\lambda = 1.54051$ for copper lamp),
β – line broadening at half the maximum intensity (FWHM),
θ – Bragg angle.

The analysis of the results shows that the materials are composed of two phases: anatase and rutile, and the anatase phase is predominant. Thermal stabilization of the photoactive coating at the temperature of 150 °C does not cause any changes in the crystalline structure of the materials analyzed. The diffraction spectra of fresh and thermally treated TiO_2 used in the studies are practically the same which can be observed in figure 3. The crystallite size determined according to the Scherrer method equals 9.4 and 9.0 nm for fresh and thermally treated materials, respectively.

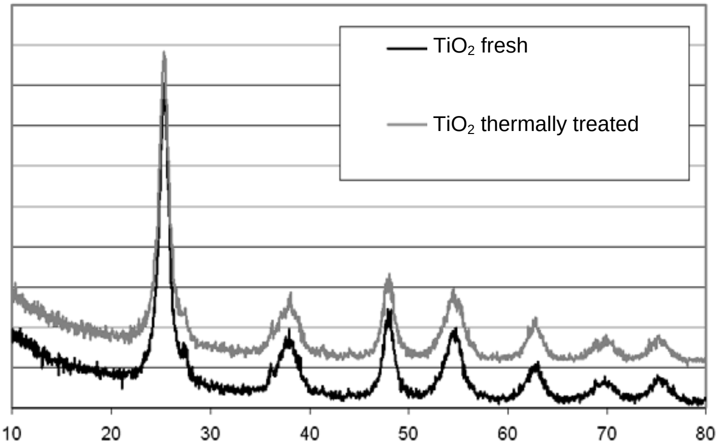

Fig. 3. Diffraction spectra of fresh and thermally treated TiO_2 used in the studies

3.1.2. BANDGAP ENERGY AND FLATBAND POTENTIAL MEASUREMENTS

UV/Vis DRS method was used to determine the bandgap energy of photocatalytic materials. Diffuse reflectance spectra were collected with Perkin-Elmer Lambda 12 spectrophotometer, equipped with 5-cm dia. integrating sphere. The samples were ground with barium sulphate in an agate mortar in the ratio of ca. 1:25 (w/w). Barium sulphate was also used as a reference. Spectra were transformed according to the Kubelka–Munk function. In order to calculate the bandgap energies of the titania samples, the transformation, appropriate for indirect bandgap semiconductors, was applied (figure 4). The fresh material (JGD1) shows a slightly lower E_g value equal to 3.26±0.03 eV as compared with that of thermally treated material (JGD2) – 3.30±0.03 eV. The latter sample is slightly grey and shows a weak, broad absorption band extending from 700 to 800 nm.

Flatband potential measurements (i.e. the measurements of the potential of the lower edge of the conduction band or the so-called quasi-Fermi level potential) were performed according to the method described by ROY et al. [19] and developed by MACYK et al. [20]. The method is based on the pH-dependence of the flatband potential of TiO_2: $E_{fb}(\text{pH}) = E_{fb}(\text{pH} = 0) - k\,\text{pH}$, where $E_{fb}(\text{pH})$ is the flatband potential at a given pH and k is a factor, usually equal to 59 mV.

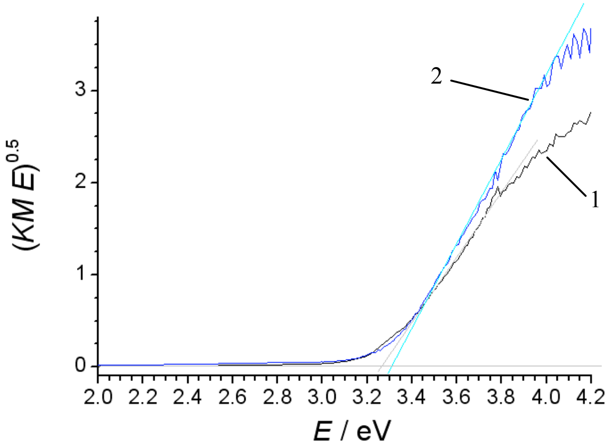

Fig. 4. Transformed diffuse reflectance spectra of indirect bandgap semiconductors, $(KM \times E)^{1/2}$ vs. λ
1 – JGD1 (3.26 eV), 2 – JGD2 (3.30 eV)

Flatband potentials were determined in the cell illuminated by the XBO-75 lamp. The cell was filled with 50 cm^3 of KNO_3 solution (0.1 mol/dm^3) containing 25 mg of the photocatalyst and 15 mg of $MV(PF_6)_2$. The suspension was stirred and purged with argon prior and during the measurement. pH was adjusted with HNO_3 and NaOH solutions and monitored with pH-meter. Large-surface platinum plate was used as a working electrode and Ag/AgCl as the reference one. The method was based on the measurements of voltage between these electrodes upon irradiation as a function of pH.

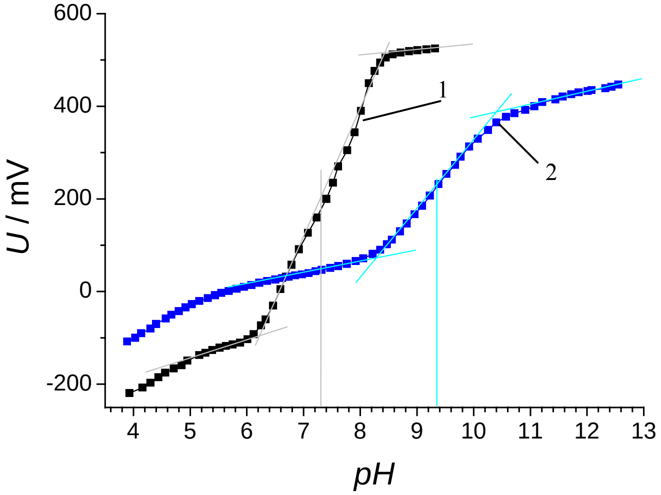

Fig. 5. Titration curves recorded for TiO_2 suspensions in 0.1 M KNO_3 in the presence of MV^{2+}
1 – JGD1 (pH_0 = 7.3), 2 – JGD2 (pH_0 = 9.3)

The results of the sample measurements are shown in figure 5. Inflection points correspond to pH_0 values of 7.3±0.2 and 9.3±0.2 for JGD1 and JGD2, respectively. The flatband potentials at pH = 7 are –0.43±0.01 V and –0.31±0.01 V vs. NHE for JGD1 and JGD2, respectively.

3.1.3. FTIR

FTIR method was used to determine the surface properties of photoactive materials. The FTIR spectra were collected with Jasco spectrometer equipped with Harric attachment for diffuse reflectance studies.

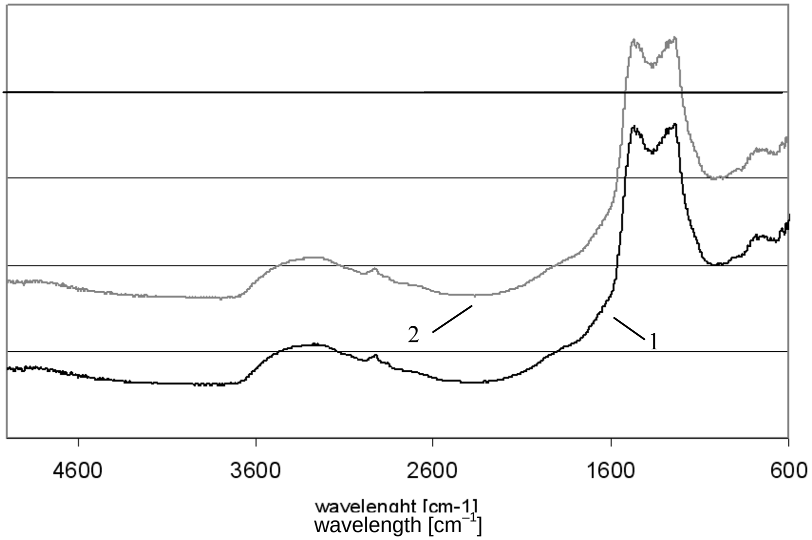

Fig. 6. FTIR spectra of fresh and thermally treated photoactive coating
1 – fresh, 2 – thermally treated

Figure 6 shows FTIR/DR spectra of fresh and thermally treated photoactive coating. The analysis did not show any significant changes on the surface of the materials analyzed.

3.1.4. DETERMINATION OF TiO_2 AMOUNT IMMOBILIZED ON THE GLASS FABRIC

The amount of titanium dioxide immobilized on the glass fabric was determined according to the procedure described below. The photoactive refill was cut into small fragments with specified dimensions. The pieces of fabric were placed in a weighed evaporating dish together with ethanol and sonicated for 1 h in order to remove titanium dioxide particles from the fabric. After that the pieces of fabric were removed from the suspension of TiO_2 in ethanol and after evaporation of alcohol the dish was weighed again. This procedure was repeated four times. On the basis of these analyses the amount of titanium dioxide immobilized on the glass fabric was found to be 1 g/m^2.

The amount of TiO_2 on the spent refill used for the photocatalytic decomposition of AR18 in water was analysed as well. The material subjected to analysis originated from the refill used in 11 tests of the photocatalytic decomposition of AR18 in water. The activity of this refill was about 2-fold lower than that of the fresh one. Washing out of the photocatalyst from the glass fabric support was considered to be a reason for the activity drop. The analysis results showed that the amount of photocatalyst on the spent fabric was higher compared with that on the fresh one and equal to 1.1 g/m^2. This result may suggest that on the photocatalyst surface the deposits are formed. In order to confirm this suggestion, the photocatalyst removed from spent fabric was subjected to FTIR analysis. Since the amount of titanium dioxide on spent fabric did not decrease it can be inferred that the photoactive coating is stable. A decrease in photocatalytic activity was probably the result of deposition of decomposition products on the surface of the photocatalyst. Figure 7 shows the spectra of fresh and spent photocatalysts. The spectrum of a spent material shows evident absorption bands in the range of 1510–1340 and 3032–2840 cm^{-1}. These bands can be assigned to –C=O and $–CH_3$ groups on the surface of the photocatalyst [21], [22]. Hence, the results of FTIR analysis confirm that on the photocatalyst surface the deposits are formed.

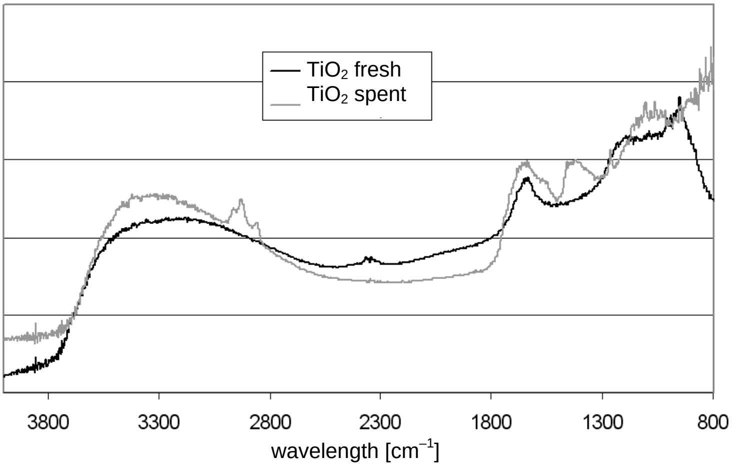

Fig. 7. FTIR spectra of fresh and spent photocatalyst

3.2. PHOTOACTIVITY TESTS

The photocatalytic degradation of dyes was carried out for their initial concentration equal to 10 mg/dm^3. The volume of the treated solution was 2.5 dm^3.

At the beginning of the studies, blank experiments were performed. Blank tests conducted in the dark revealed no discoloration of the dye solutions. A direct photolysis was also negligible. The reactions of photocatalytic decomposition of dye were conducted until the solution became colourless.

The changes in dye concentrations were monitored by UV/Vis spectroscopy. Discoloration of the solutions during the process is the result of a decrease in dye concentration and also the cleavage of –N=N– bonds which determine the colour of azo-dyes. Figure 8 presents the spectra of dye solutions recorded during the photocatalytic process. As can be seen, the decay of both UV and Vis region absorption bands is observed during the photocatalytic process, indicating a decrease in the concentration of aromatic units and chromophore groups containing azo unit in the solution.

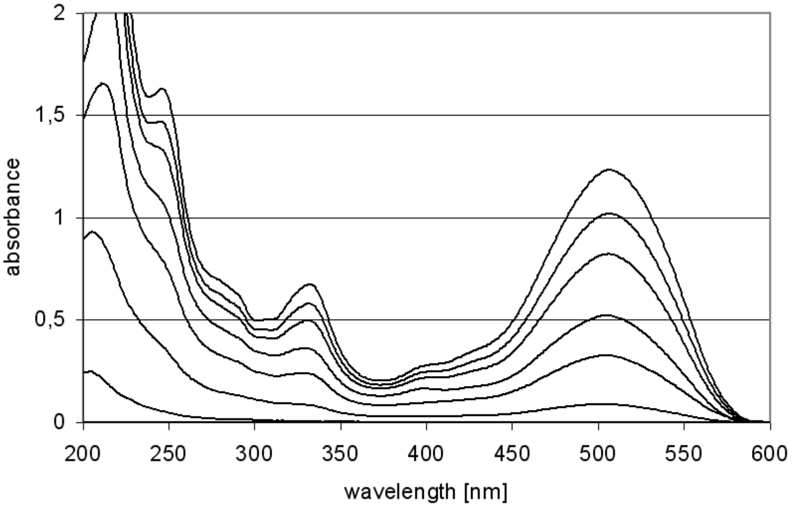

Fig. 8. UV/Vis example spectra of AR18 solutions recorded during photocatalytic process; initial concentration – 10 mg/dm^3, reaction time – 13 h, from top to bottom: 0 h, 2 h, 4 h, 6 h, 8 h, 10 h, 12 h, 13 h

Figure 9 presents the changes in dye concentration during the photocatalytic process for the four tests performed with the same photoactive refill. The dye concentration decreases with the time of the process. The colour removal is most effective during the first hours of the process. Thereafter its rate decelerates; however, the complete discoloration of the solution was achieved. During the first test a complete discoloration of the solution was observed in a relatively short time of 13 hours. In the second test, the time of complete colour removal was only slightly longer – 14 hours. The third and fourth tests showed the same time of discoloration as the second one.

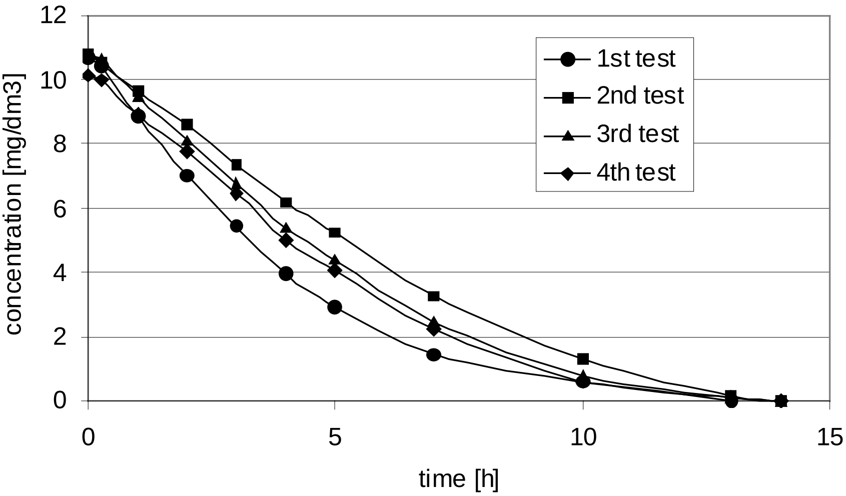

Fig. 9. Changes in dye concentration during photocatalytic process

Starting from the fifth test, the photocatalytic activity of titania coating began to decrease gradually. During the eleventh test, the time of discoloration of the dye solution was doubled – it took 30 hours to obtain the colorless solution. Concluding, it can be stated that the lifetime of the photoactive refill is about 200 hours and after that time the refill should be replaced with a new one.

4. SUMMARY

The preparation of the titania coating from the ethanolic solution followed by thermal stabilization gives a durable binding of titania to the glass fabric. In our studies, the mild conditions of the preparation do not affect significantly the properties of titanium dioxide. Simultaneously, the low temperature of 150 °C used for the thermal stabilization of the coating appeared to be sufficient to give a strong immobilization of titania on the glass support.

The results of the studies revealed that the titania coating shows a high photocatalytic potential for the decomposition of the model organic compound (Acid Red 18) in water. The coating prepared exhibits high stability in repeated cycles of water treatment. The photoactive refill in the reactor allows its continuous work without the necessity of replacing reactor or its parts. When the photocatalyst activity decreases, only the photoactive refill can easily be replaced. The application of glass fabric is advantageous since it is resistant to UV radiation and, contrary to the natural fabrics, it does not undergo any photocatalytic decomposition.

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