Research Article

Immobilized TiO₂ for Phenol Degradation in a Pilot-Scale Photocatalytic Reactor

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Received 4 June 2012; Accepted 6 September 2012

Academic Editor: Wenhong Fan

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Phenol degradation was carried out in a photocatalytic pilot plant reactor equipped with a UV/vis mercury lamp. The total volume of treated water was equal to 1.35 m³. TiO₂ P25 was used as a photocatalyst and it was immobilized on two different supports: (i) a steel mesh and (ii) a fiberglass cloth. Moreover, the performance of commercially available Photospheres-40 was examined. In addition, an experiment in the absence of a photocatalyst was conducted. The commercially available Photospheres-40 were found to be inadequate for the presented application due to their fragility, which in connection with vigorous mixing and pumping led to their mechanical destruction and loss of floating abilities. The highest effectiveness of phenol decomposition and mineralization was observed in the presence of TiO₂ supported on the fiberglass cloth. After 15 h of the process, phenol and total organic carbon concentrations decreased by ca. 80% and 50%, respectively.

1. Introduction

Nowadays significant contamination of surface water and groundwater with various organic compounds coming from both industry and agriculture is observed. A number of the contaminants are resistant to biological degradation, and they are not susceptible to removal in conventional water treatment processes such as coagulation, flocculation, and filtration [1]. Therefore, in many cases, novel, efficient and cost-effective methods of water treatment should be applied. The processes should assure complete mineralization of all the toxic species present in the raw water without leaving behind any hazardous residues [2, 3].

Advanced Oxidation Processes (AOPs) seem to be one of the most promising methods for removal of various organic contaminants. Among others, photocatalysis has been especially extensively investigated. The most commonly used photocatalyst is titanium dioxide. This is due to many merits revealed by the material such as relatively low cost, high photocatalytic activity, and chemical stability [4–6]. One of the major disadvantages of using TiO₂ is its troublesome separation from purified medium after the photocatalytic process. For that reason, attempts to immobilize the powdered

TiO₂ on various supports have been undertaken. One of the best known methods of photocatalyst immobilization is deposition of TiO₂ powder on a glass surface by the dip-coating technique. TiO₂ can firmly adhere to the glass surface due to the difference in the electrostatic charge. Besides various types of glass, other materials, including quartz, sand, stainless steel, silica, activated carbon, alumina, and polymers, zeolites, are used for TiO₂ immobilization [7, 8]. These supports can be prepared in various forms and shapes, such as cylinders, tubes, sheets or plates, and beads and mesh. Both dip coating and sol-gel precipitation of TiO₂ on the support are the most common methods of photocatalyst immobilization. However, other procedures such as direct oxidation of titanium metal by both electrochemical or thermal methods or electrophoretic coating of stainless steel can be also applied [9, 10].

The presented studies were focused on application of immobilized TiO₂ for removal of phenol from water in a pilot-scale photocatalytic reactor. Phenol was chosen as a model contaminant since it is one of the serious pollutants present in water. This compound exhibits high toxicity for human beings and causes severe environmental problems. Due to its hazardous properties, numerous investigations

(a)

(b)

FIGURE 1: Schematic diagram (a) and photograph (b) of the pilot-scale photocatalytic installation: (1) photoreactor with UV/vis mercury lamp, (2) water/wastewater tank, (3) pump; (4) air compressor.

are focused on phenol removal from water and wastewater [7, 11–18]. The aim of the presented research was evaluation of possibility of application of TiO_2 immobilized on steel mesh, fiberglass cloth, and microspheres (Photospheres-40, Microspheres Technology) in a pilot plant photocatalytic reactor. On a basis of the obtained results, the most beneficial and efficient configuration of the system was proposed.

2. Experimental

2.1. Pilot-Scale Photocatalytic Reactor. In order to make the system relocatable and thus easily reaching sources of the polluted water, the pilot-scale photocatalytic installation was built inside of a mobile container (Figure 1). The main component of the installation was a photoreactor (1) equipped with a UV/vis mercury lamp (Ultralight AG, Germany). The lamp power was set at a level of 6 kW, and the corresponding UV irradiation intensity was ca. 330 W/m^2 . For safety reasons, the pilot-scale installation was grounded because of high power usage. During the process, the phenol solution was pumped from the wastewater tank (2) (total volume of 1.5 m^3) to the photoreactor (total volume of 0.6 m^3 , working volume of 0.06 m^3) with a flow rate of $10 \text{ m}^3/\text{h}$ by means of an impeller pump (3). The effluent water flowed out of the photoreactor gravitationally to the tank. The process was realized in a batch mode with complete recycle. The water in the tank (2) was continuously aerated with use of an air compressor (4) with a flow rate of $40 \text{ m}^3/\text{h}$. A diffuser was mounted in the bottom of the tank (2) to provide a uniform distribution of air bubbles. Inside the photoreactor (1) a small amount of O_3 was generated in the presence of the UV lamp. The ozone concentration in water was $\sim 30 \mu\text{g}/\text{dm}^3$.

Both the phenol solution and air flowed in a closed loop. In this way, a release of volatile compounds outside the plant

could be avoided. Moreover, the undesirable volatile species were decomposed in situ by ozone in the closed air loop, which allowed reducing the formation of odors.

The installation was not equipped with any heat exchanger, therefore the solution temperature was monitored. The temperature during all experiments varied from 15°C at the beginning to 35°C at the end of the process. To find out if such changes affect the efficiency of phenol decomposition, additional short-term (2 h) experiments were performed, during which the temperature was maintained at 15, 25, or 35°C . The results revealed that within the investigated range the temperature had no noticeable influence on the process performance.

At the beginning of each experiment, the wastewater tank (2) was filled up with 1.35 m^3 of a fresh tap water. Subsequently, phenol was added to the tank to achieve initial concentration of $25 \text{ mg}/\text{dm}^3$. The resulting concentration of total organic carbon (TOC) was $22 \text{ mg}/\text{dm}^3$.

The experiments were realized in four different modes:

- (i) mode 1: without photocatalyst addition;
- (ii) mode 2: in the presence of Photospheres-40;
- (iii) mode 3: in the presence of TiO_2 P25 supported on a steel mesh;
- (iv) mode 4: in the presence of TiO_2 P25 supported on a fiberglass cloth.

The effectiveness of photodegradation was evaluated on a basis of changes of phenol and TOC concentrations in the treated water, with the time of the photocatalytic process.

2.2. Photocatalysts

2.2.1. Photospheres-40. The commercial Photospheres-40 were purchased from Microsphere Technology Ltd., Ireland.

The Photospheres-40 are hollow silica microspheres coated with titanium dioxide. Due to their low density (0.22 g/cm^3), the microspheres possess a floating ability [19]. According to the manufacturer, the mean diameter of the spheres is $45 \mu\text{m}$. The X-ray fluorescence (XRF) analysis revealed that the TiO_2 concentration in the sample used in the experiments was ca. 12.2 wt.%.

At the beginning of the experiment, 135 g (0.1 g/m^3) of the Photospheres-40 were added to 1.35 m^3 of the phenol solution.

2.2.2. Aeroxide TiO_2 P25. The commercially available Aeroxide TiO_2 P25 purchased from Evonik (Germany) was applied in the experiments with a photocatalyst immobilized on the steel mesh and fiberglass cloth. The physicochemical characteristics of TiO_2 P25 can be found elsewhere [20].

2.3. Photocatalyst Immobilization Procedure

2.3.1. Immobilization of TiO_2 P25 on a Steel Mesh. A commercially available steel grid ($200 \text{ cm} \times 90 \text{ cm}$) with mesh size of $1.25 \text{ cm} \times 1.25 \text{ cm}$ was used as the support. TiO_2 was immobilized on the grid according to the procedure described in the patent application [21]. In brief, a mixture of a defined amount of TiO_2 P25 and the white photocatalytic paint (TITANIUM FA, Pigment, Poland) was spread on the mesh. Painting was repeated three times and after each stage the wet surface of the paint was additionally powdered with TiO_2 P25 photocatalyst. Three units of the support were prepared in the same way. Due to a large mesh size of the applied support, the bottom of the photoreactor (1.8 m^2) was painted additionally using the same procedure. The steel mesh covered with TiO_2 was loosely mounted in the bottom part of the photoreactor. Total amount of TiO_2 utilized in such a system was ca. 560 g.

2.3.2. Immobilization of TiO_2 P25 on Fiberglass Cloth. The photocatalyst was immobilized on a commercially available fiberglass cloth ($160 \times 95 \text{ cm}$) by its immersion in a suspension of TiO_2 in ethanol (50 g/dm^3) and subsequent drying at 80°C . The coating procedure was repeated three times. Such obtained fiberglass cloth was placed on the bottom of the photoreactor. Total amount of TiO_2 P25 supported on the fabric was ca. 23 g. During examination of the effectiveness of phenol decomposition in the presence of TiO_2 immobilized on the fiberglass, the bottom of the photoreactor was not covered with the photocatalytic layer.

2.4. Analytical Methods. Phenol concentration was determined by using UV-vis spectrophotometry (Jasco V630, Japan, $\lambda_{\text{max}} = 270 \text{ nm}$). Total organic carbon (TOC) concentration was measured with application of IL 505 TOC/TN analyzer (Hach Lange Company). The ozone concentration was monitored by 9185sc amperometric ozone sensor (Hach Lange Company). Moreover, conductivity and pH of the treated phenol solution were continuously registered.

The XRD diffraction patterns were recorded using the Philips X'Pert PRO diffractometer with $\text{CuK}\alpha$ radiation.

FIGURE 2: Changes of phenol and TOC concentration in time of UV irradiation in the absence of a photocatalyst.

The XRF analysis was performed with application of the Epsilon 3 spectrometer (PANalytical). The FTIR spectra were measured using the Jasco FT-IR 430 (Japan) spectrometer, equipped with a diffuse reflectance accessory from the Harrick Company (USA). The SEM microphotographs and SEM-EDS analysis were performed with application of the Hitachi SU-70 FE-SEM scanning electron microscope.

3. Results and Discussion

3.1. Phenol Degradation in the Absence of a Photocatalyst (Mode 1). In the first stage of the investigations, a reference experiment in the absence of a photocatalyst was performed. As was mentioned in Section 2.1 in the presence of the mercury lamp used in the research an “in situ” generation of ozone was observed. This was related to the fact that the lamp emitted UV radiation at wavelengths below 210 nm , which is of sufficient energy to convert atmospheric oxygen to ozone [22]. However, the lamp emitted also radiation at 254 nm , which is absorbed by ozone. For that reason, both generation and destruction of O_3 took place in the investigated system. These two simultaneous phenomena affected the amount of ozone in the photoreactor. The concentration of O_3 in water was found to be rather low (ca. $30 \mu\text{g/dm}^3$) but cannot be regarded as negligible. Thus, degradation of phenol in the absence of a photocatalyst can be attributed to both, action of ozone and action of UV light.

Figure 2 presents changes of phenol and TOC concentrations in water during the discussed experiments. It can be observed that both phenol decomposition and mineralization proceeded well. After 15 h almost 65% of phenol was decomposed and 43% of total organic carbon was removed. It should be also noted that mineralization of phenol started about 5 h later compared to its decomposition. This suggests occurrence of an initial stage of the process during which only aromatic ring cleavage took place and it was followed by formation of by-products with lower molecular weights. Complete mineralization of these compounds started from

FIGURE 3: Changes of phenol (a) and TOC (b) concentration in time in the presence of Photospheres-40.

the 6th hour of irradiation, as can be found from appropriate changes of TOC concentrations.

During degradation of phenol, an increase of solution conductivity from $539 \mu\text{S}/\text{cm}$ at the beginning to $871 \mu\text{S}/\text{cm}$ at the end of the experiment was also observed. Electrical conductivity corresponds to the ionic activity of a solution in term of its capacity to transmit current. Thus, the increase of the conductivity of the treated phenol solution could be regarded as a measure of the increasing amount of ionic products and by-products formed during photodegradation of phenol.

Phenol degradation was also accompanied by a slight increase of solution pH from pH 8.2 at the beginning to pH 8.4 at the end of the process. Such insignificant change of pH might be attributed to the buffering properties of tap water resulting from the bicarbonate/carbonate equilibrium [23].

The results presented in Figure 2 are consistent with the literature data. It was already reported that the synergic effect of the combined O_3/UV system results in very effective degradation of phenol [24]. Moreover, the efficiency of this hybrid system was found to be significantly higher compared to a separate action of O_3 or UV [25].

3.2. Phenol Degradation in the Presence of Photospheres 40 (Mode 2). The second stage of the research was focused on the effectiveness of phenol photodegradation in the presence of the commercially available Photospheres-40. The process was conducted for 15 h. In order to evaluate the possibility of reusing the photocatalyst, 3 cycles of phenol removal were realized. To avoid losses of Photospheres-40, water was not removed from the installation during the whole experiment. Therefore, before the 2nd and 3rd cycles, the working solution was additionally irradiated until a complete phenol degradation was achieved (typically for 25–30 h). After that a defined amount of phenol was added to the tank to attain the initial concentration of $c_0 = 25 \text{ mg}/\text{dm}^3$ and the next photodegradation cycle was started. The obtained results are presented in Figures 3(a) and 3(b).

No significant difference between phenol decomposition in the three cycles during the initial 5 h was observed (Figure 3(a)). However, considering the final 5 h of the process, the removal of phenol in the 2nd cycle proceeded more efficiently compared to the 1st and 3rd ones. After 15 h of irradiation, the concentration of phenol decreased by 55% and 57% in the 1st and 3rd cycles, respectively. For comparison, nearly 76% decrease was found after the 2nd cycle. The mineralization proceeded less efficiently than photodecomposition of the model compound (Figure 3(b)). Moreover, the difference of the effectiveness of organic carbon removal in the three cycles was not as significant as in case of phenol decomposition. At the end of cycles 1–3, the concentration of TOC decreased by ca. 37, 48, and 41%, respectively.

Analogous to the experiment conducted in mode 1 (Section 3.1), certain increase of the solution conductivity with time was observed. At the end of cycles 1–3, the conductivity amounted to 846 , 977 and $932 \mu\text{S}/\text{cm}$, respectively. Changes in pH of the treated water were found to be insignificant, which remains in agreement with the results attained in the absence of a photocatalyst. The pH increased from pH 8.2 to pH 8.4–8.5, regardless of the cycle.

The difference in the effectiveness of phenol removal during the subsequent cycles might be explained as follows. The concentration of the photocatalyst in cycle 1 was exceeding the critical value and therefore the so-called screening effect took place [26–28]. This is a well-known phenomenon, which results in hindering of light penetration. Since the fresh Photospheres-40 possessed a floating ability, they remained on the surface of the treated solution. Thus, a shield which blocked UV light from entering to the deeper parts of the solution was created. The amount of floating spheres in the cycle 2 was lower than in the 1st cycle, due to their partial damage (see the discussion below). As a result, the UV light could be more efficiently utilized by the photocatalyst and the degradation rate increased. The low efficiency of phenol removal observed during the 3rd

FIGURE 4: SEM microphotographs of Photospheres-40 before (a) and after (b) experiment.

cycle can be attributed to a significant destruction of the Photospheres-40. The visual observation of the photocatalyst in the installation revealed constant decrease in the amount of the spheres floating on the surface, along with the time of the process. Hence, the crushing of the Photospheres-40 caused loss of their floating properties and led to their settling on the bottom of the tank in cycle 3. The mechanical damage was accompanied by a change of the color of the spheres from white to brown. This may suggest formation of deposits on their surface.

In order to confirm the rightness of the above explanations concerning the changes of photocatalytic activity of the Photospheres-40, the SEM, FTIR, and XRD analyses of the spheres collected from the installation at the end of the experiments were carried out.

Figure 4 presents SEM photographs of the fresh Photospheres-40 and the photocatalyst after 3 cycles of phenol degradation. The as-received spheres (left photograph) exhibit wide range of diameters, ranging from ca. 15 to ca. 70 μm. Although these spheres were unused, it can be observed that some of them were already crushed. This suggests their high fragility.

The appearance of the Photospheres-40 after 3 cycles of phenol degradation in the pilot-scale photoreactor is shown in Figure 4(b). It can be clearly seen that all the spheres were completely destroyed. This reliably explains the loss of their floating abilities and a decrease of their activity, which were discussed above.

Moreover, the XRD analysis revealed the presence of calcium and magnesium carbonates in the sample collected after the experiments. These deposits could be also responsible for the decrease of the photocatalyst activity in time.

In Figure 5 the FTIR/DRS spectra of Photospheres-40 before and after the experiments are presented. The higher intensity of the bands corresponding to the -OH vibrations ($3300\text{--}3500\text{ cm}^{-1}$) in the spectrum of the exploited photocatalyst compared to the unused one might be attributed to the increase of wettability of the destroyed spheres. The bands observed at $1630\text{--}1640\text{ cm}^{-1}$ can be assigned to the molecular water bending mode [20]. In the spectrum of the used Photospheres-40, the additional bands at $1550\text{--}1600\text{ cm}^{-1}$ and at 1780 cm^{-1} are observed and these can

FIGURE 5: FTIR/DRS spectra of Photospheres-40 before and after experiment.

be ascribed to C=O groups [29]. These groups could be attributed to the presence of by-products of phenol decomposition, adsorbed on the spheres surface. In a similar way, the occurrence of new bands at $2950\text{--}2800\text{ cm}^{-1}$ can be explained. The bands at 2940 , 2975 , and 2865 cm^{-1} , could be assigned to the stretching vibrations of aliphatic and aromatic -CH_3 and $\text{-CH}_2\text{-}$ groups. In the region of $1000\text{--}1250\text{ cm}^{-1}$ the bands characteristic for Si-O-Si stretching vibrations can be observed [29]. Moreover, a disappearance of the sharp intensive band at 1275 cm^{-1} in case of the used sample was found. The presence of this band in the FTIR spectrum of the fresh spheres could be ascribed to Si-CH_3 vibrations. This suggests that the Photospheres-40 were contaminated with some organic compounds, whose presence might be due to the applied procedure of TiO_2 immobilization (probably the sol-gel method).

The analysis of the Photospheres-40 collected from the photocatalytic pilot plant confirmed their complete damage and explained the loss of photoactivity. The obtained results revealed that the spheres should not be applied in photoreactors in which they are exposed to a mechanical damage, such as reactors equipped with pumps. The Photospheres-40 were found to be very susceptible to crushing and, therefore, did not fulfill their basic role, which is possibility of recovery and

FIGURE 6: SEM microphotograph of the cross section of the steel mesh wires covered with the photocatalytic layer.

reuse in subsequent runs. To apply the Photospheres-40 in a large-scale photocatalytic installations, a special construction of the photoreactors should be considered. The installations should assure retaining of the spheres out of pumps and other elements possibly contributing to their damage.

3.3. Phenol Degradation in the Presence of TiO_2 P25 Supported on a Steel Mesh (Mode 3). The third stage of the investigations was focused on the evaluation of the effectiveness of phenol decomposition in the presence of TiO_2 P25 immobilized on the steel mesh. Figure 6 shows SEM microphotographs of the cross section of the wires covered with the photocatalytic layer. It was found that the thickness of the coating varied from ca. 0.01 to 0.5 mm. Higher magnification of the layer (Figure 7(a)) revealed that its structure was porous and nonuniform. The SEM-EDX color mapping of the photocatalytic coating (Figures 7(b)–7(h)) showed that the small agglomerated particles contained Ti, whereas the larger species with various shapes contained Ca and Mg. Ground limestone (CaCO_3) is a commonly used paint additive, thus the presence of Ca can be attributed to the applied paint composition. In a similar way, the presence of Mg, which in the form of MgCO_3 is often present as limestone impurity, can be explained. The coating contained also Si and C also originating from the photocatalytic paint used for TiO_2 immobilization.

The steel mesh covered with the photocatalytic layer was mounted in the photoreactor and applied for phenol decomposition. The experiments realized in mode 3 were conducted for 15 h. Differently from the mode 2, the treated phenol solution was removed from the tank after the cycle 1 and a fresh tap water was introduced to the system. Subsequently, phenol was added to water in amount sufficient to achieve initial concentration of 25 mg/dm^3 . Concentrations of phenol and TOC in the treated water were measured every 1 hour, and the collected results are presented in Figures 8(a) and 8(b), respectively.

Efficiencies of phenol decomposition in both cycles were comparable (Figure 8(a)) and after 15 hours of irradiation concentration of the contaminant was reduced by ca. 56%.

However, the extent of mineralization observed during cycle 1 was lower compared to the cycle 2. The decrease of TOC concentration after termination of the cycles was ca. 24 and 44%, respectively (Figure 8(b)). These observations allowed us to assume that during the first cycle the organic ingredients of the used paint were washed out by the treated phenol solution and thus contributed to the overall TOC concentration. As a consequence, the mineralization proceeded slower in the first cycle than in the second one.

After 15 h of irradiation, conductivity increased to $922 \mu\text{S/cm}$ during the cycle 1 and to $942 \mu\text{S/cm}$ during the cycle 2. The pH increased by 0.2 pH units, which is consistent with the previously described experiments.

No visual changes were observed in the structure of the photocatalytic layer after exposing it to the photodegradation cycles. Since the rate of phenol decomposition in the two runs was almost the same, it can be concluded that the proposed procedure can be successfully applied for photocatalyst immobilization.

3.4. Degradation of Phenol in the Presence of TiO_2 P25 Supported on a Fiberglass Cloth (Mode 4). During the last stage of the research, the fiberglass cloth coated with TiO_2 P25 particles was used. Figure 9 shows SEM microphotographs of this material. The structure of the coating differed significantly from the structure of the layer prepared with application of the photocatalytic paint. In the former case, the thickness of the photocatalytic layer did not exceed $2 \mu\text{m}$, but in most analyzed samples it was below $1 \mu\text{m}$. Moreover, the porosity of the photocatalytic coating was very low. It should be also emphasized that TiO_2 particles in case of the coating on the fiberglass cloth were not covered with any additional layers, as it was in case of the photocatalytic layer prepared with the paint addition.

The TiO_2 immobilized on the fiber glass cloth was applied in two 15 hours—long cycles of phenol degradation and mineralization. Similarly as in the mode 3, the system was emptied after the first cycle and subsequently the tank was refilled with a fresh tap water containing phenol. The results collected during these experiments are presented in Figures 10(a) and 10(b).

During both cycles, decomposition and mineralization of phenol proceeded with a comparable efficiency. The 15-hour-long irradiation caused significant decrease, by ca. 80%, in phenol concentration. At the same time, TOC amount was lowered to ca. 50% of the initial level. As distinct from the mode 3, no elution of organic carbon from the photocatalyst support was observed. This may be concluded on a basis of the changes in the concentration of total organic carbon in both cycles. From this point of view, the procedure of TiO_2 immobilization on the glass fabric seems to be more beneficial.

Changes of pH and conductivity during the process runs were similar to those found during experiments carried out according to the other modes. Hence, conductivity did not exceed $852 \mu\text{S/cm}$, whereas pH increased from pH 8.1 to 8.5.

The visual observation of the fiberglass cloth after the experiment revealed certain deformation (folding) of

FIGURE 7: SEM microphotograph of the cross section of the photocatalytic layer coated on the steel mesh (a) and SEM-EDX color mapping of selected inorganic elements detected in the coated mesh (b–f); (b) Fe, (c) Ca, (d) Ti, (e) Mg, (f) Si, (g) O, (h) C.

FIGURE 8: Changes of phenol (a) and TOC (b) concentration in time in the presence of TiO_2 P25 immobilized on steel mesh.

FIGURE 9: SEM microphotographs of the cross sections of the glass fibers covered with the photocatalytic layer; (a) lateral cross section and (b) longitudinal cross section.

FIGURE 10: Changes of phenol (a) and TOC (b) concentration in time in the presence of TiO_2 P25 immobilized on a fiberglass cloth.

the mat. This resulted from a high flexibility of the material. However, it should be stressed that changes in the cloth shape did not affect the efficiency of phenol removal. The results shown in Figure 10 reliably support this statement.

3.5. Degradation of Phenol in Different Modes—Comparative Considerations. In order to compare the effectiveness of phenol decomposition in different modes investigated in this work, the initial reaction rates (r_0) were calculated. The results obtained within the initial 5 h in the first cycles were taken into account. The r_0 values (in g/h) were as follows: mode 1: 0.97; mode 2: 1.15; mode 3: 1.31; mode 4: 1.61. Apparently the highest rate of phenol decomposition was determined in the system operating in the mode 4, employing TiO_2 P25 immobilized on a fiberglass cloth. For comparison, the lowest r_0 value was calculated for the degradation conducted in the absence of a photocatalyst (mode 1). The initial degradation rate obtained in the presence of the commercially available Photospheres-40 was higher than the rate in mode 1; however, it was lower compared to the r_0 values calculated for the modes employing TiO_2 P25.

Additionally, the effectiveness of phenol decomposition and mineralization after 15 h of experiments realized in different modes, was compared (Figure 11). In general, the values obtained in the first cycles were taken into account. Exception is mode 3, where the second cycle was considered for TOC degradation. This is because the TOC removal in the first cycle of mode 3 was not reflected by the mineralization of phenol. The reason for that was the secondary contamination with organic compounds washed out from the paint explained in earlier sections of this work.

The presented results confirm the highest effectiveness of phenol removal during experiments carried out in the mode 4. This well correlates with the r_0 values given above. The 15-hour-long process conducted in this mode resulted in 80% reduction in phenol concentration and 50% removal of TOC from the treated water.

Elimination of phenol during 15 h of the process realized in the absence of a photocatalyst (mode 1) appeared to proceed more efficiently than during experiments conducted in modes 2 and 3. Furthermore, removal of phenol in the presence of either the Photospheres-40 (mode 2) or the

FIGURE 11: Comparison of the effectiveness of photodegradation and mineralization of phenol after 15 h of irradiation. Legend: mode 1—without photocatalyst addition; mode 2—in the presence of Photospheres-40; mode 3—in the presence of TiO_2 P25 supported on a steel mesh; mode 4—in the presence of TiO_2 P25 supported on a fiberglass cloth.

photocatalyst immobilized on the steel mesh (mode 3) was comparable.

Considering results shown in Figure 11, the efficiency of phenol degradation could be put in the following order: mode 4 > mode 1 > mode 3 > mode 2. However, this remains in disagreement with the r_0 values, which tend to decrease in the following order: mode 4 > mode 3 > mode 2 > mode 1. The difference refers to the mode 1. This mode was the least effective when the initial 5 h of the experiments were considered, but more efficient when the entire process was taken into account. These results might suggest that the effectiveness of phenol decomposition in case of mode 1 increased with a progress of the process.

No significant difference in the mineralization degree was observed during conducting experiments according to modes 1 and 3 (Figure 11). The least efficient configuration turned out to be the one in which commercial Photospheres-40 were used.

4. Conclusions

The photocatalytic degradation and mineralization of phenol in a pilot-scale photoreactor was investigated. Four different process modes were analyzed and compared. As found, straight application of a high voltage UV lamp accompanied by ozone generation (mode 1) allows to achieve a relatively high degree of phenol degradation and mineralization. After 15 h of irradiation, phenol and TOC concentrations decreased for about 65% and 43%, respectively.

Efficiency of phenol degradation can be significantly improved by application of TiO_2 P25 immobilized on the fiberglass cloth (mode 4). The initial rate r_0 of phenol decomposition in this mode was for ca. 65% higher compared to mode 1 (1.61 versus 0.97 g/h).

Application of TiO_2 P25 immobilized on a steel mesh (mode 3) was found to be less beneficial compared to the photocatalyst supported on a fiberglass cloth. The main disadvantage of this configuration was washing out of some organic ingredients of the photocatalytic paint used for immobilization of a photocatalyst. As a result, TOC removal in the first cycle was ineffective (24%). However, the efficiency of mineralization in the subsequent cycle was significantly higher (44%). Nonetheless, phenol removal was still lower compared to that attained using the most efficient mode 4 (56% versus 80%).

The obtained results revealed that fragile structures, such as Photospheres-40, are not promising materials for application in the pilot plant photocatalytic reactor used in the experiments. Vigorous mixing of water and application of an impeller pump contributed to severe mechanical destruction of the spheres and loss of their floating abilities.

In view of the above, TiO_2 supported on a fiberglass cloth reveals the highest potential for application in the pilot scale photoreactor.

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