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APPLICATION OF TITANIA COATING AS PHOTOACTIVE REFILL IN THE REACTOR FOR PURIFICATION OF WATER CONTAMINATED WITH ORGANICS

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The aim of the present work was to remove organic impurities from water using a reactor with photoactive refill. Application of the photoactive refill solves the problem of the replacement of the reactor or its parts when the photocatalyst activity decreases. In case of photocatalytic activity drop, only the photoactive refill can easily be replaced. Titanium dioxide coating was immobilized on the glass fabric as a thin layer from the alcoholic suspension followed by thermal stabilization.

The results of studies revealed that the titania coating shows a high photocatalytic potential for the decomposition of the model organic compounds (azodye Acid Red 18, phenol and methylene blue) in water. The coating exhibits high stability in repeated cycles of water treatment.

keywords: photocatalysis, titania coating, photoactive refill, water purification

1. INTRODUCTION

Methods used for purification of coloured wastewaters can be in general divided in two groups: (i) chemical or physical methods and (ii) biological methods. The physical methods include precipitation methods (coagulation, flocculation, sedimentation),

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adsorption (activated carbon, silica gels), filtration, reverse osmosis and the like. Reduction, oxidation, ion exchange and neutralization are example chemical methods. Biological treatment can be operated in aerobic or anaerobic conditions.

Advanced oxidation processes, especially photocatalysis, gained much interest last years since they are able to deal with the problem of organic pollutant destruction in aqueous systems [1-10]. Processes of the photocatalytic degradation of organic impurities in majority operate in the systems where the photocatalyst is suspended in the reaction mixture. However, in this case the photocatalyst should be separated from 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 [11-19]. 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 advantage of providing a good contact of the treated medium with the photocatalyst surface and also of allowing deeper light penetration in the reactor. A flexible textiles seemed to be an adequate support for the photoactive titania coatings. However, textiles are organic materials and can undergo the photocatalytic degradation themselves.

The aim of the present work was to remove organic impurities from water using a reactor with photoactive refill. Titanium dioxide was immobilized on the base material as a thin layer from the alcoholic suspension followed by thermal stabilization. The glass fabric was applied as a support for the titania coating.

2. MATERIALS AND METHODS

The commercial anatase form of titanium dioxide produced by Chemical Factory „Police" (Poland) was used as a photocatalyst. In order to evaluate the photoactivity of the prepared titania coating, decomposition behavior of methylene blue (MB), phenol and azo-dye Acid Red 18 (AR18) was studied. MB and phenol were chose since these compounds are widely used as a model compounds in the photocatalytic studies, whereas AR18 is commonly used azo-dye and was the subject of previous investigations of this paper author [20-24].

The process of photocatalytic oxidation was conducted using a laboratory installation (Figure 1) whose main component was the flow reactor (Trojan Technologies, Canada) with a refill covered with a titania coating. 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 centre. The photoactive refill was also placed inside the reactor in such a way as to stick the inner walls of the reactor. The photocatalyst was fixed to the glass fabric according to the following procedure. The suspension of TiO_2 in ethanol was sonicated for 1 h with a frequency of 40 kHz. The glass fabric was immersed in such prepared suspension and then dried for at 105°C. The procedure was repeated twice. After that the coating was stabilized by thermal treatment at the temperature of 150°C overnight. The excess of the immobilized photocatalyst was rinsed with the water flowing through the reactor before the photocatalytic process. The solution of organics was pumped to the reactor by peristaltic pump from the container and than circulated through the reactor with the flow rate of 36 dm^3/h. The solution circulated in the reactor for 15 minutes without illumination to reach the adsorption equilibrium. The adsorption onto photocatalyst surface was low, only about 5 % (by weight).

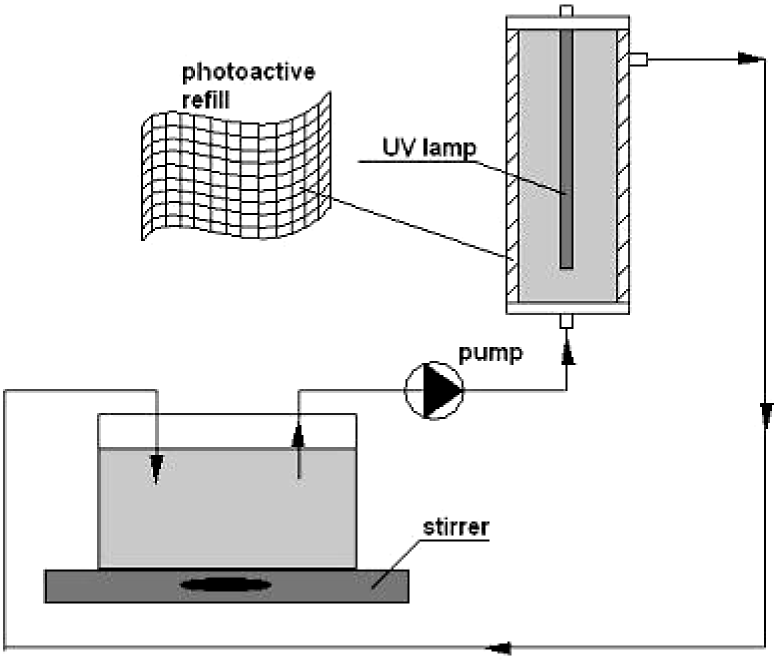

Fig. 1. The scheme of installation for the process of photocatalytic oxidation of MB, phenol and AR18.

The changes of reactants concentration in the solution were determined by absorbance measurement at the maximum absorption wavelength of 664, 270 and 507 nm, respectively for MB, phenol and AR18. (Jasco V-530 spectrometer, Japan). Total organic carbon (TOC) concentration was measured by "multi N/C 2000" analyzer (Analytik Jena, Germany). Total dissolved solids

(TDS) content, conductivity and pH of the solution (Ultrameter 6P, Myron L Company, USA) were also monitored during the process.

3. RESULTS AND DISCUSSION

At the beginning of the studies, blank experiments were performed. No decomposition occurred when an aqueous solution of studied compounds flowed through the reactor in the dark and the direct photolysis was also negligible (0,5 – 1,5%).

Figures 2 – 4 show the changes in concentration, respectively for MB, phenol and AR18, during the photocatalytic process. In case of all studied organic compounds, the concentration decreased the fastest in the first 10 hours of the process performance.

In case of MB, the initial dye concentration in the solution was equal to 5 mg/dm^3 and the total volume of the reaction solution was 2.5 dm^3. Three consecutive tests applying the same photoactive refill were performed (Fig. 2).

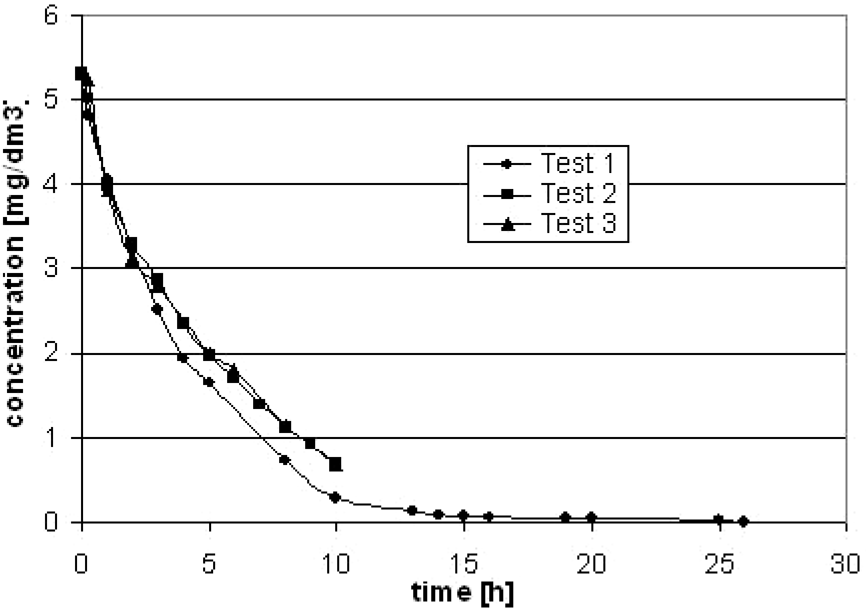

Fig. 2. Changes in concentration of MB during the photocatalytic process (three consecutive tests applying the same photoactive refill).

The dye concentration decreases with the time of the process. As can be seen from Figure 2, the color removal is the highest during the first hours of the process. After that, the rate of color removal decelerates however a complete discoloration of the solution was achieved. The first test was conducted until the solution was colourless while the time of next tests was set to be 10 hours. The best results were obtained in the first test where after 10 h of the process performance, the decrement of concentration of MB was 94.7%. The complete discolouration of the solution during this test was obtained in 26 hours. The next two tests also gave very good results. During the second test, the concentration of MB decreased from 5.3 mg/dm3 to 0.68 mg/dm3 giving 87% decrement of concentration. The third test showed similar result as the second one. Such a good results obtained in relatively short time indicate that the photoactive refill applied in the studies shows high photocatalytic activity and this activity is stable in the repeated cycles of water treatment.

Figure 3 presents the changes in phenol concentration during the photocatalytic process for three tests performed with the same photoactive refill. The initial phenol concentration applied in the studies was equal to 20 mg/dm^3 and the total volume of the reaction solution was 2.5 dm^3. During the first test, the phenol decomposition degree was equal to 64.4% after the first 5h of the photocatalytic process and complete phenol decomposition was obtained in 23h. In the second tests, the phenol concentration in the solution after 10 h of illumination was a little higher comparing to the first one; however, the third tests showed comparable time of decomposition as the second one.

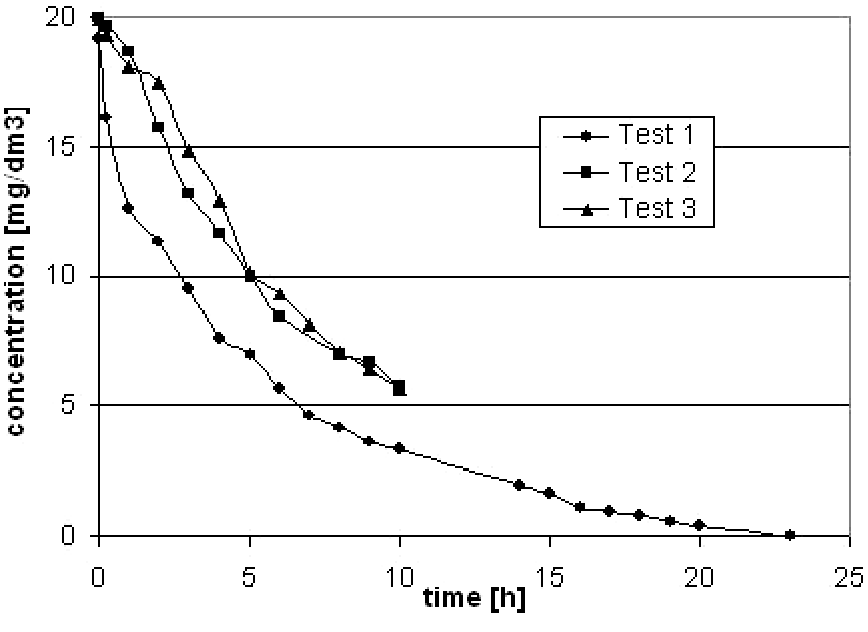

Fig. 3. Changes in concentration of phenol during the photocatalytic process (three consecutive tests applying the same photoactive refill).

For AR18, the results of five separated tests applying the same photoactive refill are presented in Figure 4. The initial AR18 concentration applied in the studies was equal to 10 mg/dm^3 and the total volume of the reaction solution was 2.5 dm^3. Similarly as for MB and phenol, the best results were obtained in the first run. The degree of degradation equal to 72% was achieved already after 5h while the degradation was completed after 15h of the photocatalytic process. The average value of concentration decrement after 5h of the process during the tests from 2 to 5 was about 60%.

Just as it was observed for MB and phenol, the activity of the photoactive refill decreased after the first usage and stabilized at a certain level during the next runs. However, starting from the sixth test, the time required for complete discoloration of AR18 solution elongated and during the eleventh test was doubled comparing to the firs one. Therefore, it can be stated that the lifetime of the photoactive refill amounts to about 200 hours and after that time the refill should be replaced with a new one.

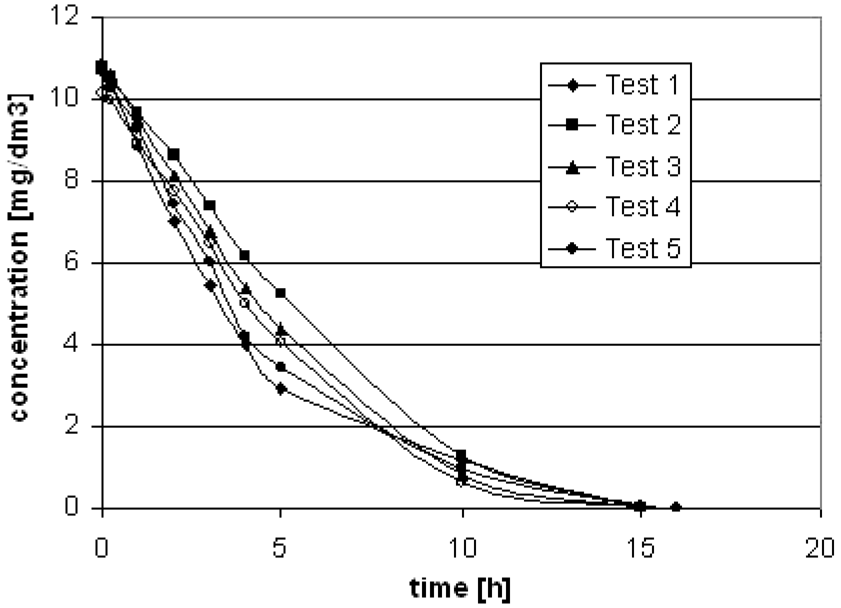

Fig. 4. Changes in concentration of AR18 during the photocatalytic process (five consecutive tests applying the same photoactive refill).

Except for the concentration of the studied compounds, the TOC, TDS, conductivity and pH of the reaction solutions have also been monitored during the photocatalytic process. Changes of these parameters give a wider picture of the organics degradation process since they do not always undergo the complete mineralization. The degradation of the primary structure is analytically observed as decrease in concentration but the degradation products can still remain in the reaction mixture. Figure 5 shows the changes of TOC, TDS, conductivity and pH during the first test conducted with AR18 solution. The tendency of changes for the other tests conducted with AR18 and also with MB or phenol was similar.

The TOC concentration in the reaction solution for all the studied cases was decreasing during the photocatalytic process however a complete TOC removal was not achieved. This indicates incomplete mineralization of the treated compounds. In order to obtain the complete mineralization of organics leading to inorganic compounds, the time of the photocatalytic reaction should be elongated. It should be yet noticed that the values of TOC concentration in all the studied cases meet the legal regulation concerning the TOC concentration in water. The values of TDS and conductivity gradually increased during the process. This indicates the increase of dissolved compounds and ions in the reaction mixture showing also the progressive degradation of the initial compounds. The progressive degradation of organics was also confirmed by pH decrease (from 6.03 to 5.56) indicating generation of such decomposition products as carboxylic and mineral acids.

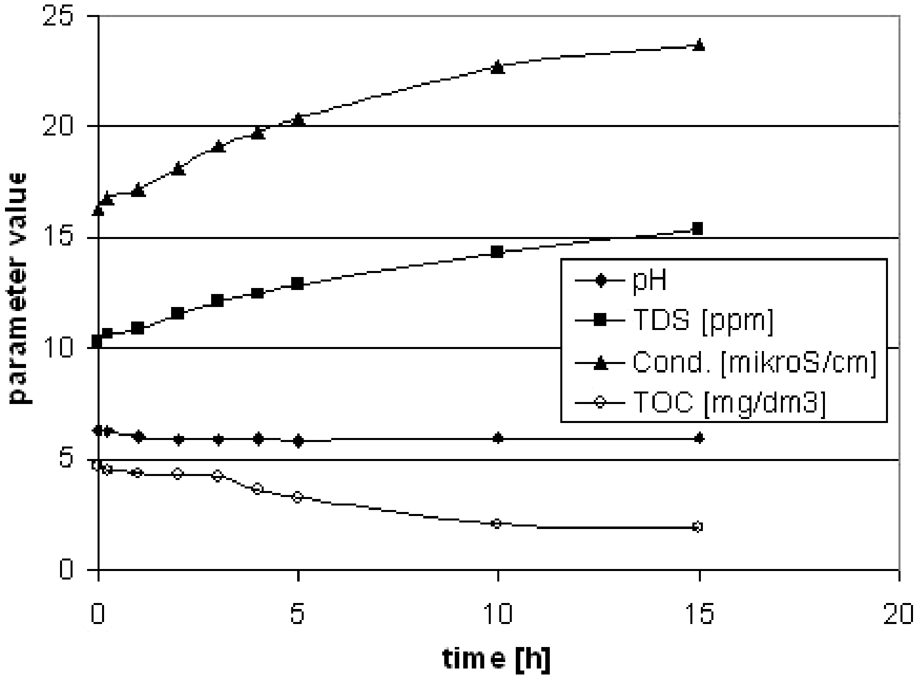

Fig. 5. Changes of TOC, TDS, conductivity and pH during the first test with AR18 solution

4. CONCLUSIONS

The results of the studies revealed that the titania coating shows high photocatalytic potential for the decomposition of the model organic compounds (methylene blue, phenol and Acid Red 18) in water. The coating prepared exhibits high stability in repeated cycles of water treatment. The photoactive refill solves the problem of reactor or its parts replacement necessity. The lifetime of the photoactive refill amounts to about 200 hours and when the photoactivity decreases, only the photoactive refill can easily be replaced. The application of glass fabric is advantageous since it is resistant to UV radiation and on the contrary to the natural fabrics, it does not undergo any photocatalytic decomposition.

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