

Water purification using a novel reactor with the photoactive refill

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The aim of the presented work was the removal of organic dye, Acid Red 18, from water using a novel reactor with the photoactive refill. Titanium dioxide was immobilized on the base material as a thin layer from the alcoholic suspension followed by thermal stabilization. The prepared coating exhibits high stability in repeated cycles of water treatment. The complete removal of colour was achieved in a relatively short time of 14 hours. The proposed reactor with the photoactive refill solves the problem of the necessity of the replacement of the reactor or parts of the reactor when the photocatalysts activity decreases. In the case of activity drop of the photocatalyst, only the photoactive refill can be easily replaced.

Keywords: titanium dioxide, photocatalysis, flow reactor, photoactive coating, organic dyes.

INTRODUCTION

Organic dyes are one of the largest groups of pollutants in wastewaters produced from textile and other industrial processes. The color of the wastes is the most apparent indicator of waste pollution. The presence of even small amounts of dyes is clearly visible and influences the water environment considerably. The conventional techniques used for the treatment of color wastewaters are biological oxidation and physical-chemical methods, like coagulation or activated carbon adsorption. The disadvantage of these commonly used traditional methods results from the fact that they usually are not destructive but only transfer the contamination from one phase to another one. The development in the field of chemical water purification has led to an improvement in the oxidative degradation processes applying catalytic and photochemical methods. They are called advanced oxidation processes. Chemical reactions carried out under light illumination in the presence of inorganic semiconductors, that is to say photocatalytic reactions, are an alternative method for conventional water treatment technologies. Photocatalytic reactions allow in many cases a complete degradation of organic pollutants in very small and not noxious species, without using chemicals, avoiding sludge production and its disposal¹⁻⁷.

The photocatalytic processes can be conducted using the catalyst suspended in the reaction medium or immobilized on various supports. The advantage of water suspension is a much better contact between the photocatalyst and dissolved impurities comparing to the reactors with the immobilized catalyst bed. On the other hand, in this case the step of catalyst's separation is necessary, which increases the overall costs of the process. Although the suspended systems show high photocatalytic activity, the problem of catalyst particles' separation emerges in the practical applications. The photocatalyst particles are usually so small that gravitational separation is not possible. The photocatalyst can be immobilized on the adequate solid support, which eliminates the step of separation⁸⁻¹¹. However, in this case, there is a necessity to replace a reactor or its parts when the photocatalytic material loses the activity.

The aim of the presented work was removal of organic dye, Acid Red 18, from water using a novel reactor with photoactive refill. Titanium dioxide was immobilized on the base material as a thin layer from the alcoholic suspension

followed by thermal stabilization. In the case of activity drop of the photocatalyst, only the photoactive refill can be easily replaced.

MATERIALS AND METHODS

An anatase form of titanium dioxide produced by Chemical Factory "Police" (Poland) was used as a photocatalyst. 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 the light fastness equal 4 (8-grade ISO Blue Wool Scale). The chemical structure of AR18 is presented in Figure 1. The support for titania photoactive coating was a glass fabric. A glass fabric with the dimensions of about 19 x 24 cm, followed by drying for 1 hour at the temperature of 105°C. After cooling, the fabric was reimmersed in the ethanolic suspension of TiO₂, dried and then placed in the furnace at the temperature of 200°C for 24 hours. The glass fabric with coating was a photoactive refill placed in the reactor where the process of water purification was conducted.

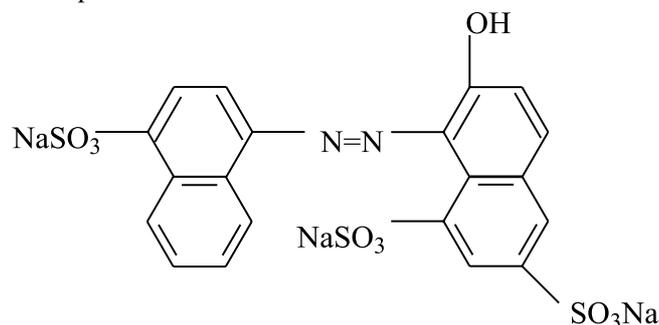


Figure 1. The chemical structure of Acid Red 18

The process of photocatalytic oxidation of AR18 was conducted using a laboratory installation (Figure 2) where the main component of the system 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 the centre. The photoactive refill was also placed inside the reactor in a way to stick the inner walls of the reactor. The excess of the immobilized photocatalyst was rinsed by flowing water through the reactor

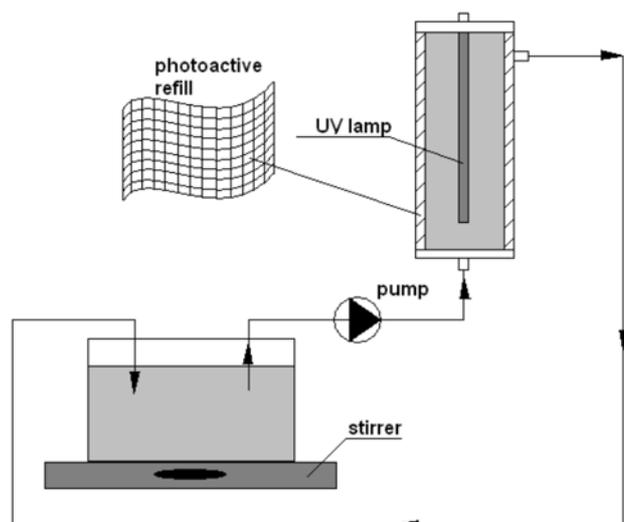


Figure 2. The scheme of the installation for the process of photocatalytic oxidation of AR18

before photocatalysis, so only a thin layer of photocatalyst remained on the fabric.

The solution of AR18 was pumped to the reactor by a peristaltic pump from the container and was circulated through the reactor with the flow rate of $36 \text{ dm}^3/\text{h}$ until the solution was colourless. The solution of dye circulated in the reactor for 15 minutes without illumination to obtain the adsorption equilibrium. The adsorption of dye onto the photocatalyst's surface was low, even less than 1% (by weight).

The changes of dye concentration in the solution were determined by absorbance measurement at maximal absorption wavelength 507 nm (Jasco V-530 spectrometer, Japan). The total organic carbon (TOC) concentration was measured by the "multi N/C 2000" analyzer (Analytik Jena, Germany). The total content of the dissolved solids (TDS), the conductivity and pH of the solution (Ultrameter 6P, Myron L Company, USA) were also monitored during the process.

RESULTS AND DISCUSSION

The experiments of the photocatalytic degradation of dyes were conducted for the initial concentration of dyes equal to $10 \text{ mg}/\text{dm}^3$. The volume of the treated solution was 2 dm^3 .

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

Figure 3 presents the changes in dye concentration during the photocatalytic process for the four tests performed with the same photoactive refill. The concentration of dye decreases with the time of the process. The removal of colour is the highest during the first hours of the process. After that, the rate of colour removal decelerates, however the complete discoloration of the solution was obtained. During the first test the 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.

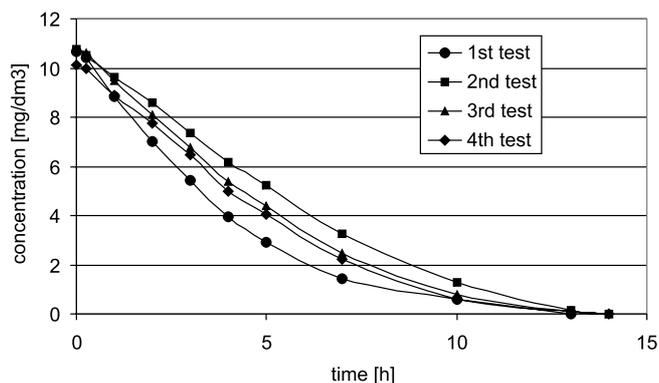


Figure 3. The changes in dye concentration during the photocatalytic process

The changes in dyes concentrations were monitored by UV/Vis spectroscopy. Discoloration of the solutions during the process is the result of the decrease of dye concentration and also the cleavage of $-N=N-$ bonds which determine the colour of azo-dyes. Figure 4 presents the spectra of dye solutions recorded during the photocatalytic process. As it can be seen from Figure 4, decay of both UV and Vis region absorption bands is observed during the photocatalytic process indicating the decrease of concentration of aromatic rings and chromophore groups containing the azo unit in the solution.

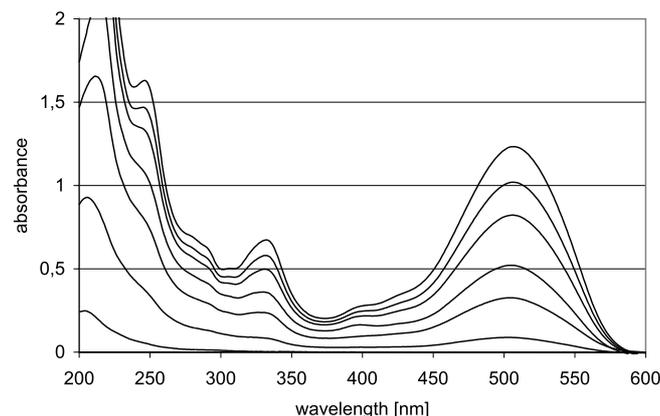


Figure 4. The spectra of dye solutions recorded during the photocatalytic process

Decolorization of the solution does not give a complete data on the dye degradation. Figure 5 presents the changes of TOC concentration during the process. The TOC removal in the first hours of the process was slower and then it accelerated. It acts contrary to the removal of the colour. Discoloration of the solution was faster at the beginning of the process. This observation might suggest that in the first hours of the process, when the fast decolorization occurs, a high quantity of decomposition products is formed and the mineralization process is decelerated. TOC analysis revealed the presence of organic carbon in the solution even after the complete discoloration of the solutions. The TOC concentration determined at the end of the process amounted to 1.65, 1.54, 1.43 and 1.48 mg/dm^3 for the first, second, third and fourth test, respectively. Although the removal of TOC was not complete, the obtained values meet the legal regulations in respect of TOC concentration in water.

The changes of conductivity and TDS during the photocatalytic process are shown in Figure 6. The conductivity and TDS values tend to increase with the time of the process. The

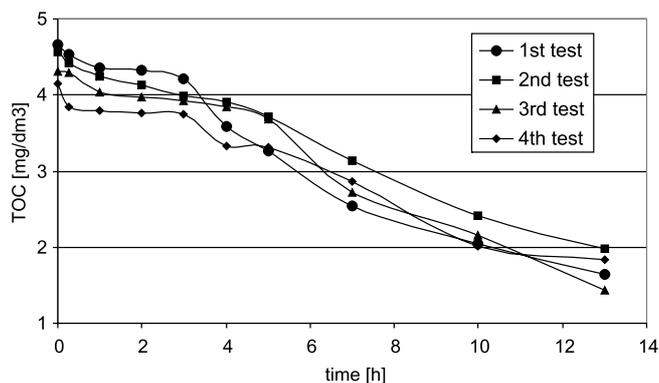


Figure 5. The changes of TOC concentration during the photocatalytic process

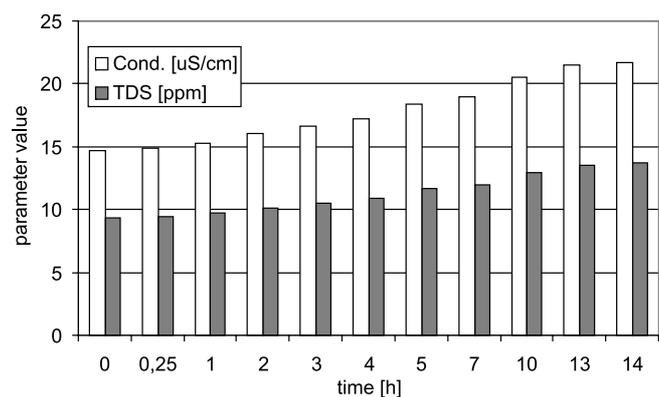


Figure 6. The changes of conductivity and TDS during the photocatalytic process

initial concentration of TDS in the solution during the test amounted to 9.32 ppm and after the 13 hours of the process performance it reached the value of 13.69 ppm. The initial conductivity amounted to 14.72 $\mu\text{S}/\text{cm}$ and at the end of the process the value of this parameter was 21.69 $\mu\text{S}/\text{cm}$. This indicates the mineralization of organic molecules and increase of the dissolved species present in the solution. The presented data refer to the fourth photocatalytic test. For the other three tests, the tendency of the changes was similar.

The pH of the solution (data not shown) tends to decrease during the process. The drop of the pH value indicates the formation of acid products like CO_2 and H_2SO_4 originating from the mineralization of the dye as well as from sulfonate groups present in the structure of the dye.

CONCLUSIONS

The results of the studies revealed that the obtained titania coating shows a high photocatalytic activity toward the decomposition of AR18 in water. The prepared coating exhibits high stability and a negligible decrease of photoactivity in repeated cycles of water treatment has been observed. The complete removal of colour was achieved in the relatively short time of 14 hours. It was found that not only the decolorization but also mineralization of the dye was effective in the process. After a total decolorization of AR18 solution ca. 65% of TOC was removed.

The results of the presented studies showed that the photocatalytic removal of azo-dye Acid Red 18 can be successfully conducted using a flow reactor with the photoactive refill. The proposed reactor with the photoactive refill solves the problem of the necessity of the replacement of the reac-

tor or parts of the reactor when the photocatalysts activity decreases – only the photoactive refill can be easily replaced.

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LITERATURE CITED

- Hoffman, M.R., Martin, S.T., Choi, W. & Bahnemann, D.W. (1995). Environmental Applications of semiconductor Photocatalysis. *Chem. Rev.* 95(1), 69 – 91. DOI: 10.1021/cr00033a004
- Linsebigler, A.L., Lu, G. & Yates, Jr.J.T. (1995) Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* 95(3), 735 – 758. DOI: 10.1021/cr00035a013
- Schiavello, M. (1997). Heterogeneous photocatalysis. John Wiley & Sons, Chichester, New York, Wienheim, Brisbane, Singapore, Toronto.
- Mills, A. & LeHunte, S. (1997). An overview of semiconductor photocatalysis. *J. Photochem. Photobiol. A: Chem.* 108(1), 1 – 35. DOI: 10.1016/S1010-6030(97)00118-4
- Herrmann, J.-M. (1999). Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catal. Today* 53(1), 115 – 129. DOI: 10.1016/S0920-5861(99)00107-8
- Fujishima, A., Rao, T.N. & Tryk, D. (2000). Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C: Photochem. Rev.* 1(1), 1 – 21. DOI: 10.1016/S1389-5567(00)00002-2
- Kaneko, M. & Okura, I. (2002). Photocatalysis. Science and Technology. Kodansha Ltd., Tokyo, Springer-Verlag Berlin Heidelberg, New York.
- Fernández, A., Lassaletta, G., Jiménez, V.M., Justo, A., González-Elipe, A.R., Herrmann, J.-M., Tahiri, H. & Ait-Ichou, Y. (1995). Preparation and characterization of TiO_2 photocatalysts supported on various rigid supports (glass, quartz and stainless steel). Comparative studies of photocatalytic activity in water purification. *Appl. Catal. B: Environ.* 7(1-2), 49 – 63. DOI: 10.1016/0926-3373(95)00026-7
- Grzechulska, J. & Morawski, A.W. (2003). Photocatalytic labyrinth flow reactor with immobilized P25 TiO_2 bed for removal of phenol from water. *Appl. Catal. B: Environ.* 46(2), 415 – 419. DOI: 10.1016/S0926-3373(03)00265-0
- Balasubramanian, G., Dionysiou, D.D., Suidan, M.T., Baudin, I. & Lainé, J.-M., Evaluating the activities of immobilized TiO_2 powder films for the photocatalytic degradation of organic contaminants in water. (2004). *Appl. Catal. B: Environ.* 47(2), 73 – 84. DOI: 10.1016/j.apcatb.2003.04.002
- Venkata Subba Rao, K., Subrahmanyam, M. & Boule, P. (2004). Immobilized TiO_2 photocatalyst during long-term use: decrease of its activity. *Appl. Catal. B: Environ.* 49(4), 239 – 249. DOI: 10.1016/j.apcatb.2003.12.017.