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Water Purification Using a Novel Reactor with Photoactive Refill

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Abstract The aim of the presented work was the removal of organic impurities from water using a novel reactor with photoactive textile refill. Titanium dioxide was immobilized on the base textile as a thin layer using sodium silicate as a binding material. The results of studies revealed that the titania–silicate coatings show a high photocatalytic activity towards the azo-dye Acid Red 18 decomposition in water. The prepared coatings exhibit high stability in repeated cycles of water treatment

Keywords Photocatalysis · Titania–silica coatings · Azo-dyes · Water purification

1 Introduction

Water and wastewater purification is one of the most promising application of photocatalytic processes since many of toxic impurities, both organic and inorganic, undergoes a complete mineralization to harmless final products during the photocatalytic process. The process of photodegradation in water phase with TiO_2/UV system can be successfully applied for removal of organic compounds such as: humid acids, carboxylic acids and derivatives, dyes, phenols, pesticides, surface active compounds and others from water and wastewater. Many books and review papers were devoted to this matter [1–10]. The classical methods, such as activated carbon adsorption, membrane separation or coagulation usually just transfer contamination from one phase to another and do not lead to a complete elimination of separated pollutants.

Heterogeneous photocatalysis is at present at a preindustrial level of development. Purification of water and wastewater by means of photocatalytic processes at industrial level is technically practicable. The basic investigations in the field of photocatalysis are now objected to learn about the mechanism of photocatalytic reactions, comparison of different process/reactors configurations and searching for materials with higher than titanium dioxide photocatalytic activity.

Titanium dioxide, the most often used photocatalyst, can be applied in the suspension or immobilized on various supports. In the suspended systems the step of separation of the catalyst is necessary, what increases the overall costs of the process. Therefore, attempts to immobilize the catalyst on different supports have been made [11–15]. The literature data indicate that application of silicate materials as a binder for titanium dioxide particles provides very good results. The silica/titania mixed oxides have been reported to be more active than pure titania photocatalyst [15–20]. The addition of silica to titania enhances the thermal stability and the phase transformation of titania from anatase to rutile form [21] and also increases the surface area [16] and surface acidity [22].

The aim of the presented work was removal of organic impurities from water using a novel reactor with photoactive refill. Titanium dioxide was immobilized on the base material as a thin layer using silicic acid as a binding material.

2 Experimental

The commercial anatase form of titanium dioxide produced by the Chemical Factory “Police” (Poland) was used as a

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photocatalyst. Acid Red 18 (AR18) produced by the Chemical Factory “Boruta-Kolor” (Poland) was used as a model azo-dye. AR18 is a monoazo dye with a light fastness equal 4 (8-grade Blue Wool Scale). The chemical structure of AR18 is presented in Fig. 1. The support for titania–silica photoactive coating was a glass fabric. Titanium dioxide was immobilized on the base material using orthosilicic acid as a binder. The glass fabric with titania–silica coating was a replaceable photoactive refill placed in the reactor where the process of water purification was conducted.

The process of photocatalytic oxidation of AR18 was conducted using a laboratory installation (Fig. 2). The main component of the system was the flow reactor (Trojan Technologies, Canada) with a refill covered with a titania-silica coating. The mercury lamp emitting UV radiation in the range of 250–800 nm, with maxima at 254, 436 and 546 nm, was positioned in the center of the reactor. The photoactive refill was also placed inside the reactor in a way to stick the inner walls of the reactor. The refill was prepared by spreading a thin layer of titania suspended in water solution of silicone binder with the help of brush. The excess of the immobilized photocatalyst was rinsed by water flowing through the reactor before photocatalysis, so only a thin layer of photocatalyst remained on the fabric.

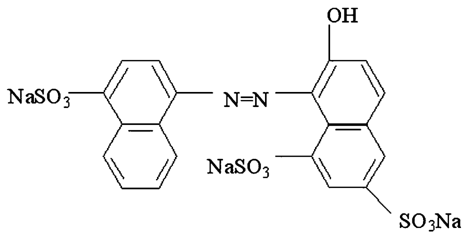

Fig. 1 The chemical structure of Acid Red 18

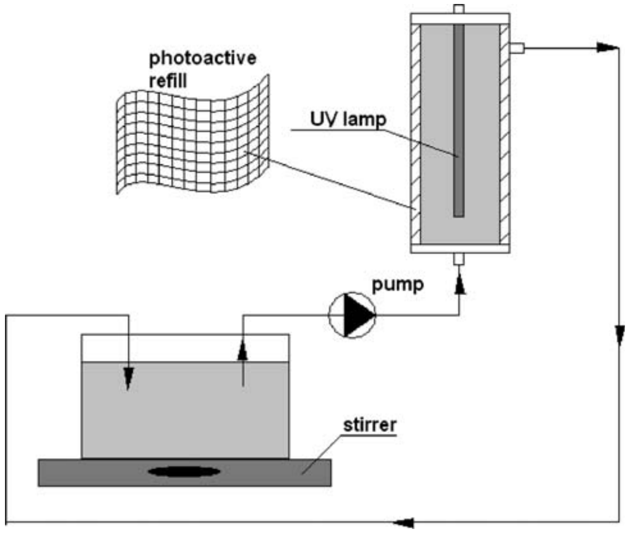

Fig. 2 The scheme of installation for the process of photocatalytic oxidation of AR18

The solution of AR18 was pumped from the container to the reactor by peristaltic pump and was circulated through the reactor with the flow rate of 36 dm^3/h until the solution was colorless. 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). Total organic carbon (TOC) concentration was measured using “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.

The solution of dye was circulated through the reactor for 15 min without illumination to obtain the adsorption equilibrium. The adsorption of dye onto photocatalyst surface was low (about 1 wt.%).

3 Results and Discussion

The experiments of the photocatalytic degradation of dye were conducted for the initial concentration of dye equal to 10 mg/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 that no discoloration of the dye solutions took place. The direct photolysis was also negligible. The reactions of photocatalytic decomposition of dye were conducted until the solution was colorless.

Figure 3 presents the changes in dye concentration during three runs of the photocatalytic process performed with the same photoactive refill. The concentration of dye decreased with the time of the process. As can be seen from Fig. 3, the highest removal of color was obtained during the first hours of the process. After that, the color removal decelerates; however, the complete discoloration of the solution was obtained. During the first run a complete

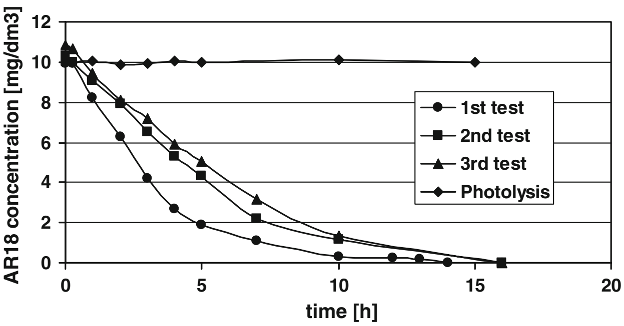

Fig. 3 The changes in dye concentration during the photocatalytic process

discoloration of the solution was observed in a relatively short time of 13 h. In the second run, the time of a complete color removal was only slightly longer—13.75 h. The third run showed comparable time of discoloration as the second one.

The changes of dye concentration were monitored by UV/vis spectroscopy. Discoloration of the solution during the process resulted from a decrease of dye concentration as well as the cleavage of –N=N– bonds which determine the color of azo-dyes. Figure 4 presents the UV/vis spectra of Acid Red 18 recorded during the photocatalytic process. The absorption bands in visible region are attributed to chromophore groups containing azo unit, whereas absorption in ultraviolet region is associated with the presence of aromatic rings in dye molecule. As can be seen from Fig. 4, a decrease of absorption bands in both, UV and vis regions, was observed during the photocatalytic process.

Decolorization of the solution does not provide a complete data on the dye degradation. Figure 5 presents the changes of TOC concentration during the process. As can be seen from Fig. 5, the TOC removal during the first hours of the process was slow and then it accelerated. It is on the contrary to the removal of colour. Discoloration of the solution was faster at the beginning of the process. This observation might suggest that during the first hours of the process, when the fast decolorization occurs, 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 concentrations at the end of the process amounted to 1.65, 1.54 and 1.43 mg/dm^3 for the first, second and third run, respectively. Although the removal of TOC was not complete, the obtained values meet the legal regulations with respect to TOC concentration in water.

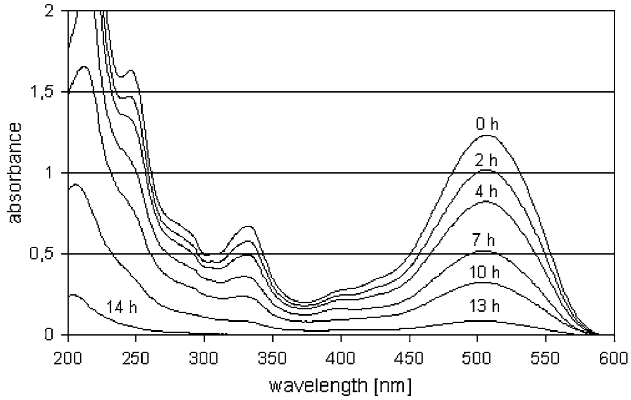

Fig. 4 The spectra of dye solutions recorded during the photocatalytic process

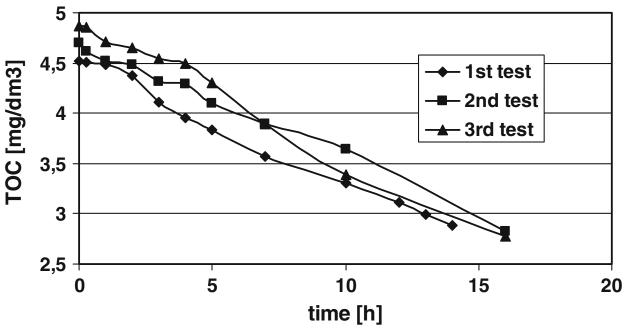

Fig. 5 The changes of TOC concentration during the photocatalytic process

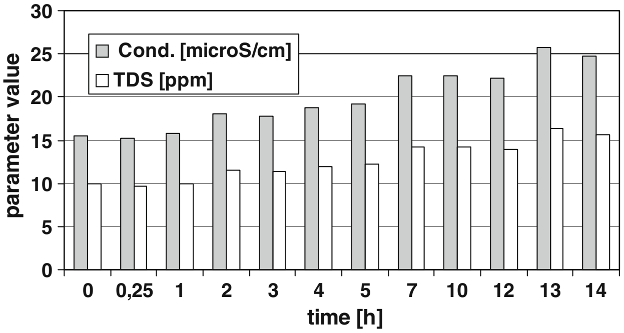

Fig. 6 The changes of conductivity and TDS during the photocatalytic process

The changes of conductivity and TDS during the photocatalytic process are shown in Fig. 6. The conductivity and TDS values tend to increase with the time of the process. The initial concentration of TDS in the solution during the first run amounted to 10.32 ppm and after 13 h of the process performance it reached the value of 14.87 ppm. The initial conductivity amounted to 16.28 µS/cm and at the end of the process the value of this parameter was 23.6 µS/cm. This indicates the increase of number of dissolved species present in the solution. For the other two runs, the changes of conductivity and TDS values were 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 mineralization of the dye as well as from sulfonate groups present in the structure of the dye.

4 Conclusions

The results of the studies revealed that the titania–silica coating shows a high photocatalytic activity toward decomposition of AR18 in water. The prepared coating exhibited high stability since a negligible decrease of photoactivity in the repeated cycles of water treatment was observed. The complete removal of color was achieved in a relatively short time of about 14 h. It was found that not only decolorization but also mineralization of 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 solves the problem associated with a replacement of the reactor or the parts of the reactor when the photocatalysts activity decreases because only the photoactive refill can be easily replaced.

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