

# Photocatalytic Degradation of Textile Dyes in aTiO<sub>2</sub>/UV System

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This study is focused on development of a method of TiO<sub>2</sub> immobilization, convenient for the wastewater remediation (especially for the degradation of textile dyes) and cheap for an industrial operation. An influence of selected operational parameters on process performance was verified. Methylene Blue was chosen as the model dye, however, a possibility of decolorization of other dyes was also tested. Two different ways of TiO<sub>2</sub> immobilization were examined. An application of polyvinylalcohol (PVA) revealed to be more convenient for our purposes than application of the polyacrylamide (PA), as the observed degradation rate was much faster with the PVA. When TiO<sub>2</sub> was immobilized in PA gel, the effects of the volumetric flow rate of the treated liquid through the photoreactor, wavelength of the UV light and the amount of immobilized TiO<sub>2</sub> on decolorization process were negligible. Higher light intensity made the dye degradation substantially faster.

## 1. Introduction

Synthetic dyes are used almost in all branches of the consumer goods industry. About 10 000 tons of dyes are produced per year (Double and Kumar, 2005). Inevitably, there are dye losses (approximately 12 % of used amount) during manufacturing and processing operations (Peternel et al., 2007). The effluents from these operations are usually highly colored, toxic, carcinogenic or mutagenic. As the most of the synthetic dyes is resistant to the light or other degradative environmental conditions, it is necessary to remediate these effluents before they are released to the environment. However, common wastewater treatment plants are ineffective in removal of dyes from the wastewaters. One of possible options to modify these facilities to get better outcome is an application of the Advanced Oxidation Processes (AOPs), i.e., chemical methods based on generation of highly reactive hydroxyl radicals (Peternel et al, 2007).

The AOPs includes heterogeneous photocatalysis capable of a degradation of a wide range of organic compounds including the dyes (Haarstrick et al., 1996; Lachheb et al., 2002). Semiconductors such as ZnO or TiO<sub>2</sub> are often used as catalytic agents because of their high stability, low costs, high efficiency and nil toxicity. In our study we used TiO<sub>2</sub>, which exhibits higher catalytic activity under the UV light irradiation than ZnO (Peternel et al., 2007). Other possible AOPs to degrade organic pollutants and dyes are O<sub>3</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV and Fe<sub>2</sub>O<sub>3</sub>/UV processes. Photocatalytic activity of TiO<sub>2</sub> can be substantially affected by its crystalline structure. Tanaka et al. (1991) reported that catalytic activity of the anatase is much higher than the catalytic activity of the rutile. Besides crystalline structure the catalytic activity of TiO<sub>2</sub> can be also influenced by its particle size. Xu et al. (1999) observed increased degradation rate as the particle size of TiO<sub>2</sub> decreased.

A mechanism of the photocatalytic degradation of organic compounds and dyes can be described by following steps (Vautier et al., 2001):

Absorption of photons by TiO<sub>2</sub> and production of photoholes and electron pairs



Oxygen ionosorption



Neutralization of  $OH^-$  by photoholes



Reaction of an organic pollutant with  $OH^{\cdot}$  radical or directly with the holes



The first step of the previous mechanism can be carried out only by photons with the energy higher than the bandgap energy of  $TiO_2$  (for rutile:  $h\nu \geq E_g = 3.2$  eV). It corresponds to the light wavelength  $\lambda < 388$  nm (Wonyong et al., 2000). In a case of the colored pollutants it is also possible to use visible light to achieve  $TiO_2$  photocatalytic degradation. The visible light absorbing chromophores of the dye absorb photons creating excited dye molecule. From the excited dye, the electron is injected into the conduction band of  $TiO_2$ , leaving cationic dye radical (Prevot et al., 2001; Yiming et al., 2001). If there are no visible light absorbing species in the effluents, it is possible to use other photo-sensitizing techniques. For example, Eunyong et al. (2003) observed dechlorination of  $CCl_4$  on  $TiO_2$  modified by ruthenium-complex sensitizers ( $TiO_2/Ru^{II}L_3$  or  $Pt/TiO_2/Ru^{II}L_3$ ) irradiated by visible light, while no dechlorination was observed on  $TiO_2$  or  $Pt/TiO_2$ . This research is very important as the visible light forms substantial part of the solar radiation, which is available for free and in an inexhaustible amounts. It makes industrial applications of photochemical degradation of pollutants economically attractive.

The most of experiments on the  $TiO_2$  photocatalytic degradation of pollutants were carried out using dispersed  $TiO_2$  particles (Xu et al., 1999; Wang et al., 2006). However, for technological applications an usage of the immobilized  $TiO_2$  is much more advantageous, despite the dispersed  $TiO_2$  exhibits higher photocatalytic degradation efficiency. The main advantage of the immobilized catalyst resides in the fact that no additional equipment or energy to separate the catalytic particles from the treated stream are required. There are many options to immobilize the  $TiO_2$  particles. For example, Haarstrick et al. (1996) used immobilized  $TiO_2$  on the quartz sand in a fluidized bed photoreactor. Wonyong et al. (2000) used  $TiO_2$  immobilized on glass plates. The way of the catalyst immobilization can seriously influence the photocatalytic degradation efficiency and costs of the entire treatment process. Therefore, the aim of this study was to find convenient methods of  $TiO_2$  immobilization with a perspective to degrade textile dyes in waste waters and to examine influences of chosen operational conditions on the dye degradation process.

## 2. Material and methods

### 2.1 Chemicals

The anthraquinone dye Remazol Brilliant Blue R (RBBR), the azo dye Reactive Orange 16 (RO16), the Methylene Blue (MB) and  $TiO_2$  containing 99 % of the anatase were purchased from Sigma-Aldrich. All other chemicals used in the experiments were gained from local sources and were of the analytical grade.

### 2.2 Photocatalytic reactor

Textile dye degradation experiments were carried out in the experimental equipment schematically depicted in Figure 1. The basic part of the apparatus is the photoreactor with the immobilized  $TiO_2$ . The body of the reactor was made of the polycarbonate. The body was covered with the UV light transparent quartz glass. The inner dimensions of the reactor are: 70 mm × 45 mm × 3 mm (length × width × depth). The inner space of the reactor was divided by 3 spacers to ensure required liquid flow pattern.

The immobilized  $TiO_2$  (see section 2.3) was irradiated through the quartz glass by UV-lamps. Three UV-lamps were tested in our experiments: 500 W high pressure mercury lamp, 6 W lamp (UVGL 58, UVP) and 4 W lamp (UVGL-25, UVP). The last two lamps emitted monochromatic light at wavelengths 254 or 365 nm, respectively, and were placed directly at the surface of the quartz glass. Only a half of the 6 W lamp was used to irradiate the inner space of the photoreactor.

The stock solution (simulated waste water) containing dissolved dye was pumped from a bottle by the peristaltic pump (Lambda Multiflow) through the reactor with the immobilized  $TiO_2$  and then it was returned back to the bottle. The volumetric flow rate of the liquid was set to 0.5 mL min<sup>-1</sup> or to 2 mL min<sup>-1</sup>. The entire volume of the liquid in the apparatus equalled 65 mL. The stock dye solution in the bottle was stirred by the magnetic stirrer and the concentration of the dye in the liquid was measured by the immersion probe of the UV-VIS spectrophotometer.

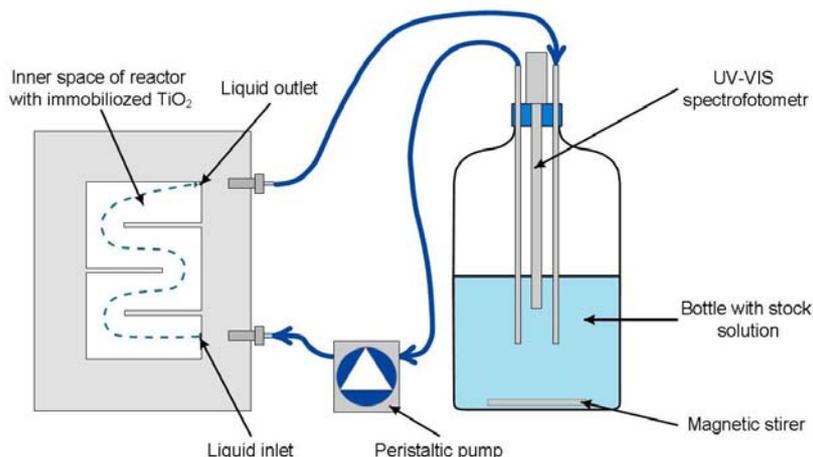


Figure 1: Experimental set-up

### 2.3 TiO<sub>2</sub> immobilization

Two different ways of TiO<sub>2</sub> immobilization were used in this study: i) entrapment in polyacrylamide and ii) entrapment in polyvinyl alcohol. Polyvinyl alcohol particles were prepared by dropping a dispersion of 1 % (w/w) of TiO<sub>2</sub> in 10 % (w/w) polyvinyl alcohol solution by syringe needle to the saturated boric acid solution. The formed particles were then thoroughly washed with the distilled water. To prepare a layer (thickness 1 mm) of the polyacrylamide containing 1 % (w/w) of TiO<sub>2</sub> in the reactor 1.25 mL acrylamide solution containing 15 % (w/w) acrylamide and 0.75 % (w/w) bisacrylamide, 0.75 mL 0.05 mM phosphate buffer (pH = 8), 1.675 mL distilled water and 37.5 mg TiO<sub>2</sub> were mixed together and poured onto the reactor plate. The acrylamide polymerization was then initiated by adding 6.25  $\mu$ L TEMED and 62.5  $\mu$ L 10 % (w/w) ammonium persulphate solution.

### 2.4 Dyes concentration assay

The concentrations of dyes were determined spectrophotometrically at 490 nm for RO16, 592 nm for RBBR and 665 nm for MB.

## 3. Results and discussion

First we carried out experiments with TiO<sub>2</sub> immobilized in the polyacrylamide in the form of a thick layer (1 mm) on the bottom of the reactor. Above the polyacrylamide layer was the layer of the flowing liquid (thickness of 2 mm) containing the dye. In these experiments the volumetric liquid flow rate was set to 2 mL min<sup>-1</sup> and initial concentration of the dye MB was adjusted to 50 mg L<sup>-1</sup>. The inner space of the reactor was irradiated by the UV light at wavelength 365 nm (lamp power 3 W). Figure 2 shows the time dependence of MB concentration in the liquid during these experiments. Already before irradiation of the reactor by the UV light (at the time  $t = 0$  hours) significant decrease of the MB concentration was observable. There are two possible causes of this observation: a) adsorption of the dye on the walls of the bottle, the reactor and tubes, or b) an absorption of the dye in the polyacrylamide layer. To find out, which of these two options is the real reason for the initial rapid dye concentration decrease another experiment was carried out. We immobilized TiO<sub>2</sub> in a polyacrylamide layer in Petri dishes (layer thickness 1 mm, area 62 cm<sup>2</sup>) and onto this layer solutions with various initial dye concentrations were poured (25 mL) and the system was allowed to reach equilibrium without any UV light irradiation (see Figure 2 - inset). Using initial and equilibrium dye concentrations, known liquid volume and the surface area of the gel layer it is possible to evaluate amount of the dye adsorbed in the polyacrylamide layer in the reactor. We found that less than 1 % of the dye is adsorbed in the polyacrylamide layer while on the walls of bottle, reactor and tubes about 76 % of the initial amount of dye present in the liquid adsorb. However, during the photodegradation process the most of the adsorbed dye desorbs back to the liquid. The dye adsorption to the walls of experimental apparatus is a reason of low dye concentration in the solution and therefore of the low degradation rate of MB. Therefore, it would be convenient to use another materials to build the experimental apparatus (dye adsorbs especially to silicon tubes and sealings). However, the MB was adsorbed also to the glass bottle and Teflon stirrer.

To evaluate possibility of repeated applications of TiO<sub>2</sub> immobilized in the polyacrylamide, three degradation cycles with the same polyacrylamide layer were carried out (see Figure 2). It is obvious that degradation rate of the dye increases, especially between the 1<sup>st</sup> and the 2<sup>nd</sup> degradation cycle. There are few possible explanations: At the start of the 1<sup>st</sup> degradation cycle the polyacrylamide layer is flat, but during the experiments its surface becomes wavy. Therefore, some parts of the polyacrylamide layer are closer to the quartz glass and there is thinner layer of the liquid, which absorbs UV light. There can be also larger surface area as a consequence of a physical degradation of the polyacrylamide layer surface (especially by the liquid flow). The higher degradation rate of MB can be also caused by photocatalytic degradation of the polyacrylamide as a result of TiO<sub>2</sub> irradiation by UV light, which could make pores in the polyacrylamide gel more convenient for penetration of MB molecules making adsorption on TiO<sub>2</sub> particles easier. Albarelli et al. (2009) observed similar behaviour of Ca-alginate beads containing TiO<sub>2</sub> and proposed similar explanations.

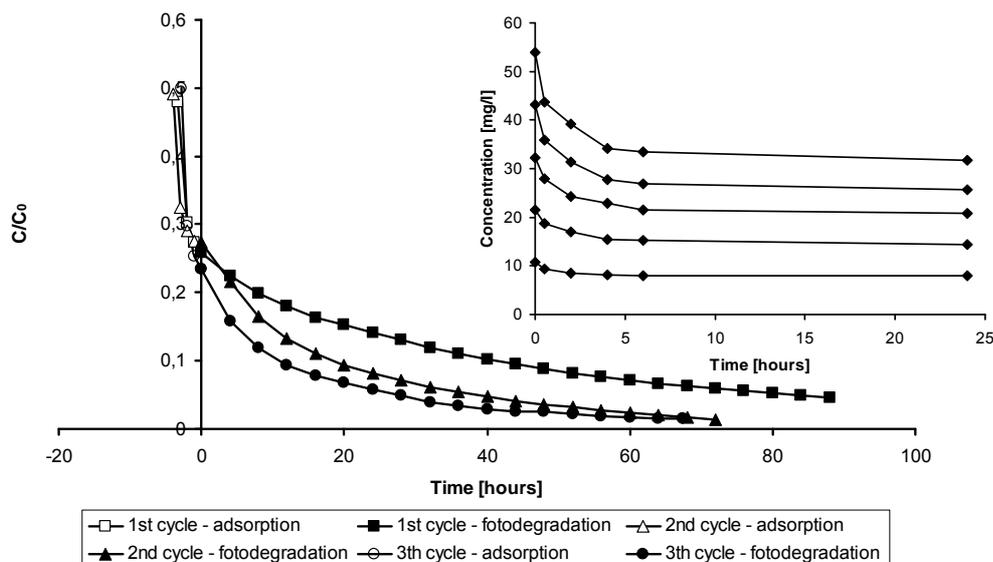


Figure 2: Time dependence of relative MB concentration (UV light 365 nm, 3 W, polyacrylamide, 2 mL min<sup>-1</sup>, initial MB conc. 50 mg L<sup>-1</sup>); inset: adsorption of MB to polyacrylamide layers in Petri dishes

We were also interested in influence of chosen process parameters to MB photodegradation rate. One of these parameters was the liquid volumetric flow rate through the photoreactor. The result of the higher volumetric liquid flow rate is the higher mass transfer rate between the liquid and the polyacrylamide layer and therefore also faster MB degradation. Nevertheless, there was just a negligible change of the degradation rate when the volumetric flow rate of the liquid through the photoreactor was increased from 0.5 to 2 mL/min (data not shown). Therefore we can suppose that mass transfer between the liquid and the polyacrylamide layer is not the rate limiting step at least within this range of the liquid volumetric flow rate. Another parameter that could influence degradation rate of the dyes is the wavelength of the UV light irradiating the TiO<sub>2</sub> particles. Therefore we used two UV light wavelengths (254 nm and 365 nm, both 3W) to degrade MB (keeping other conditions constant), but no remarkable difference in the degradation rate was observed. To verify influence of the amount of TiO<sub>2</sub> immobilized in the polyacrylamide on the MB degradation rate, experiments (liquid volumetric flow rate 2 mL min<sup>-1</sup>, initial MB concentration 20 mg L<sup>-1</sup>, 4 W UV lamp, wavelength 254 nm) with the polyacrylamide layer containing original (1 % w/w) and three times higher quantity of TiO<sub>2</sub> were performed. However, no increase of the degradation rate was observed (see Figure 3). Possible explanation of this phenomenon is: the most of TiO<sub>2</sub> particles settle during the gel polymerization to the bottom of layer therefore only a small portion of TiO<sub>2</sub> remains on a top of the gel layer, where it can be used for the photodegradation. The polyacrylamide layer containing 3 % (w/w) of the TiO<sub>2</sub> was irradiated also by 500 W high pressure mercury lamp. The relative intensity irradiation spectrum of this lamp is shown in Figure 3. However, only a small part of 500 W lamp power was really used to irradiate the photoreactor and only 13 % of output power was irradiated at wavelengths shorter than 388 nm, which is suitable for production of  $h_{\nu b}^+ + e_{cb}^-$  pairs in TiO<sub>2</sub> (Wonyong et al, 2000). However, in this case the light with the longer wavelength than 388 nm could contribute to photodegradation of dyes (see section 1). The higher irradiation intensity had positive effects to the degradation rate. It took less than 25

hours to completely decolorize the stock solution (see Figure 3). In these experiments a somewhat modified experimental set-up was used, therefore the relative equilibrium MB concentration in the stock solution before the photodegradation process gained higher value.

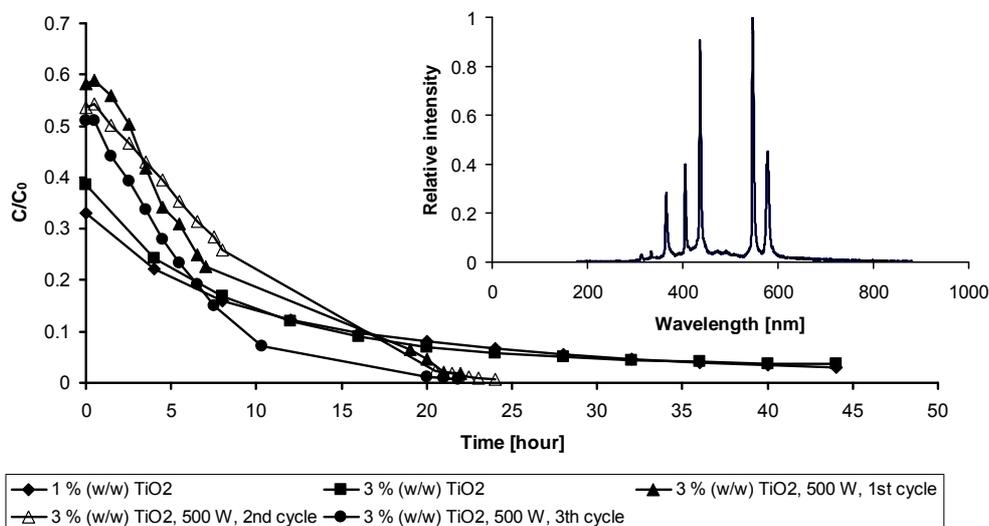


Figure 3: Time dependence of relative MB concentration during photodegradation (4 W UV lamp - 254 nm or 500 W high pressure mercury lamp, after adsorption of dye to walls of apparatus)

Besides MB also other textile dyes were subjected to photodegradation by TiO<sub>2</sub> immobilized in the polyacrylamide layer. With the RO16 only 34 % decolorization in 90 h was achieved (initial dye concentration 50 mg L<sup>-1</sup>, initial adsorption to polyacrylamide and walls 6 %). The RBBR dye was degraded significantly faster: 79 % decolorization within 90 h (initial concentration 50 mg L<sup>-1</sup>, initial adsorption to polyacrylamide and walls 6 %). The lower degradation rate of these dyes, compared to the MB, can be caused by their higher resistance to photodegradation or by their higher molecular weight (MB: 319.85 g mol<sup>-1</sup>, RO16: 617.54 g mol<sup>-1</sup>, RBBR: 626.54 g mol<sup>-1</sup>). For molecules with higher molecular weight it is more difficult to penetrate the small pores of polyacrylamide and adsorb to the surface of TiO<sub>2</sub> particles that is necessary for the photodegradation.

Except the polyacrylamide layer we tried to immobilize the TiO<sub>2</sub> within the spherical particles made of the polyvinyl alcohol (PVA). These particles had diameter 2-3 mm. In Figure 4 an adsorption of MB to the

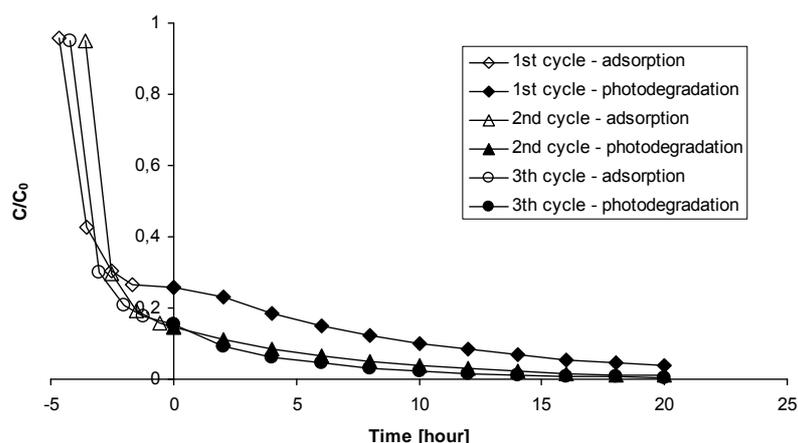


Figure 4: Relative concentration of MB during its adsorption to PVA particles and consecutive photodegradation (flow rate 2 mL min<sup>-1</sup>, initial MB conc. 20 mg L<sup>-1</sup>, 4 W UV lamp, wavelength 254 nm)

PVA particles and the following photodegradation is shown (liquid volumetric flow rate  $2 \text{ mL min}^{-1}$ , initial MB concentration  $20 \text{ mg L}^{-1}$ , 4 W UV lamp, wavelength 254 nm). Degradation of MB was much faster compared to the degradation in the polyacrylamide layer. It took less than 20 h to get almost 100 % decolorization. The faster decolorization rate in comparison to polyacrylamide is probably caused by easier diffusion of MB within the PVA and therefore higher adsorption of MB to the surface of  $\text{TiO}_2$  particles.

#### 4. Conclusions

Two ways of  $\text{TiO}_2$  immobilization for application in photocatalytic degradation of textile dyes were tested in this study. The application of polyacrylamide proved not to be effective enough for this purpose. The very low MB degradation rate was independent of the liquid volumetric flow rate through the photoreactor, the wavelength of the UV light and the amount of  $\text{TiO}_2$  immobilized in the polyacrylamide. However, the higher irradiation intensity made the dye degradation faster. The  $\text{TiO}_2$  immobilized in the PVA proved to be more suitable for MB decolorization. Nevertheless, the decolorization rate is very low in comparison to decolorization with the  $\text{TiO}_2$  freely dispersed in the treated liquid or other degradation methods, such as biodegradation by white rot fungi.

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