

## Dye decomposition on P25 with enhanced adsorptivity

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The preparation method and the activity of the TiO<sub>2</sub>-P25/N doped photocatalyst based on commercial titanium dioxide (TiO<sub>2</sub> Aeroxide® P-25 Degussa, Germany) are presented. For the TiO<sub>2</sub>-P25/N preparation TiO<sub>2</sub>-P25 and gaseous ammonia were kept in a pressure reactor (10 bars) for 4 hours at the temperature of 200°C. This modification process changed the chemical structure of the TiO<sub>2</sub> surface. The formation of NH<sub>4</sub><sup>+</sup> groups was confirmed by the FTIR measurements. Two bands in the range of ca. 1430 – 1440 cm<sup>-1</sup> attributed to bending vibrations of NH<sub>4</sub><sup>+</sup> could be observed on the FTIR spectra of the catalysts modified with ammonia and the band attributed to the hydroxyl groups at 3300 – 3500 cm<sup>-1</sup>, which were not reduced after N-doping. The photocatalytic activity of the photocatalysts was checked through the decomposition of two dyes under visible light irradiation. The modified TiO<sub>2</sub> thus prepared samples were more active than TiO<sub>2</sub>-P25 for the decomposition of dyes under visible light irradiation.

**Keywords:** visible-light active photocatalyst, N-doped, titanium dioxide, azo dye.

### INTRODUCTION

Photocatalytic reactions on the surface of titanium dioxide (TiO<sub>2</sub>) have attracted much attention in view of their practical applications to environment<sup>1-3</sup>. TiO<sub>2</sub> has the advantages due to its high chemical stability, no toxicity, and a relatively low-price, but a serious disadvantage is that only the UV light can be used for photocatalytic reactions. Therefore, it is of great interest to find the ways to extend the absorption wavelength range of TiO<sub>2</sub> to a visible region without the decrease of photocatalytic activity. Several research groups succeeded in Pt, Fe, S, Ln, N and Cd doping into the TiO<sub>2</sub> photocatalyst to obtain photoresponse under the visible light<sup>4-9</sup>. Asahi et al. reported that the N-doped TiO<sub>2</sub> showed a significant shift of the absorption edge to a lower energy in the visible light region<sup>10</sup>. The substitution doping of N atom was the most effective because its p states contributed to the band-gap narrowing by mixing with O 2p.

Ihara et al.<sup>11</sup> prepared the vis-active photocatalyst by the calcination of the hydrolysis products of Ti(SO<sub>4</sub>)<sub>2</sub> with the NH<sub>3</sub> aq solution. The catalyst absorbed light in the blue (400 nm) to bluish-green (500 nm) region, due to its vivid yellow color. The authors stated that the vis-activity could be realized on polycrystalline particles, not on the well-crystallized particles. The nitrogen-doped titania was prepared by planetary ball milling of TiO<sub>2</sub> Degussa P-25 titania with ammonium carbonate by Yin et al.<sup>12</sup>. TiO<sub>2</sub> Degussa P-25 showed an absorption edge at 408 nm corresponding to the band gap of 3.04 eV. The powders prepared by planetary milling of TiO<sub>2</sub> Degussa P-25 with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> showed two absorption edges at 400 – 408 nm (3.04 – 3.10 eV), and at 540 – 565 nm (2.19 – 2.30 eV). The first and second edges are related to the band structure of the original titania and the newly formed N 2p band which was located above the O 2p valence band, respectively.

Silveyra et al.<sup>13</sup> prepared N-doped TiO<sub>2</sub> Degussa P-25 by thermal treatment under the nitrogen enriched atmosphere. The N-TiO<sub>2</sub> presented a slight displacement in the absorption edge of light towards the visible radiation range. The authors proved that reducing the energy of the band

gap in N-doped catalysts increased their photocatalytic activity.

Wang et al.<sup>14</sup> obtained N-doped TiO<sub>2</sub> by treating nanotube titanic acid (NTA, H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> · H<sub>2</sub>O) in the NH<sub>3</sub> flow, which had higher visible light photocatalytic activity than the prepared N – doped TiO<sub>2</sub> Degussa P-25 under the same conditions.

In the case of photocatalytic dyes decomposition the literature suggests two different direct photocatalytic reaction mechanisms<sup>15</sup>. The first one is the Langmuir-Hinshelwood process. This mechanism is based on the production of electrons and holes by the photoexcitation of the catalyst. Then, the hole is trapped by the adsorbed molecule (AM<sub>ads</sub>) in order to form a reactive radical state. On the one hand, these reactive groups (AM<sub>ads</sub><sup>+</sup>) can decay when recombination with electron occurs and, on the other hand, its chemical reaction yields to the products and regenerates the original state of the catalyst surface (S). A different photocatalytic reaction mechanism is named the Eley-Rideal process. This process starts with the photogeneration of free carriers and the subsequent trapping of the holes by surface defects (i.e. „potential” surface active centers) S to produce the surface-active centers S<sup>+</sup>. These surface-active centers can, then react with the molecule (chemisorption) to form species (S-M)<sup>+</sup> that further decompose yielding the photoreaction products or can recombine with electrons, which represents their physical decay.

The aim of the presented work was to obtain a visible-light active TiO<sub>2</sub> photocatalyst, containing nitrogen, based on commercial titanium dioxide (TiO<sub>2</sub> Aeroxide® P25 Degussa, Germany) prepared by an evaluated pressure method. The photocatalytic activity of the obtained catalyst was estimated on the basis of the decomposition of the diazo dye (Reactive Black 5) and the poliazo dye (Direct Green 99).

**Table 1.** Comparison of isotherm constants and adsorption capacity of different adsorbents for phenol adsorption

Azo dyes	Structural formula	Molecular weight (g/mol)	$\lambda_{\max}$ (nm)
Reactive Black 5		992	597
Direct Green 99		1169	625

## EXPERIMENTAL

### Materials

Titanium dioxide Aeroxide® TiO<sub>2</sub>-P25 (Degussa, Germany) was used for modification. This titanium dioxide has a specific surface area of 50 m<sup>2</sup>/g and is composed of 80% anatase and 20% rutile<sup>16</sup>. The average sizes of the anatase and rutile elementary particles are 25 and 85 nm, respectively.

The commercially available Reactive Black 5 diazo dye and the Direct Green 99 polyazo dye, produced by The Chemical Factory Boruta – Color Sp. z o.o. (Poland), were used as the model compounds. In Table 1 the structural and molecular formulae and the max wavelengths of the azo dyes used for decomposition, are presented.

### Preparation of modified photocatalyst samples

4 g of Aeroxide® TiO<sub>2</sub>-P25 was placed in a pressure reactor (type BLH-800 Berghof, Germany, scheme published<sup>17</sup>). The reactor was closed and gaseous ammonia was introduced through the inlet valve, then the reactor was heated up to 200°C in. After that, the catalyst was kept at this temperature for 4 hours under the pressure of 10 bars. After that time the reactor was cooled down to the room temperature and the valves were opened. The obtained catalysts were dried in the oven for 18 hours at 105°C. After drying the photocatalyst was ground in the agate mortar before use. All the experiments were carried out with the use of double distilled water.

### Experimental procedures and techniques

The photocatalysts were characterized by the UV-VIS/DR technique with the use of the spectrophotometer (Jasco V-530 Japan), equipped with the integrating sphere accessory for diffuse reflectance spectra (BaSO<sub>4</sub> was used as reference).

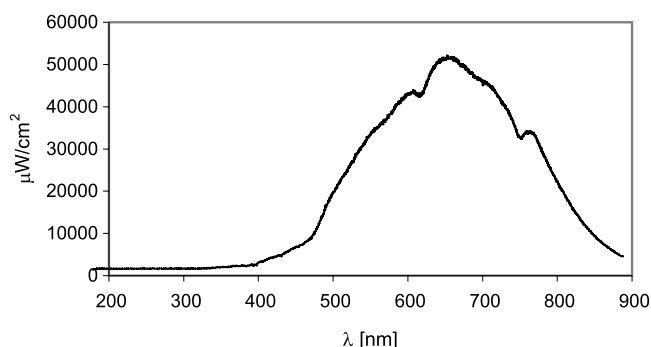
The surface properties of the photocatalysts were examined on the basis of the FTIR/DRS spectra. The measurements were performed using the Jasco FTIR 430 (Japan) spectrometer, equipped with a diffuse reflectance accessory (Harrick, USA).

The analysis of the OH radicals formation on the photocatalyst surface under UV irradiation were performed by the fluorescence technique, using terephthalic acid, which readily reacted with the OH radicals to produce a highly fluorescent product, 2-hydroxyterephthalic acid. The intensity of the peak attributed to 2-hydroxyterephthalic acid was known to be proportional to the amount of the OH radicals formed. The selected concentration of the

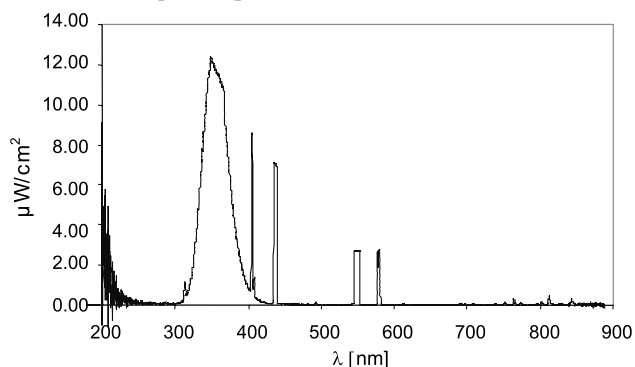
terephthalic acid solution was 10<sup>-4</sup> M. It has been proved that under such experimental conditions (low concentration of terephthalic acid, less than 10<sup>-3</sup> M, room temperature), the hydroxylation reaction of terephthalic acid proceeds mainly by the OH radicals<sup>18</sup>. For this experiment, TiO<sub>2</sub>-P25 and TiO<sub>2</sub>-P25/N samples of 0.02 g were magnetically stirred in 100 ml of the prepared terephthalic acid solution under UV irradiation. Sampling was performed in every 10 min. The solution, after the filtration through the membrane filter (pore size 0.45 μm) was analyzed in the fluorescence spectrophotometer (Hitachi F-2500). The product of terephthalic acid hydroxylation, 2-hydroxyterephthalic acid, gives a peak at the wavelength of about 424 nm by the excitation with the wavelength of 314 nm.

The reactions of the photocatalytic decolourisation of azo-dyes (Reactive Black 5 (RB) and Direct Green 99 (DG)) were carried out in a glass batch photoreactor containing 500 cm<sup>3</sup> of a model solution and 0.1 g of photocatalyst. The initial concentrations of Reactive Black 5 and Direct Green 99 solutions were equal to 5mg/dm<sup>3</sup>. The solutions were mixed with a magnetic stirrer during the reaction process. Firstly, the solution mixture was stirred for 15 min in the dark in order to get the equilibrium of dyes adsorption. Then the solution was irradiated for 5 hours using a 100 W lamp (Philips) as the Vis light source. The illumination intensity at the irradiation plate was equal to 400 W/m<sup>2</sup> for Vis and 0.09 W/m<sup>2</sup> for UV. It should be noticed that the intensity of the UV radiation in the experiment was very low (0.02% of the total illumination, whereas in solar radiation it equals to 5.52%). Due to this its influence can be considered as negligible. The activity of the photocatalysts was tested also under the UV light irradiation (6 x 20W UV lamp, Philips), with the radiation intensity of about 100 W/m<sup>2</sup> Vis and 154 W/m<sup>2</sup> UV. The illumination intensities were measured with the LB-901 illumination meter equipped with PD 204AB (Macam Photometrics Ltd.) and CM3 (Kipp & Zonen) external sensors. The emission spectra of the 100 W lamp (Philips) is presented in Fig. 1a and the 6 x 20 W UV lamp in Fig. 1b. The emission spectra were measured with the meter of radiation intensity and UV and Vis distribution USB4000 (Ocean Optics, Netherlands).

The photocatalysts were separated from the solutions using a centrifugal clarifier (Universal 320, Hettich Zentrifugen, Germany). The concentrations of model compounds were determined by UV absorbance measurement (Jasco V-530, Japan) at the wavelength of 597nm



**Figure 1a.** The emission spectrum of the visible light (100 W lamp, Philips)



**Figure 1b.** The emission spectrum of the UV light (6 x 20 W lamp, Philips)

(Reactive Black 5) or 624nm (Direct Green 99). The percentage of the decomposition of azo dyes was calculated from the equation:  $D = \frac{C_0 - C}{C_0} \cdot 100\%$ , where D is

the decomposition rate of azo-dye,  $C_0$  is the initial solution concentration and C is the solution concentration after 5 hours of irradiation.

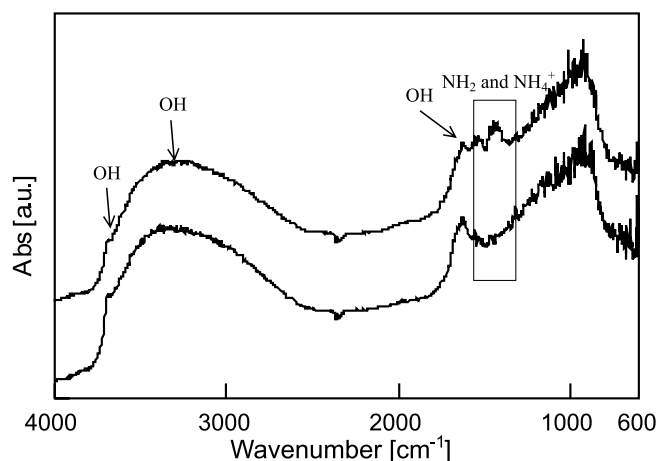
The content of total organic carbon (TOC) in the solution was measured using a Multi N/C Analyzer (Analytic Jena, Germany).

## RESULTS AND DISCUSSION

The Aeroxide® TiO<sub>2</sub>-P25 (Degussa Germany) is a well-known photocatalyst with very high photocatalytic activity and therefore is often used by many researchers.

The modification of TiO<sub>2</sub> photocatalysts under elevated pressure in the ammonia atmosphere is a new way of the preparation the titania doped photocatalysts. The modification of TiO<sub>2</sub> by ammonia, earlier studied by the group of Morawski<sup>19-21</sup>, showed that doping of nitrogen to TiO<sub>2</sub> through the calcinations of TiO<sub>2</sub> in an ammonia atmosphere, under the atmospheric pressure leads to receive the N-doped TiO<sub>2</sub> of higher photoactivity rather than the not modified TiO<sub>2</sub>.

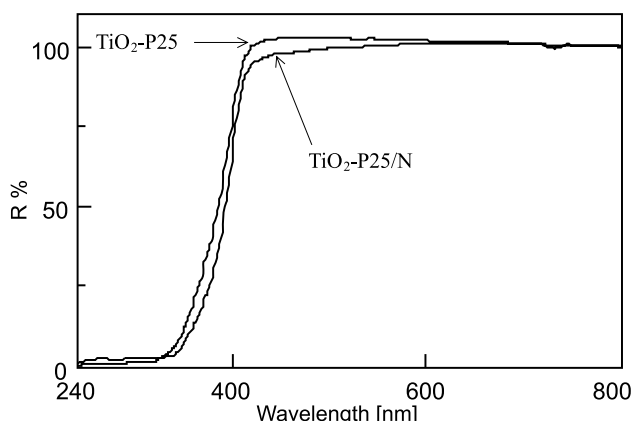
Modification of TiO<sub>2</sub> carried out under elevated pressure leads to the introduction of new groups to the surface of TiO<sub>2</sub> without the reduction of surface hydroxyl groups. The FTIR spectra of the modified and unmodified TiO<sub>2</sub>-P25 are presented in Fig. 2. The bands at 3695 cm<sup>-1</sup>, assigned to the stretching of a hydroxyl group chemisorbed on the surfaces defect site, the bands in the range of 3300 – 3500 cm<sup>-1</sup> assigned to hydroxyl groups for both the dissociated and molecularly adsorbed water and at 1623 cm<sup>-1</sup> assigned to the molecular water bending mode<sup>22</sup>. The



**Figure 2.** The FTIR/DRS spectra of the modified and unmodified TiO<sub>2</sub>-P25

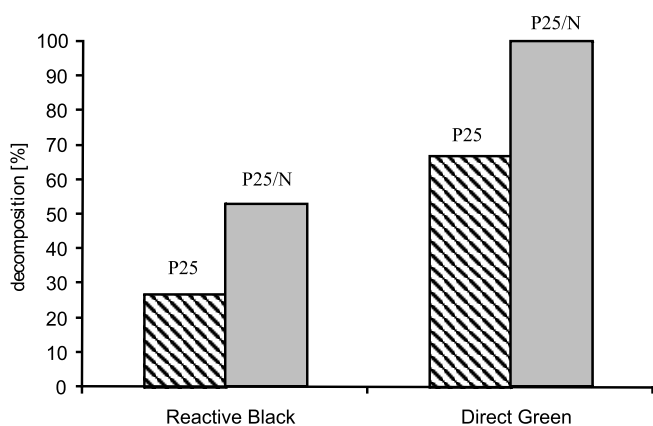
changes in the intensity of surface hydroxyl groups at 3300 – 3500 cm<sup>-1</sup> were not observed on the FTIR spectra of the N-doped on the FTIR spectra of the N-doped TiO<sub>2</sub>. The spectra of the catalyst modified with ammonia exhibit new bands at ca. 1430 – 1440 cm<sup>-1</sup> that could be attributed to the bending vibrations of NH<sub>4</sub><sup>+</sup> and at ca. 1535 cm<sup>-1</sup> associated to NH<sub>2</sub> groups<sup>23</sup> or NO<sub>2</sub> and NO<sup>11</sup>.

In Fig. 3 the UV-VIS/DR spectra of the unmodified and the N-doped TiO<sub>2</sub> catalysts are presented. It can be observed that there is no essential change in the character of the spectra in spite of the presence of ammonia, only insignificant decreasing of the reflectance in the visible region (400 – 650 nm) on the spectrum of TiO<sub>2</sub>-P25/N catalysts can be noticed. The decrease of reflectance is probably caused by the change of the colour of the obtained catalysts; the catalyst after the modification under the elevated pressure was yellowish. According to Suda et al.<sup>24</sup> the observed tendency may be due to the concentration of the nitrogen atoms in the TiO<sub>2-x</sub>N<sub>x</sub> particles.



**Figure 3.** The UV-VIS/DR reflection spectra of the nitrogen modified and unmodified TiO<sub>2</sub>-P25

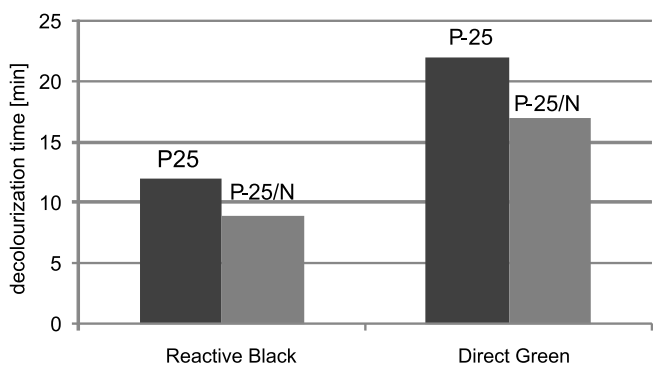
The photocatalytic activity of the TiO<sub>2</sub>-P25 and TiO<sub>2</sub>-P25/N was checked by azo dyes decolourisation under the visible light irradiation. At the beginning of the investigation the blank experiments were carried out, it demonstrated that Reactive Black 5 and Direct Green 99 were not degraded in the aqueous TiO<sub>2</sub> suspension in the dark, but when they were irradiated with visible light in the absence of TiO<sub>2</sub>. Fig. 4 shows the results of the photocatalytic activity for the undoped and the N-doped TiO<sub>2</sub>-P25. The TiO<sub>2</sub>-P25/N exhibited the best decolourisation efficiency with 100% of DG 99 decolorized in 5 hrs,



**Figure 4.** Photocatalytic decomposition of Reactive Black 5 and Direct Green 99 on  $\text{TiO}_2\text{-P25}$  and  $\text{TiO}_2\text{-P25/N}$  under the visible light

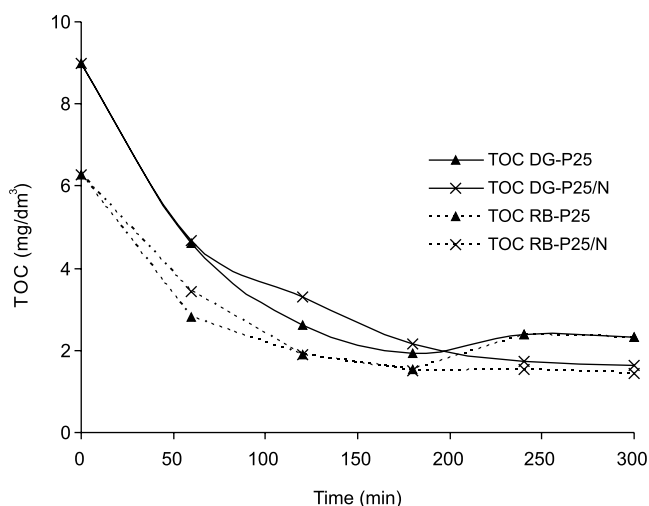
while undoped  $\text{TiO}_2$  showed 67% efficiency. Similarly as during the degradation of DG 99, the  $\text{TiO}_2\text{-P25/N}$  catalyst was more effective in RB 5 decolorization. The percentage of the decolourisation for the modified photocatalyst amounted to 53%, whereas for  $\text{TiO}_2\text{-P25}$  only 27%.

The photocatalytic activity of the modified and unmodified P25 was checked during azo dyes decomposition under the UV light irradiation. The „decolourisation time” of the dye solution was measured. Two different azo dyes were used for the photocatalytic activity tests: diazo dye (Reactive Black) and poliazo dye (Direct Green). The „decolourization time” is the time when the colour of the solution disappears, it means when the destruction of the chromophore group ( $\text{R1-N=N-R2}$ ) occurs. In Fig. 5 the „decolourization time” of the azo dyes is presented. The „decolourization time” of the dyes solutions using the nitrogen-modified  $\text{TiO}_2$  was shorter than for the unmodified P-25.



**Figure 5.** The decolourization time of the di and poli azo dye solution during photocatalytic process under the UV light irradiation. Dye concentration = 5 mg/l, amount of photocatalyst = 0.2 g/l

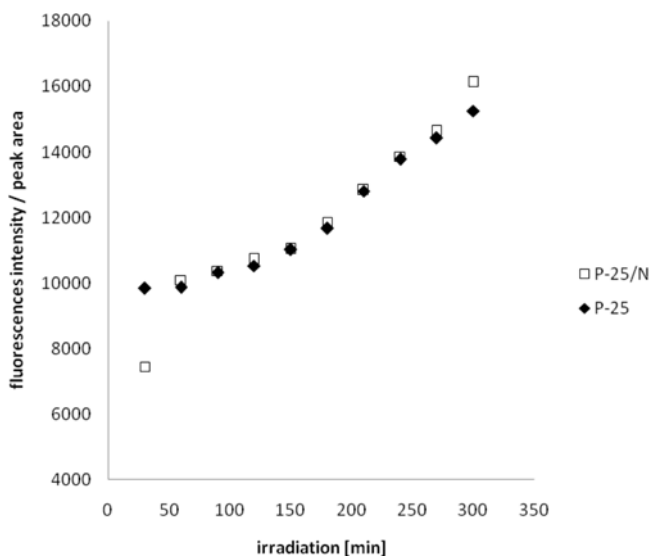
The progress of the photocatalytic reaction was measured by the UV-VIS spectroscopy and the TOC measurements. The decreasing in the TOC of the decolourised slurry with the time of the irradiation for the modified (P25/N) and unmodified (P25)  $\text{TiO}_2$  is presented in Fig. 6. The TOC concentration of the dyes solutions decreased slowly, when visible radiation was used for the decomposition. To show the differences in the mineralisation degree for the investigated catalysts the decomposition of the dyes, together with the TOC measurements, was carried out under UV radiation. In Fig. 6 the changes in TOC during the decomposition of the dyes under the UV



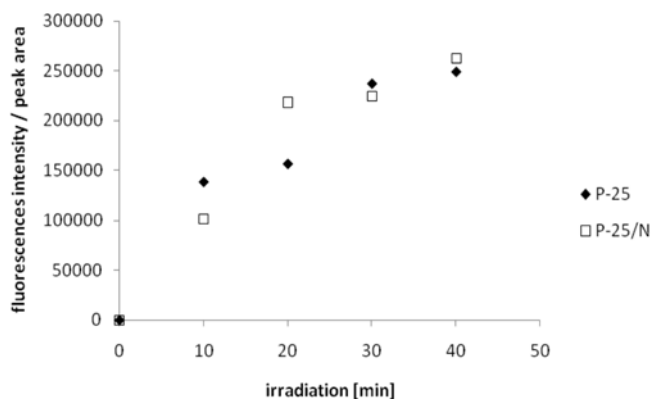
**Figure 6.** Changes in TOC concentration during the photocatalytic decomposition of Reactive Black 5 and Direct Green 99 on  $\text{TiO}_2\text{-P25}$  and  $\text{TiO}_2\text{-P25/N}$  under the UV light

radiation are shown. Finally, the TOC was degraded for RB 5 up to 77% on  $\text{TiO}_2\text{-P25/N}$  and for DG 99 – 84%, whereas on  $\text{TiO}_2\text{-P25}$  – 63 and 74%, respectively. After ca. 180 min of irradiation, an increase of the TOC concentration in the case of P25 was observed. This behaviour is, probably caused by a small desorption of the intermediates from the photocatalyst surface.

In Fig. 7 and 8 the formation of OH radicals on the surface of  $\text{TiO}_2\text{-P25/N}$  and  $\text{TiO}_2\text{-P25}$  is shown with the time of the Vis and UV irradiation, respectively. The amount of OH radicals increases with increasing the Vis and UV irradiation time, due to the generation of the OH radicals after  $\text{TiO}_2$  excitation and their reaction with terephthalic acid on the surface of  $\text{TiO}_2$  particles. Almost the same amount of the OH radicals can be observed on  $\text{TiO}_2\text{-P25}$  and the modified  $\text{TiO}_2\text{-P25/N}$ . However, this fact did not correspond to a larger efficiency of the photocatalytic activity of the N-doped  $\text{TiO}_2$  catalyst. Although the amount of the formed hydroxyl radicals on  $\text{TiO}_2\text{-P25/N}$  was the same as on  $\text{TiO}_2\text{-P25}$ , the percentage of the decomposed azo dyes was higher. Therefore, it can be supposed that the additional photocatalytic activity of the



**Figure 7.** Formation of the OH radicals with the Vis irradiation time on the  $\text{TiO}_2\text{-P25}$  and  $\text{TiO}_2\text{-P25/N}$  samples



**Figure 8.** Formation of the OH radicals with the UV irradiation time on the TiO<sub>2</sub>-P25 and TiO<sub>2</sub>-P25/N samples

modified catalyst depends on the presence of ammonia/nitrogen groups on the surface. The ammonia/nitrogen groups change the ability for the adsorption of dyes, which is the most important catalytic step. In our preliminary study it was found that on TiO<sub>2</sub>-P25/nitrogen photocatalyst there occurs the several times higher adsorption of RB and DG dyes than on the surface of pure P25. Another explanation is based on the ability of the nitrogen doped TiO<sub>2</sub> for the prevention of electron/hole (e<sup>-</sup>/h<sup>+</sup>) recombination. The direct decomposition, according to the mechanism of Langmuir-Hinshelwood and Eley-Rideal also could play role in the higher photoactivity of TiO<sub>2</sub>-P25/nitrogen.

## CONCLUSIONS

1. The modification of TiO<sub>2</sub> (P25) under the elevated pressure of gaseous ammonia leads to obtaining of the photocatalyst with nitrogen groups on the surface.

2. It was found that nitrogen modification doesn't change the amount of hydroxyl radicals produced on the photocatalyst surface but increased the adsorption capacity of the photocatalyst.

3. High adsorption capacity of photocatalyst led to the increase of the photocatalytic activity of TiO<sub>2</sub>-P25/nitrogen under the visible and UV light irradiation.

4. The direct decomposition, according to the mechanism of Langmuir-Hinshelwood and Eley-Rideal could also play role in the higher photoactivity of TiO<sub>2</sub>-P25/nitrogen.

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