

TiO₂ modified by ammonia as a long lifetime photocatalyst for dyes decomposition

Julia Choina¹, Diana Dolat¹, Ewelina Kusiak¹, Magdalena Janus^{1,2,*}, Antoni W. Morawski¹

West Pomeranian University of Technology,

¹ Institute of Chemical and Environment Engineering, Department of Water Technology and Environment Engineering, ul. Pułaskiego 10, 70-322 Szczecin, Poland,

² Department of Sanitary Engineering, al. Piastów 50, 70-310 Szczecin, Poland

* corresponding author: e-mail: mjanus@zut.edu.pl

Ammonia-modified TiO₂ (TiO₂/N), prepared in a pressure reactor was used as the well- active and long-life photocatalyst for the azo dye (Reactive Red 198) decomposition. The effect of aeration and the different value of the pH of the reaction medium on the photocatalytic degradation of Reactive Red 198 in water has been investigated. It has been reported that the degradation is greatly influenced by the reaction pH and the faster decomposition of azo dye took place at pH 3.5. When the solution was acidic, a larger amount of azo dye on the positively charged surface of TiO₂ photocatalysts was adsorbed. From the obtained results it can be seen that the effectiveness of the decolourisation of the solution was faster by using the nitrogen-modified TiO₂.

Keywords: photocatalysis, nitrogen-modified TiO₂, lifetime

INTRODUCTION

The greatest challenge for a researcher is the removal of the contamination from the wastewater generated by the industry e.g. textile industry containing considerable amounts of azo dyes. This kind of pollution has been problematic because of their toxicity and resistance to biodegradability. The conventional wastewater treatment methods are usually ineffective in the removal of these compounds. That is why new, more effective and less expensive, methods of removing wastewater pollution have been widely investigated.

Special attention has been given in this area to heterogeneous photocatalysis using TiO₂ as a photocatalyst which included adsorption of cationic and anionic dyes on TiO₂. Previous studies indicate that TiO₂ is the most effective and the most extensive photocatalyst and more frequently used as a good adsorbent in the degradation of azo dyes from water.

The most reactive form of titanium dioxide is anatase, however, it has high-energy gap ($E_G > 3.2\text{eV}$) and for this reason it could be excited only by UV light irradiation ($\lambda < 380\text{ nm}$)¹. On the other hand, rutile has lower-energy gap than anatase ($E_G < 3.1\text{eV}$), however, it has also very short recombination time, which makes it almost completely inactive as a photocatalyst. That is why nowadays, the methods of moving the absorption spectrum of anatase TiO₂ into the main part of solar spectrum ($\lambda > 380\text{ nm}$) are widely investigated. Due to TiO₂'s large band gap and the use of only 3 – 5% of the solar spectrum that reach the earth² it is necessary to develop the efficient way to not only extend the absorbance of TiO₂ into visible regions but new methods of the modification of TiO₂ to obtain a better quality of the photocatalyst are widely investigated. The development of the visible light response has a positive effect on the improvement of the photocatalytic efficiency.

It was found that substitutional N-doping was a very effective method of the preparation of the VIS – active photocatalyst. Asahi et al.⁴ obtained TiO_{2-x}N_x by sputter-

ing the TiO₂ target in N₂(40%)/Ar gas atmosphere and then subjecting it to the heat treatment at 550°C in N₂ gas for 4h. TiO₂ films were prepared in a similar way by sputtering the TiO₂ target in an O₂(20%)/Ar gas mixture and subsequently annealing it at 550 °C in O₂ gas for 4h. It was proved that TiO_{2-x}N_x film absorbed the light at the wavelengths lower than 500nm, whereas the TiO₂ film did not. The authors concluded that the visible light absorption by N-doped TiO₂ is due to the substitution of oxygen by nitrogen, which results in mixing of N(2p) and O(2p) states.

Yuan et al.⁵ prepared the nitrogen-doped TiO₂ directly by the hydrolysis of titanium tetrachloride (TiCl₄) and heating the mixture of urea and TiO₂. Ihara et al.⁶ prepared the VIS-active photocatalysts by the calcinations of hydrolysis products of Ti(SO₄)₂ previously treated with the aqueous NH₃ solution. They concluded that the oxygen-deficient sites formed in the grain-boundaries are important for the VIS-activity to emerge and nitrogen doped in the part of oxygen-deficient sites is important as a blocker for re-oxidation. Suda et al.⁷ prepared TiO_{2-x}N_x thin films by the pulsed laser deposition method (PLD). The TiO_{2-x}N_x films were activated by the visible light irradiation as well as the UV light irradiation.

Other aims are to obtain a photocatalyst with a relatively long lifetime. Tasbihi et al.⁸ examined the lifetime of the catalysts based on the TiO₂ supported on glass beads, silica gel and quartz sand, which were synthesized using the sol-gel methods. The photocatalyst supported on the quartz sand turned out to be the most efficient during the first degradation process with the efficiency of about 90% after 6h, while the TiO₂/silica gel and the TiO₂/glass beads obtained the degradation rate on the 86% and 74% level, respectively. What's more, the supported TiO₂ catalysts were found not only to be very efficient but also quite stable for the repeated use. After four times of a repeated use only a slight decrease in the activity of the TiO₂/ quartz sand and the TiO₂/silica gel was observed. Nevertheless for the TiO₂/glass beads the decrease was about 11% already in the second use, how-

ever, their subsequent studies pointed out an increase of the TiO₂/glass beads activity after it was regenerated. Tsumura et al.⁹ also tested the lifetime of the photocatalyst; they have carried out the cycling performance of Methylene Blue decomposition on the carbon-coated TiO₂ prepared from ST-01 and PVA under UV irradiation.

The lifetime of the photocatalysts is a very important parameter from the technological point of view. The best material should have high adsorption capacity, good photocatalytic activity and be stable in many cycles of the photocatalytic reaction. This significant parameter of photocatalysts has already been studied by others. Kaur et al.¹⁰ had also studied the lifetime of the TiO₂ photocatalyst. The photocatalyst was recycled four times with decreasing its efficiency from 98% to 40%. Matos et al.¹¹ has widely investigated the photocatalytic degradation of phenol in the aqueous suspended TiO₂ activated carbon (TiO₂/AC). Three consecutive runs (180 min each) were carried out to verify the potential of TiO₂/AC and the principal intermediate products' influence on the photocatalytic activity in each of the three runs. It was found out that each of the kinetic curves of phenol degradation were of the apparent first-order rate and that the rate constant decreased from 2.48 in the first run to 1.71 and 1.32 in the second and the third respectively, probably as a consequence of higher quantities of the intermediate products in each photocatalytic run. The accumulative quantities of the intermediate products (HQ and BQ) competed with phenol for the original adsorption sites and consequently led to a progressive loss of the photocatalytic activity of TiO₂. Nevertheless it was also confirmed that the TiO₂/AC system has higher photocatalytic activity during even the third run than the neat TiO₂. Janus et al.¹² has studied the lifetime of carbon-modified photocatalysts in the degradation of mono azo dye Reactive Red 198 under the UV irradiation. Not only was the influence of the number of runs on the photocatalytic activity tested but also the influence of additional aeration. The TiO₂/C photocatalyst additionally aerated was stable during 10 cycles, but the experiment conducted without additional aeration showed that the photocatalytic activity of TiO₂/C decreased. The aim of this work was to study the lifetime of nitrogen modified titanium dioxide and the influence of pH on the photocatalytic activity of the photocatalysts.

EXPERIMENTAL

Materials

Anatase titanium dioxide was used as a base material (Z.Ch. Police company, Poland). The average pore diameter for anatase TiO₂ was 39 Å and the BET surface area was 248 m²/g. Commercial titanium dioxide TiO₂-P25 was supplied by the Degussa company (Germany). TiO₂-P25 has the surface area of 50±5 m²/g and is composed of 80% anatase and 20% rutile with elementary particles 25 nm and 85 nm, respectively.

Mono azo dye Reactive Red 198 (C₂₇H₁₈ClN₇Na₄O₁₅S₅, molecular weight 968 g/mol, λ_{max}=516 nm) was used for the photocatalytic tests (The Chemical Factory Boruta-Color company (Poland)).

Preparation of modified photocatalysts samples

4 g of anatase TiO₂ and 15 ml of ammonia water (NH₃ aq) were placed in a pressure reactor (BLH-800, BERGHOF, Germany), which was presented in the earlier work¹³. The reactor was closed and heated up to 100°C, after that the mixture was kept at this temperature for 2 hours, generating the 6 bar pressure. After heating the reactor was cooling slowly to the room temperature and the valves were opened. The catalyst was dried for 20 hours at 105°C.

Experimental procedures and analyses

The surface of the photocatalysts was analyzed on the basis of the FTIR/DRS spectra. The measurements were performed using the Jasco FT-IR 430 (Japan) spectrophotometer equipped with a diffuse reflectance accessory (Harrick, USA).

The photocatalysts were characterized by the electronic spectrometer for a chemical analysis (ESCA).

The UV-VIS/DR spectra were made by Jasco V-530 (Japan) spectrophotometer equipped with the integrating sphere accessory for the diffuse reflectance spectra (BaSO₄ was used as a reference).

The photocatalytic decomposition under the UV irradiation of mono azo dye was carried out to the decolourization of the aqueous solution by the destruction of the chromophore group (R₁-N=N-R₂) of the dye¹⁴ and a complete decolourisation of the dye solution and the photocatalyst's surface. In the glass beakers, 0.1 g of the TiO₂ photocatalyst was added to 500 ml of the aqueous dye solution (Reactive Red 198) with the initial concentration of 10 mg/l. The dye solution was mixed with a magnetic stirrer during reaction. The irradiation of the solution was operated under UV light (6 lamps with the power of 20W, Phillips) with the radiation intensity of about 167 W/m² Vis and 183 W/m² UV.

All the experiments were carried out in different pH value. The pH of the dye solution was adjusted over the range pH=3.5; 6 and 7.5 using 0.1 M H₂SO₄ or 0.1 M NaOH solution. Ten cycles of the photocatalytic tests were done. After decolourization each solution contains some amount of the co-products of the dye decomposition and the photocatalyst, the next quantity of azo dye was added. Before the first and after the last photocatalytic cycle the TOC (Total Organic Carbon) measurement in the 6 pH solution (aerated and no-aerated) was carried out.

The TOC measurements of the dye solution were performed to check the rate of photomineralization. The TOC was measured with the Multi N/C 2000 analyzer (Analytik Jena, Germany).

In the lifetime tests different values of pH were used to check the influence of pH on the performance of the photocatalysis process. The influence of aeration on the photocatalytic process was also tested.

RESULT AND DISCUSSION

FTIR/DRS and XPS spectra analysis

The modification method of anatase TiO₂ by ammonia water (NH₃ aq) is a way for the increasing of its photocatalytic activity and also to increase its adsorption capacity. The modification of TiO₂ by ammonia, earlier stud-

ied by Morawski at al.¹³ significant increased its photocatalytic activity under the visible light irradiation significantly. The activity of the nitrogen-modified TiO₂ was compared with the commercial TiO₂ (P25-Degussa). The modification of TiO₂ carried out at low temperature (100°C) and pressure (6 bars) in the water ammonia atmosphere led to the introduction of new groups on the surface of anatase TiO₂. In Fig. 1 the FTIR/DRS spectra of nitrogen modified TiO₂, unmodified TiO₂ and P25 are presented. It demonstrates the bands that are positioned at 3695 cm⁻¹, assigned to the stretching of a hydroxyl group that was chemisorbed on the surface of the defect site, 3300 – 3500 cm⁻¹, assigned to hydroxyl for both the dissociated water and the molecularly adsorbed water and at 1623 cm⁻¹, for the molecular water. The spectra of the catalyst modified with ammonia also showed the new bands at 1430 – 1440 cm⁻¹ that could be attributed to the

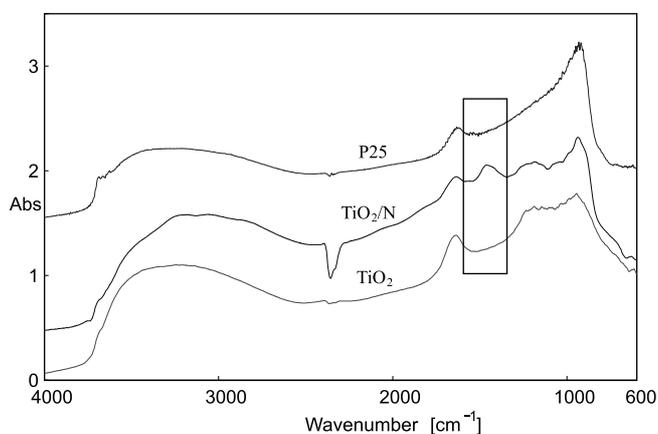


Figure 1. The FTIR/DRS spectra of the P25, modified TiO₂ and unmodified TiO₂

bending vibrations of NH₄⁺ and at 1535 cm⁻¹ associated to NH₂ groups¹⁵.

Moreover, the presence of nitrogen groups could be observed on the XPS spectra at the 403 eV binding energy (Figure 2).

UV-Vis/DR spectra analysis

In Fig.3 the UV-Vis/DR spectra of the unmodified and nitrogen modified TiO₂ and TiO₂-P25 are presented. For all the catalysts the band gap energy E_G was determined. The modification practically does not change the value of E_G which amounted 3.34 eV for the unmodified and 3.33 eV for the modified TiO₂. Only an insignificant decrease in the reflectance on the spectra in region 400 – 800 nm could be observed.

Effect of aeration and different pH value

The lifetime tests of commercial P25, the unmodified and nitrogen-modified TiO₂ photocatalysts in 10 cycles at different pH values (pH = 3.5; 6; 7.5) were carried out. In Fig. 4 the time of the decolourization all the photocatalysts at pH=3.5 solution were presented.

Low pH value can significantly cause high adsorption capacity during the adsorption of Reactive Red 198 on the TiO₂ photocatalyst's surface, because nitrogen modification changed the zeta potential of the photocatalyst surface which increased from value: -32 eV for the unmodified TiO₂ to -2.1 eV for the nitrogen modified TiO₂¹⁶. In the photocatalytic degradation of organic compounds the mechanism of the photosensitised oxidation of dyes played a very important role. The mechanism of the photosensitised oxidation of dyes suggests that excitation of the adsorbed dye takes place by a visible light irradiation to the appropriate singlet or triplet state, followed by the electron injection from the excited dye molecule into the conduction band of the TiO₂ particles. At the same time

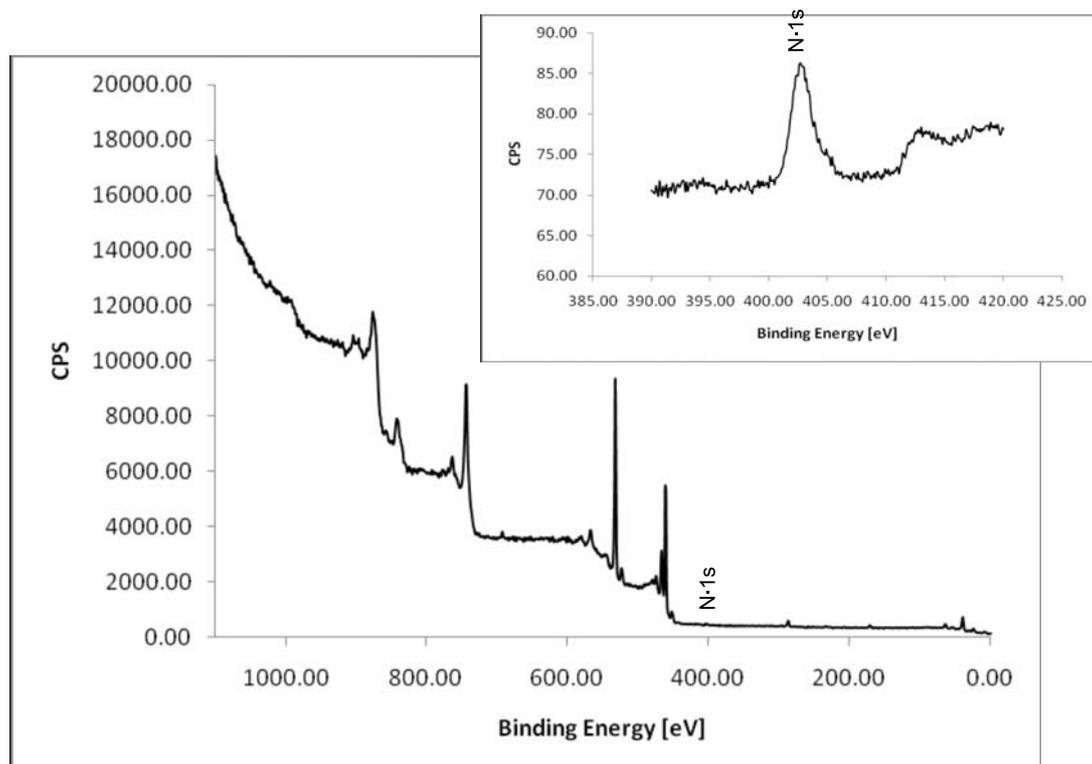


Figure 2. XPS spectra of the nitrogen modified TiO₂

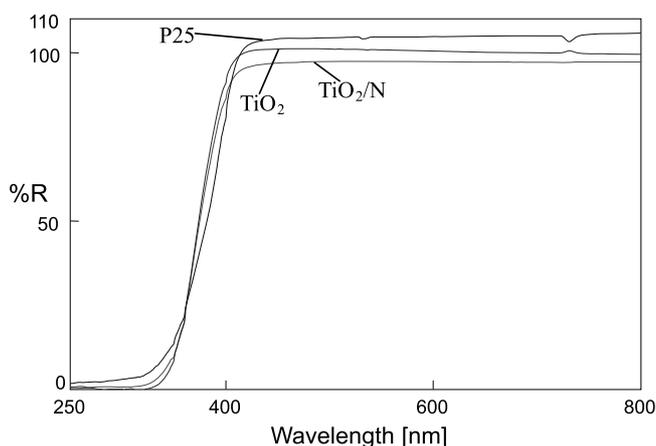


Figure 3. The UV-Vis/DR spectra of the P25, unmodified and nitrogen-modified TiO_2 photocatalysts

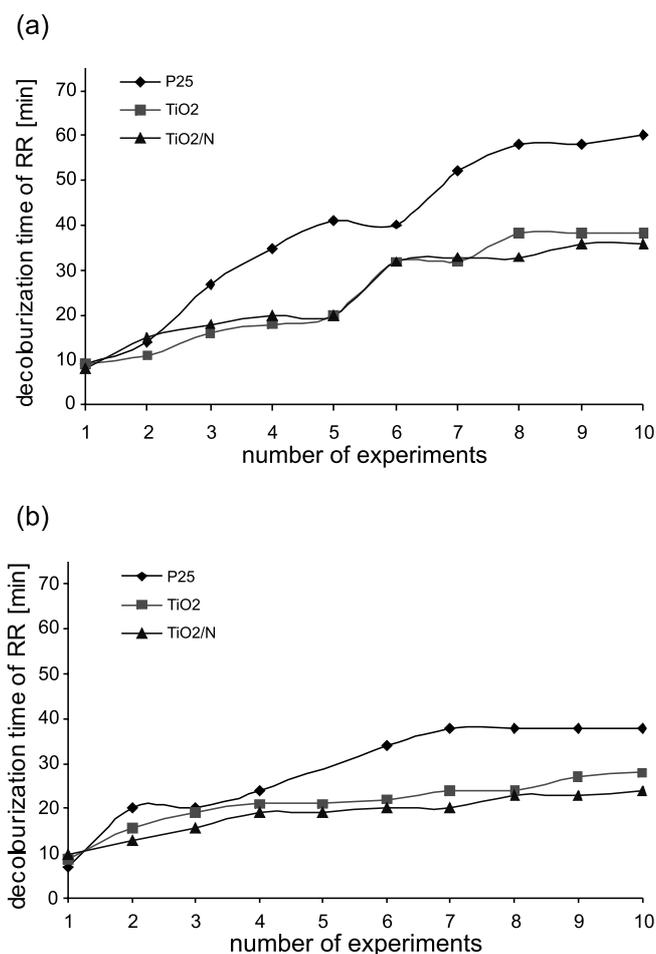
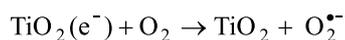
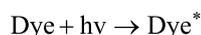


Figure 4. The photocatalytic decolourisation of Reactive Red under the UV irradiation on different photocatalysts in 10 experiments (a) in the no-aerated solution with the 3.5 pH value, (b) in the aerated solution with the 3.5 pH value

the dye is converted to the cationic dye radicals that can react with hydroxyl ions undergoing oxidation or interact effectively with $\text{O}_2^{\bullet-}$, HO_2^{\bullet} or HO^{\bullet} species to generate the intermediates that ultimately lead to CO_2 ¹⁷.



Therefore, azo dye might be easily degraded in the aqueous solution under the UV-Vis light irradiation, when the photocatalyst has high adsorption capacity. Thus, the results show that the activity of the photocatalysts was reduced when the time of the UV irradiation was longer and the time of dye decolourization was slightly increased. The adsorption capacity of the nitrogen-modified TiO_2 was higher than that of the commercial TiO_2 -P25 so the time of the decolourization was better than the P25 one. Additional aeration led to the reaction system, caused the reduction in the time of Reactive Red 198 decomposition. At pH=6 the modified TiO_2 was more efficient than the commercial P25 (Fig. 5).

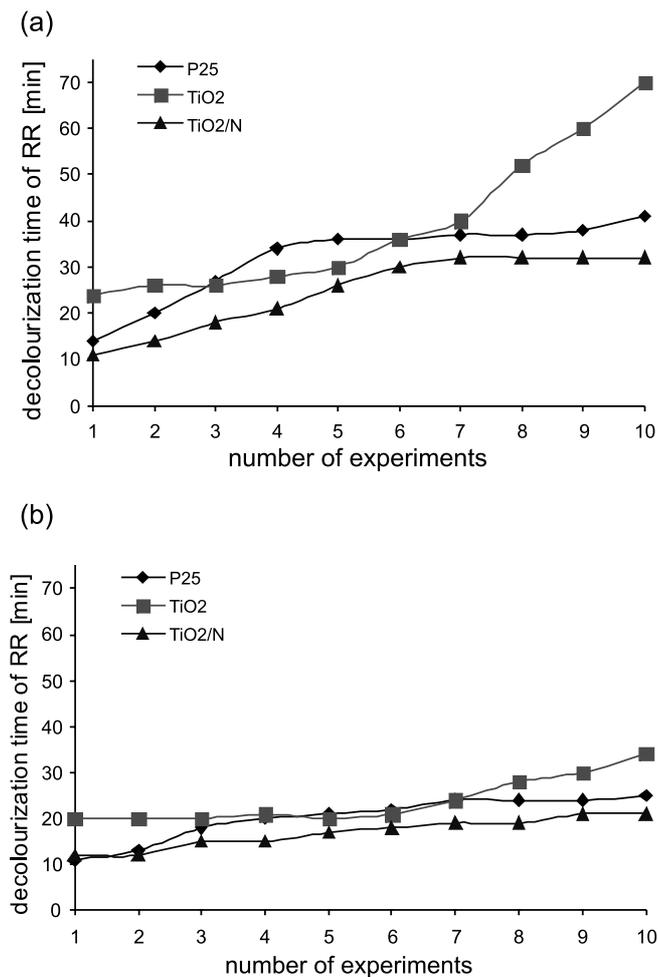


Figure 5. The photocatalytic decolourisation of the Reactive Red under the UV irradiation on different photocatalysts in 10 experiments (a) in the no-aerated solution with the 6 pH value, (b) in the aerated solution with the 6 pH value

In the case of pH=7.5 a significant difference was noted. The activity of the nitrogen-modified TiO_2 was decreased and the mechanism of the photosensitised oxidation of dye played an insignificant role. In the case of high pH value, the commercial P25 demonstrated better photocatalytic properties (Fig. 6).

Under the UV light irradiation on the TiO_2 -P25 surface more hydroxyl radicals were formed than on the surface of the unmodified and the nitrogen-modified TiO_2 , as it was shown in Fig.7. At pH=7.5 the adsorption capacity of the nitrogen-modified TiO_2 was lower and the dye was not so well adsorbed as at pH 3.5. In the alkaline

medium the amount of the OH[•] radicals produced on the photocatalyst surface was more important because adsorption did not occur.

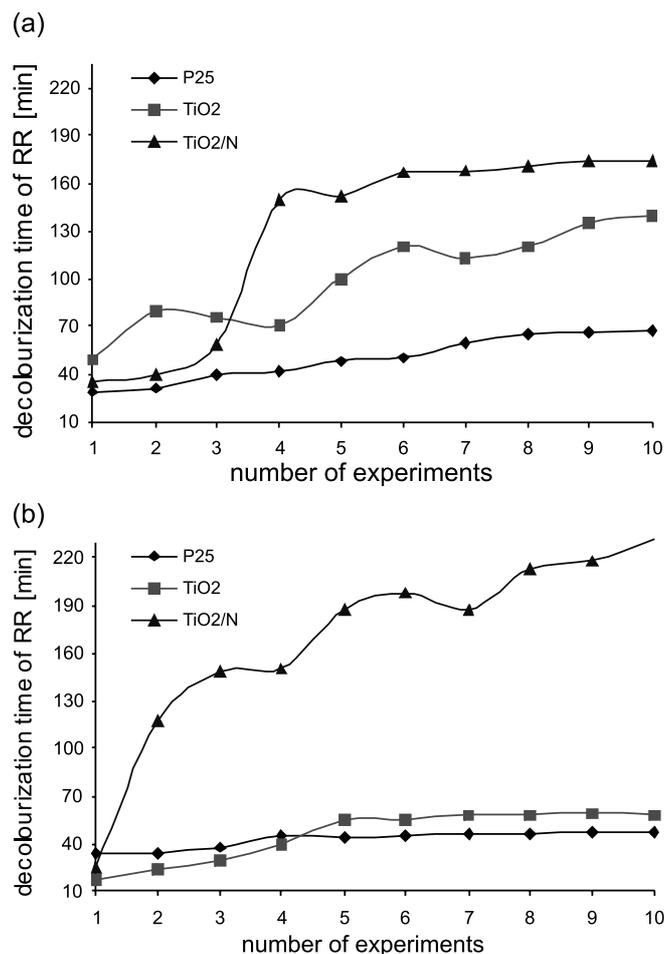


Figure 6. The photocatalytic decolourisation of the Reactive Red under the UV irradiation on different photocatalysts in 10 experiments (a) in the non-aerated solution with the 7.5 pH value, (b) in the aerated solution with the 7.5 pH value

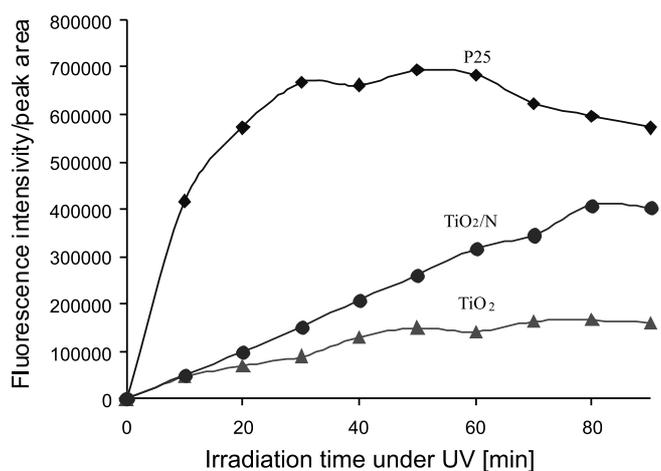


Figure 7. Formation of the OH[•] radicals under the UV light irradiation on the P25, unmodified and nitrogen-modified TiO₂ surface

TOC analysis

After the 10th cycle of decolourisation the TOC measurements were taken. The amount of the total organic carbon in the solution increased with the addition of the amount of azo dye. The rates of mineralization

were higher when the photodegradation processes without aeration were conducted (67.1% for the unmodified TiO₂, 71.3% for TiO₂/N and 74.0% for P25) than with the additional aeration (62.8% for the unmodified TiO₂, 63.5% for TiO₂/N and 68.7% for P25). The aeration decolourisation process took shorter time and there was a higher amount of the intermediate products in the solution. It is suspected that these intermediate products do not compete with the Reactive Red dye for the adsorption sites because in every consecutive run the RR adsorption was very high (for the low pH solution) and what is more the TOC value, which is analyzed from the solution, increased in every next run of the decomposition process, which indicates that the intermediate products had to remain in the solution, so it did not get adsorbed on the TiO₂ surface and certainly had no influence on the RR surface adsorption capacity.

CONCLUSION

The modification of TiO₂ was conducted in ammonia atmosphere and caused changes in the chemical structure of TiO₂ surface. The obtained photocatalyst had new bands at 1430 – 1440 cm⁻¹ attributed to the bending vibrations of NH₄⁺ and at 1535 cm⁻¹ associated to NH₂ groups. The photocatalytic degradation process by using the nitrogen-modified TiO₂ under the UV light irradiation with an additional amount of oxygen could be very efficiently applied for removing the difficult compound from the water. The results after the experiments clearly delineated the important role of the optimum reaction conditions in achieving the highest level of the degradation of Reactive Red 198 at pH=3.5. At pH = 3.5 and with additional aeration the nitrogen-modified TiO₂ is active during 10 cycles of the photocatalytic dye removal, but progressively decreasing its activity. The decolourisation time of the dye in the 10th cycle was two times longer than in the first one, but nevertheless it was shorter than for the commercial TiO₂-P25.

ACKNOWLEDGEMENT

This work was supported by Research Project NN 205012734 for 2008 – 2010.

LITERATURE CITED

- Hong, X.T., Wang, Z.P., Cai, W.M., Lu, F., Zhang, J., Yang, Y.Z., Ma, N. & Liu, Y. (2005). Visible-Light-Activated Nanoparticle Photocatalyst of Iodine-Doped Titanium Dioxide. *Chem. Mater.* 17(6), 1548 – 1552. DOI: 10.1021/cm047891k.
- Yamashita, H., Harada, M., Misaka, J., Takeuchi, M., Nappolian, B. & Anpo, M. (2003). Photocatalytic degradation of organic compounds diluted in water using visible light-responsive metal ion-implanted TiO₂ catalysts: Fe ion-implanted TiO₂. *Catal. Today.* 84(3-4), 191 – 196. DOI:10.1016/S0920-5861(03)00273-6.
- Tong, T., Zhang, J., Tian, B., Chen, F. & He, D. (2008). Preparation of Fe³⁺-doped TiO₂ catalysts by controlled hydrolysis of titanium alkoxide and study on their photocatalytic activity for methyl orange degradation. *J. Hazard. Mater.* 155(3), 572-579. DOI:10.1016/j.jhazmat.2007.11.106.
- Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. & Taga, Y. (2001). Visible-Light Photocatalysis in Nitrogen-Doped Ti-

tanium Oxides. *Science*. 293, 269 – 271. DOI: 10.1126/science.1061051.

5. Yuan, J., Chen, M., Shi, J. & Shangguan, W. (2006). Preparations and photocatalytic hydrogen evolution of N-doped TiO₂ from urea and titanium tetrachloride. *Intern. J. Hydrogen Energy*. 31(10), 1326 / 1331. DOI:10.1016/j.ijhydene.2005.11.016.

6. Ihara, T., Miyoshi, M., Iriyama, Y., Matsumoto, O. & Sugihara, S. (2003). Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping. *Appl. Catal. B, Environ.* 42(4), 403 – 409. PII: S0926-3373(02)00269-2.

7. Suda, Y., Kawasaki, H., Ueda, T. & Ohshima, T. (2004). Preparation of high quality nitrogen doped TiO₂ thin film as a photocatalyst using a pulsed laser deposition method. *Thin Solid Films*. 453 – 454, 162 – 166. DOI: 10.1016/j.tsf.2003.11.185.

8. Tasbihi, M., Ngah C.R., Aziz, N., Mansor, A., Abdullah, A.Z., Teong, L.K. & Mohammed, A.R. (2007). Lifetime and Regeneration Studies of Various Supported TiO₂ Photocatalysts for the Degradation of Phenol under UV-C Light in a Batch Reactor. *Ind. Eng. Chem. Res.* 46(26), 9006-9014. DOI: 10.1021/ie070284x.

9. Tsumura, T., Kojitani, N., Izumi, I., Iwashita, N., Toyoda, M. & Inagaki, M. (2002). Formation of the Ti₄O₇ phase through interaction between coated carbon and TiO₂. *J. Mater. Chem.* 12, 1391 – 1396. DOI : 10.1016/j.desal.2003.11.007.

10. Kaur, S., Singh, V. (2007). TiO₂ mediated photocatalytic degradation studies of Reactive Red 198 by UV irradiation. *J. Hazard. Mat.* 141(1), 230 – 236. DOI:10.1016/j.jhazmat.2006. 06.123.

11. Matos, J., Laine, J., Herrmann, J.-M., Uzcatogui, D. & Brito, J.L. (2007). Influence of activated carbon upon titania on aqueous photocatalytic consecutive runs of phenol photodegradation. *Appl. Catal. B, Environ.* 70(1-4), 461 – 469. DOI:10.1016/j.apcatb.2005. 10.040.

12. Janus, M., Kusiak, E., Choina, J. & Morawski, A.W. (2009). Lifetime of Carbon-Modified TiO₂ Photocatalysts Under UV Light Irradiation. *Catal. Lett.* 131, 606 – 611. DOI: 10.1007/ s10562-009-0022-z.

13. Wawrzyniak, B. & Morawski, A.W. (2006). Solar-light-induced photocatalytic decomposition of two azo dyes on new TiO₂ photocatalyst containing nitrogen. *Appl. Catal. B, Environ.* 62(1-2), 150 – 158. DOI:10.1016/j.apcatb.2005.07.008.

14. Konstantinou, I.K. & Albanis, T.A. (2004). TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review. *Appl. Catal. B, Environ.* 49(1), 1 – 14. DOI:10.1016/j.apcatb.2003.11.010.

15. Hadjiivanov, K. (1998). FTIR study of CO and NH₃ co-adsorption on TiO₂ (rutile). *Appl. Surf. Sci.* 135(1-4), 331-338. PII: S0169- 4332_98.00298-0.

16. Janus, M., Choina, J., Kusiak, E., Morawski, A.W. (2008). Study of Nitrogen-modified Titanium Dioxide as an Adsorbent for Azo Dyes. *Adsorption Science&Technology*. 26(7), 501 – 513.

17. Epling, G.A., Lin, C. (2002). Photoassisted bleaching of dyes utilizing TiO₂ and visible light. *Chemosphere*. 46, 561 – 570. PII: S0045-6535(01)00173-4.