

Study of Structure-Properties Relationship of TiO₂: Photodegradation of Azo Dyes, Catalyst Efficiency and Recyclability

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1. Introduction. Water pollution problems are an important issue correlated negatively with the human health and the environment. For the photocatalytic water purification processes the most important is the type of used catalyst. One of the most studied and widely used photocatalysts is titanium dioxide (TiO₂) due to its good photocatalytic activity, nontoxicity and low price. [1] TiO₂ is photocatalytically active under ultraviolet (UV)-light irradiation (<380 nm) and it is used as photocatalyst for the degradation of organic pollutants. [2,3] For dyeing processes today synthetic dyes, like azo dyes, are mainly used and they are considered to be basically non-degradable. Their degradation processes such as physicochemical treatment and oxidative techniques are not able to completely remove azo dyes from the contaminated waste waters. [4] During the degradation process dyes can be converted to their intermediate products, such as aromatic amines, that can be toxic or carcinogenic. Alternative methods for waste water treatment have been developed, such as advanced oxidation processes (AOP) from which the photocatalysis is the most popular one. This technique is based on heterogeneous photocatalytic oxidation process [5] which is promising as it uses semiconducting metal oxides that produce electron-hole pairs when being irradiated with UV light in an aqueous medium. In this work the aim was to investigate the photocatalytic efficiency in aqueous solution of variously synthesized TiO₂ in correlation with its structure and to examine its reuse efficiency during several cycles of photodegradation of azo dyes (Reactive Red 45 and Acid Blue 25). As the photocatalytic activity of TiO₂ strongly depends on its crystalline structure and composition, the study of synthesis conditions and post-treatments (calcination temperature, time and reactant concentration) was performed. Characterization of synthesized TiO₂ photocatalysts was performed by FTIR and UV/Vis spectrometry, X-ray diffraction and SEM microscopy.

2. Experimental. Synthesis of TiO₂. TiCh photocatalyst was prepared by sol-gel synthesis using 12.8 mL of tetra-n-butyl titanate (Ti(OC₄H₉)₄) (TBT) as the precursor that was introduced dropwise into 50 mL of 3 M acetic acid and stirred with magnetic stirrer (300 rpm) for 60 min. The resultant solution was then transferred into Erlenmeyer flask and heat-treated at 105 °C for 24 h. The product was taken out and washed with absolute ethanol for three times and dried in a vacuum oven at 100 °C for 12 h. The obtained TiO₂ photocatalysts (TiCh) was calcined at 400 °C, 500 °C, 600 °C for 3 h.

Synthesis of TiO₂. TiB photocatalyst was prepared by sol-gel synthesis where solution A consisted of 20 mL of tetra-n-butyl titanate (TBT) dissolved in 20 mL of anhydrous ethanol. Afterwards, 20 mL of 3 M acetic acid was drop-wise added into solution under the stirring. Solution B consisted of 2.1 mL of didecyl dimethyl ammonium chloride mixed with 60 mL anhydrous ethanol and 20 mL distilled water stirred for 15 min at room temperature. The solution B was drop-wise added to solution A. The obtained mixture was mixed at high speed with disperser (7500 rpm) than transferred in Erlenmeyer flask and heated at 85 °C in oven for 24 h until the transparent sol was obtained. The product was washed several times with distilled water dried at 100 °C for 12 h and calcined at 400 °C for 3 h.

Characterization. Infrared spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrometer within the range of 4000–650 cm⁻¹. UV/Vis reflectance measurements of the studied TiO₂ photocatalysts were made over the range 200 to 800 nm at a spectral resolution of ~0.3 – 10 nm using UV/Vis spectrometer Ocean Optics USB 2000+. Microstructure and the morphology of the studied photocatalysts were studied by using scanning electron microscopy (SEM) Tescan Vega 3 and X-ray diffraction performed on ItalStructures APD 2000, (λ (CuK α) = 1.5405 Å).

Photocatalytic activity test. The experiments were performed with the waste water containing 30 mg/L of azo dyes (Reactive Red 45 and Acid Blue 25) and 1 g/L of photocatalyst (TiCh and TiB) in the glass

water-jacketed batch reactor equipped with the Pen-Ray UVP lamp emitting irradiation in UVA region (315 to 400 nm), which was located in the middle of the reactor. The total volume of the treated solution was 75 mL in all experiments. The solution was magnetically stirred (250 rpm) in the dark for 90 min and after that it was illuminated for next 90 min to proceed with photocatalysis. Samples were taken periodically from the reactor and thereafter immediately analysed by UV/Vis spectroscopy. Decolourization and degradation of RR45 and AB25 dyes in the solution was monitored by a Perkin Elmer Lambda EZ 201 UV/VIS spectrophotometer where the absorption was measured at a wavelength of 542 nm for RR45 and at 622 nm for AB25.

Reuse of photocatalyst. Multiple experiments of photocatalysis were performed under identical photocatalytic conditions to follow the reuse efficiency of the photocatalyst. After each cycle of photocatalysis the samples were separated by decantation, dried at room temperature for 12 h and were reused in the next cycle. The efficiency of the photocatalyst over the four cycles of photodegradation is given as the percentage of degraded RR45 calculated according to the equation. Degradation (%) = $(A_0 - A) / A_0 \times 100\%$, where A_0 and A were the initial absorbance and the absorbance at the specific time of measurement, respectively.

3. Results and Discussion.

TiO₂ photocatalysts (TiCh, TiB) synthesized by the different procedures were first characterized by FTIR and UV-Vis spectrometry. In Image 1a) are presented FTIR spectra of TiCh samples calcined at various temperatures (400, 500, 600 °C) and in Image 2a) TiB and TiCh samples that differ by synthesized procedure.

procedure.

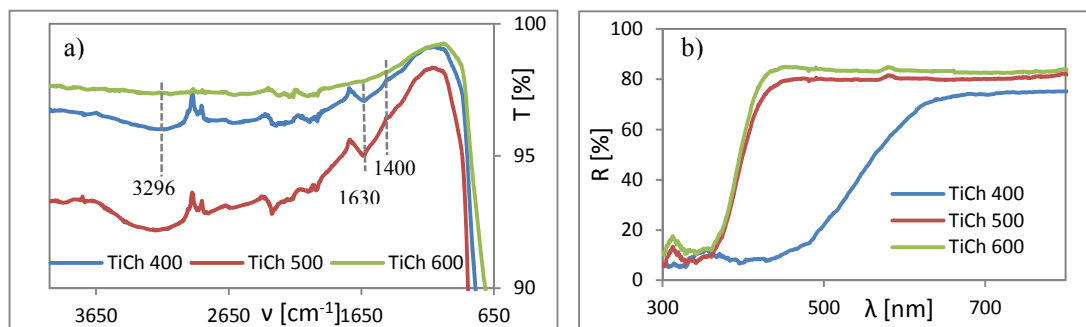


Image 1. a) FTIR spectra b) UV/Vis spectra of synthesized TiCh calcined at three different temperatures

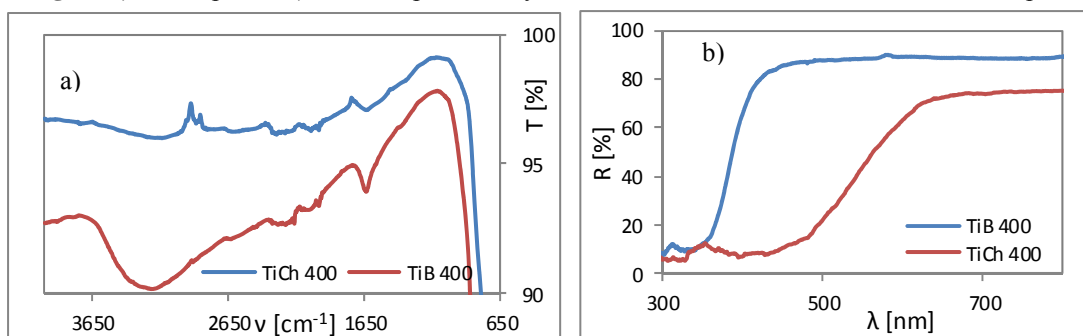


Image 2. a) FTIR spectra b) UV/Vis spectra of TCh and TiB synthesized under the different conditions

In FTIR spectra the vibration bands of TiO₂ at 3300 and 1660 cm⁻¹, attributed to the stretching and bending vibration of the OH group, can be seen. The small peak at 1400 cm⁻¹ shows stretching vibrations of Ti-O-Ti while the peak at 524 cm⁻¹ corresponding to the stretching vibration of Ti-O is not seen due to restriction range of FTIR spectrometer. It is observed that spectra of studied samples differ among themselves indicating different structures like the absence of secondary interaction between TiO₂ molecules. In Image 1b) and 2b) UV-Vis spectra can be seen and significant difference in reflectance is observed for the TiCh sample calcined at 400 °C in comparison to two other samples calcined at 500 and

600 °C. TiCh 400 exhibited the high reflectance shifted to higher wavelength to 470 nm while the typical TiO₂ broad band is in the range of 220 - 380 nm. In the SEM micrographs of TiO₂ photocatalysts in Image 3 the morphology of samples are compared and typical crystal form can be recognized. By comparing the TiB and TiCh samples synthesised by different procedure small variation in crystals are seen while by comparing the TiCh samples calcined at different temperatures increase of crystals size are observed with increase of calcination temperatures.

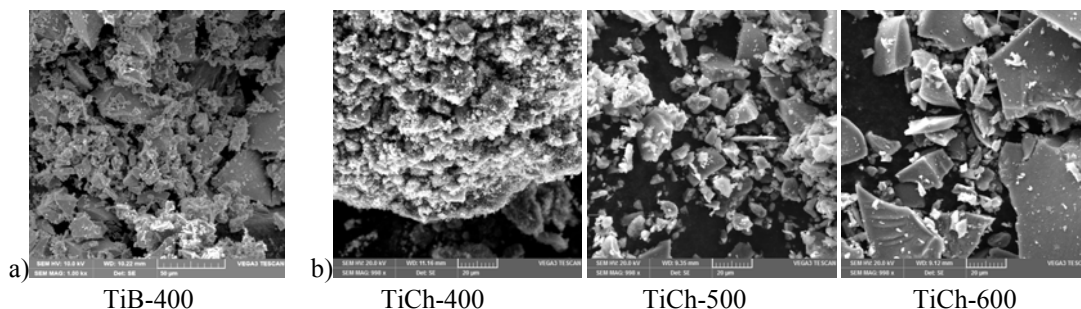


Image 3. SEM micrographs a) TiB photocatalyst calcined at 400°C b) TiCh photocatalyst calcined at three different temperatures.

The change in TiO₂ crystals size is better seen in Image 4 where X-ray analysis is shown. XRD patterns shown in Image 4 suggest the presence of anatase TiO₂ as a single phase in all 4 samples. The size of anatase crystallites was estimated by using Scherrer equation [6] as 11, 14, 18 and 34 nm for the samples TiB-400, TiCh-400, TiCh-500 and TiCh-600, respectively.

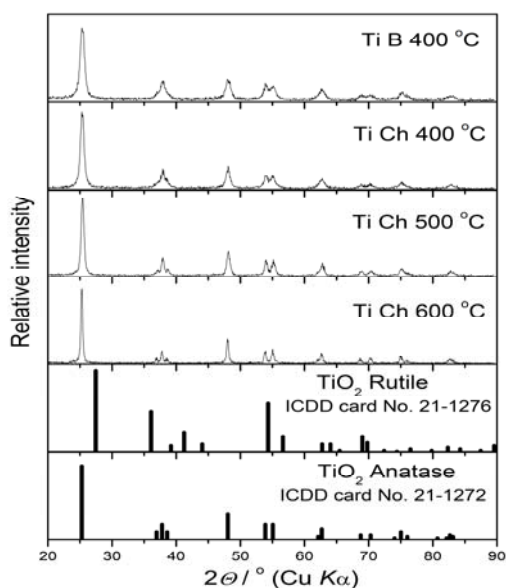


Image 4. XRD diffractogram of photocatalyst; four TiB calcined at 400°C and TiCh calcined at three different temperatures.

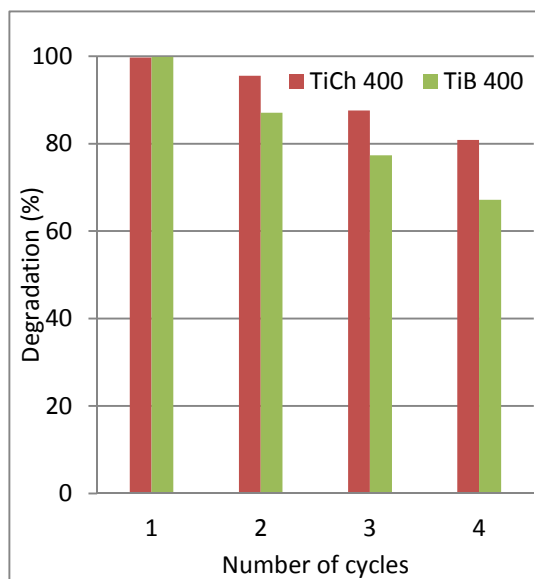


Image 6. Recycling of TiCh and TiB samples after four cycles of photocatalytic degradation of RR 45

In order to evaluate the effect of various structure of the TiO₂ photocatalysts on photocatalytic activity the process of photodegradation of Reactive Red (RR45) and Acid Blue 25 (AB25) waste water was performed. At first, process of adsorption of azo dyes onto catalysts has been carried out to ensure the adsorption/desorption equilibrium and to examine the possibility of azo dyes removal from waste water by simple adsorption mechanism (Image 5). After 90 minutes of adsorption process it is seen that very low concentration of RR45 is removed (less than 8%), by the TiCh samples (Image 5a)) calcined at different temperatures. On the other hand, the adsorption was significantly higher for the AB25 azo dye (Image 5b)) with achieved value of approximately 25% after 60 minutes for TiB 400 photocatalyst. It is

well known fact that TiO_2 is positively charged in acidic and negatively in basic medium. [7] In this work the both processes were performed at neutral medium at pH 7 because it was presuppose that the lower adsorption and the highest photocatalytic efficiency would be obtained under neutral conditions.

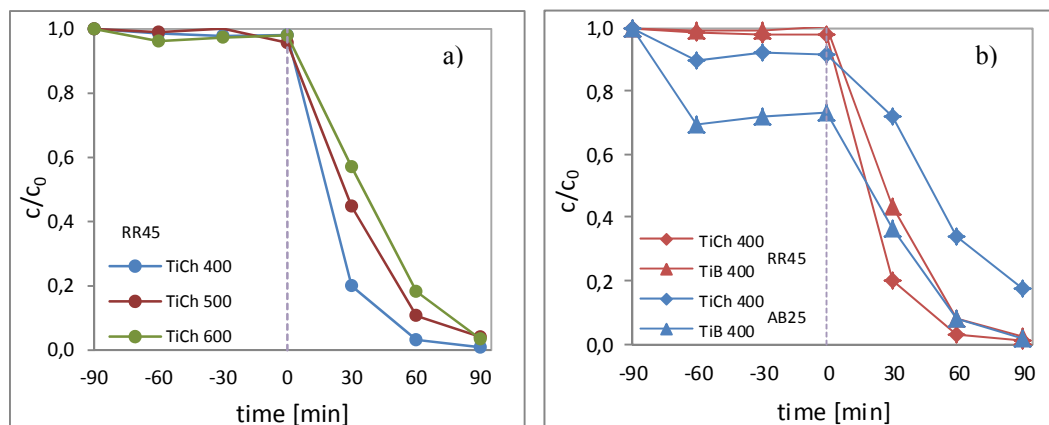


Image 5. Decolouration rate of azo dyes during the adsorption and photocatalysis by use of a) synthesized TiCh, calcined at different temperatures b) TiCh and TiB calcined at the same temperature (con. of dye RR45 and AB25 was $\gamma=30$ mg/L and photocatalysts $\gamma=1$ g/L, pH =7)

After adsorption process, actual photocatalytic activity of investigated samples in degradation of RR45 and AB25 azo dyes in water was performed (Image 5), positive part of the X axis. The obtained results indicate that all synthesized TiO_2 samples exhibit various photocatalytic activity under UVA irradiation. TiCh photocatalyst calcined at 400 °C shows the highest rate of degradation of RR45 in the first 30 minutes as more than 80 % of dye was removed while at the same time other two samples removed only 55% (TiCh500) and 40% (TiCh600) of dye. The photocatalytic activity of TiCh and TiB photocatalysts prepared under different synthesis condition also exhibited various removals of azo dyes. Thus, it is seen that the efficiency is different regarding the photocatalyst and regarding the azo dye. The highest rate of azo dye removal shows TiCh in 30 minutes for RR45 and then follows the TiB photocatalyst for AB25 dye where it can be seen that even high adsorption of AB25 dye onto its surface did not limit the degradation efficiency in photocatalytic process. In Image 6 reuse efficiency of TiCh and TiB photocatalysts in four cycles of photocatalytic degradation of RR 45 has been evaluated. It can be seen that TiCh photocatalyst is more efficient as it removed 80% of RR45 after the fourth cycle.

4. Conclusions.

From the results it was concluded that photocatalytic activity of TiO_2 photocatalyst strongly depends on its crystalline structure that is modified by the synthesis conditions and post-treatments (calcination temperature, time and reactant concentration). It was also observed that TiCh photocatalyst is more efficient to remove RR45 azo dye while TiB photocatalyst is more efficient to remove AB25 azo dye.

Acknowledgements

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5. References

- [1] L. Yang, M. Zhang, S. Shi, J. Lv, X. Song, G. He, Z. Sun, *Nanoscale Res Lett.* **9** (2014) 621.
- [2] J. M. Szeifert, J. M. Feckl, D. Fattakhova-Rohling, Y. J. Liu, V. Kalousek, J. Rathousky and T. Bein, *J. Am. Chem. Soc.* **132** (2010) 12605.
- [3] K. Park, Q. F. Zhang, B. B. Garcia, X. Y. Zhou, Y. H. Jeong, G. Z. Cao, *Adv. Mater.* **22** (2010) 2329.
- [4] D. Melgoza, A. Hernandez-Ramirez, J.M. Peralta-Hernandez, *Photochem. Photobiol. Sci.* **8**(2009)596.
- [5] Y. Gu, Y. Z. Zhang, F. Y. Zhang, J. P. Wei, C. M. Wang, Y. L. Du, W. C. Ye, *Electrochim. Acta* **56** (2010) 953.
- [6] H. P. Klug, L. E. Alexander, X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd ed., New York, Wiley, 1974, p. 687.
- [7] N. Daneshvar, D. Salari, A.R. Khataee, *J. Photochem. Photobiol. A* **162** (2004) 317.