



# Application of temperature modified titanate nanotubes for removal of an azo dye from water in a hybrid photocatalysis–MD process

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## ABSTRACT

The presented studies have focused on application of modified titanate nanotubes (TNTs) for decomposition of Acid Red 18 in water. The TNTs were prepared via hydrothermal method. The post-treatment of TNTs was carried out by calcination of the as-received nanotubes at temperatures of 400–700 °C. The photocatalytic experiments revealed that the most active towards AR18 decomposition were TNTs calcinated at 600 °C (TNT600). However, the photocatalytic activity of the calcinated titanate nanotubes, regardless of the annealing temperature applied was found to be lower than that of P25. In the second step of the investigations, the TNT600 were applied for degradation of AR18 in a photocatalytic membrane reactor coupling photocatalysis with membrane distillation. The effect of photocatalyst loading on the effectiveness of degradation of AR18 was especially investigated. After 5 h of irradiation the amount of AR18 was lowered for ca. 67, 80 and 97% for TNT600 loadings of 0.1–0.5 g/dm<sup>3</sup>, respectively. The mineralization of the organics was significantly lower than the decolorization of the solution. The amount of TOC after 5 h of the experiment decreased for 20, 27 and 57%, for 0.1–0.5 g TNT600/dm<sup>3</sup>, respectively. Amongst products and by-products of AR18 photodegradation organic acids (formic, acetic and oxalic) and inorganic ions (nitrite, nitrate, ammonia and sulfate) were detected. The product of the hybrid process (distillate) was high quality water with conductivity in the range of 2.3–3 μS/cm.

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## 1. Introduction

Over the last several years a great deal of interest has been focused on a new type of photocatalytic reactors, taking advantage of photodegradation of pollutants in water and membrane technology. These reactors, called photocatalytic membrane reactors (PMRs) seem to be a very promising method of solving problems concerning separation of photocatalyst as well as products and by-products of photodecomposition from the reaction mixture.

Photocatalytic membrane reactors exhibit some advantages with respect to conventional photoreactors, such as [1]: (I) confining of the photocatalyst in the reaction environment by means of the membrane; (II) control of a residence time of molecules in the reactor; (III) realization of a continuous process with simultaneous catalyst and products separation from the reaction environment. Moreover, application of a PMR instead of a conventional photoreactor allows avoiding some additional operations, such as coagulation–flocculation–sedimentation which are necessary in order to remove catalyst from the treated solution. One benefit from this is energy saving and reducing the size of installation. Another one is possibility of reusing of the photocatalyst in further

runs, what is practically impossible when the conventional separation system composed of coagulation–flocculation–sedimentation steps is applied.

Most of the PMRs described in the literature combine photocatalysis with pressure driven membrane processes such as microfiltration (MF) [2–17], ultrafiltration (UF) [18–24] and nanofiltration (NF) [1,25–30]. However, when a catalyst in suspension is applied, the membrane fouling is observed, especially in case of MF and UF membranes. Moreover, the quality of permeate is not very high, because small molecules can pass easily through the membranes used, even in case of NF.

Recently new types of photocatalytic membrane reactors combining photocatalysis with dialysis [31] and pervaporation (PV) [32] have been described. In our earlier publications [33–40] we have presented a new type of PMR utilizing photocatalysis and direct contact membrane distillation (MD, DCMD). One of the main advantages of the above-mentioned configuration was high quality of the product (distillate). Moreover, no membrane fouling due to the presence of photocatalyst particles was observed.

TiO<sub>2</sub> is the most often used photocatalyst due to its considerable photocatalytic activity, high stability, non-environmental impact and low cost. Since Kasuga et al. [41,42] described a novel hydrothermal method for formation of titanate nanotubes (TNTs), the investigations on preparation and properties of these species have attracted attention of numerous researchers. Amongst various

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possible applications, including supports, ion-exchange, adsorption, dye sensitized solar cells, and others, photocatalysis seems to be of special interest. However, the data concerning the photocatalytic activity of the as-synthesized TNTs are inconsistent [43–53]. Yu et al. [44] investigated photocatalytic oxidation of acetone in air in the presence of TNTs synthesized hydrothermally at 150 °C for 48 h. The authors found that prior to calcination, the nanotubes showed no photocatalytic activity. Similar observations were published by Qamar et al. [45]. The researchers reported that the as-prepared nanotubes, with or without sodium content, showed no photocatalytic activities towards amaranth degradation. Baiju et al. [46] presented results on the photocatalytic degradation of Methylene Blue (MB) on a mixed nanobelts–nanotubes titanate obtained via hydrothermal method at 150 °C for 30 h. The authors found that the sample exhibited very high adsorptivity towards MB. However, the photocatalytic activity was very low. On the other hand, significant activity of titanate nanotubes towards HCHO degradation under UV light was reported by Nakahira et al. [48]. According to Xiao et al. [49], titanate nanotubes synthesized hydrothermally at 130 °C for 24 h revealed photocatalytic activity toward Rhodamine B (RhB) degradation with efficiency similar to that of P25. Photocatalytic activity of as-prepared TNTs towards Methylene Blue (MB) degradation and oxidation of NO to NO<sub>2</sub> was reported by Inagaki et al. [50]. Similarly, Geng et al. [51] observed photodegradation of MB in the presence of TNTs. Jiang et al. [52] found significant photocatalytic activity of TNTs during photodecomposition of Acid Red 3B. Moreover, the authors reported that TNTs washed with HCl solution were significantly more active than TNTs washed with water. Recently, Costa et al. [53] reported a considerable photocatalytic activity of titanate nanotubes during degradation of indigo carmine dye, although it was lower than that of anatase TiO<sub>2</sub>. The inconsistencies in the reports on the photocatalytic activity of TNTs obtained by the hydrothermal method might result mainly from different precursors used (amorphous TiO<sub>2</sub>, anatase, rutile, mixture of both phases, such as P25, etc.) and reaction conditions applied (temperature, time, etc.). Another reason might be that the obtained product contained unreacted anatase phase, from which the sample gained the photocatalytic activity.

Recently, different attempts to improve the photoactivity of TNTs have been made. They include post-thermal treatment, post-hydrothermal treatment, acid modification and others [43]. The literature data on the influence of post-thermal treatment on the photoactivity of TNTs are rather limited. However, most of the already published results suggest that calcination of TNTs significantly improves their photoactivity. For example, Lee et al. [54] found that TNTs with low sodium content calcinated at 300–600 °C exhibited high photoactivity towards decomposition of basic dye BV10; however, the reaction rate constants determined for P25 were higher. Qamar et al. [45] reported that titanate nanotubes calcinated at 500 °C were almost as active as P25 during photodecomposition of amaranth. According to Yu et al. [44] TNTs calcinated at 400 and 500 °C exhibited much higher activity towards degradation of acetone in air than P25.

Taking into consideration all the above-mentioned inconsistencies it seems to be important to continue the investigations on the photocatalytic properties of TNTs and products of their calcination. The presented research has been focused on the verification of the literature data concerning photocatalytic activity of the as-received TNTs and TNTs modified by post-thermal treatment. During the first part of the studies the thermal modification of titanate nanotubes obtained from TiO<sub>2</sub> P25 by hydrothermal method was conducted. The effect of different calcination temperatures on the photocatalytic activity of the temperature modified samples towards degradation of model azo dye Acid Red 18 (AR18) was investigated and compared to that of P25. In the second part of

the research the effectiveness of the removal of AR18 from water in the photocatalytic membrane reactor coupling photocatalysis and MD was investigated. The effect of catalyst loading on the degradation rate of the dye and the permeate quality was especially determined.

## 2. Materials and methods

### 2.1. Preparation of TNTs

#### 2.1.1. As-received TNTs

TNTs were synthesized using the hydrothermal method reported for the first time by Kasuga et al. [41,42], and later developed by others [43–57]. The main differences between the procedures used are the substrate type and concentration, NaOH and HCl concentrations, reactor volume as well as reaction time and temperature. However, the overall idea of the hydrothermal method is in every case similar to that presented by Kasuga et al. [41,42]. The procedure applied in this study was as follows. Commercial TiO<sub>2</sub> P25 (Evonik, former Degussa, Germany) was used as a starting material for TNTs preparation. The P25 consists of 75% of anatase and 25% of rutile. The BET surface area of P25 is ca. 50 m<sup>2</sup>/g and the crystallite size of anatase is 25 nm (all data according to the manufacturer). 1.5 g of P25 was introduced to a Teflon-lined autoclave (70 cm<sup>3</sup>) containing 60 cm<sup>3</sup> 10 M NaOH. The suspension was ultrasonically treated for 1 h in order to allow good dispersion of TiO<sub>2</sub> particles in the reaction mixture. After that the autoclave was heated statically at 130 for 24 h. After the heat treatment the NaOH solution was decanted and the obtained precipitate was dispersed in 0.5 dm<sup>3</sup> of 0.1 M HCl. After 1 h the precipitate was separated from the HCl solution and dispersed again in 0.5 dm<sup>3</sup> of fresh 0.1 M HCl. After the next 2 h the precipitate was washed thoroughly with deionized water (Simplicity, Millipore) until the conductivity of washing solution reached the value of 1 μS/cm or less. Eventually, the precipitate was dried in air at 80 °C for 24 h. Such obtained titanate nanotubes were denoted later as “TNT-0”.

#### 2.1.2. Temperature modified TNTs

The as-received nanotubes (TNT-0) were calcinated in air for 1 h at different temperatures ranging from 400 to 700 °C (the samples are therefore denoted later as TNT400; TNT500; TNT600; TNT700). Heating rate was 10 °C/min. After calcination the samples were ground in an agate mortar and applied in the photocatalytic experiments.

### 2.2. Characterization of TNTs

Transmission electron microscopy (TEM) images were recorded using FEI Tecnai F20 microscope. Samples were prepared by dispersing the powder in acetone by ultrasonic treatment, and then dropping the suspension onto a copper grid (400 mesh). X-ray diffraction (XRD) analyses were performed using a powder diffractometer Philips X’Pert PRO (Cu Kα, 35 kV, 30 mA). TiO<sub>2</sub> anatase over rutile ratio was calculated from:

$$\text{anatase content } A = \frac{1}{1 + 1.26(I_R/I_A)} \quad (1)$$

where  $I_A$  and  $I_R$  are the diffraction intensities of the (101) anatase and (110) rutile crystalline phases at  $2\theta = 25.3^\circ$  and  $27.4^\circ$ , respectively. The average anatase crystallite diameter  $D$  (nm) was determined using the Scherrer’s equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where  $K = 0.9$  is a shape factor for spherical particles,  $\lambda$  is the wavelength of the incident radiation ( $\lambda = 1.54056 \text{ \AA}$ ),  $\theta$  is half of the

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