

# Decolorization of crystal violet over TiO<sub>2</sub> and TiO<sub>2</sub> doped with zirconia photocatalysts

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## Abstract

Titania based catalyst and TiO<sub>2</sub> doped with zirconia were prepared by modified sol-gel method. The synthesized catalysts samples were characterized by BET, XRD, SEM and FTIR techniques. Photocatalytic activity was tested in the reaction of crystal violet (CV) dye decolorization/decomposition under UV light irradiation. The effect of several operational parameters, such as catalyst dosage, initial dye concentrations, duration of UV irradiation treatment and number of reaction cycles were also considered. The obtained results indicated faster dye decolorization with the increase of the catalyst amount and a decrease of initial CV concentrations. An influence of doping with zirconia on the physico-chemical properties of bare titania was studied. The doping procedure had affected photocatalytic properties of the final catalytic material, and had improved photocatalytic performances of doped catalyst on crystal violet decolorization/degradation in comparison to bare titania.

**Keywords:** crystal violet, decolorization/degradation, doping, heterogeneous catalysts, process parameters, titania.

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Organic dyes present in water originate from textile and other industries may cause severe environmental damage and thus they are major ecological problem confronted by scientists nowadays [1]. Crystal violet is triphenylmethane dye that has been widely used in paper, leather and printing industry. It is toxic, has a mutagenic effect, which includes, but is not limited, to water organisms, and it is also considered to be cancerogenic [2,3].

Traditional methods such as thermal destruction, biodegradation and various adsorption processes are ineffective for removal of organic pollutants. Biological treatments take too much time; thermal treatments are energetically inefficient, while adsorption processes comprise mass transfers of reactants and/or products over interfaces [4].

Heterogeneous photocatalysis is one of the most promising (new) technologies for waste water treatments, especially if organic pollutants (dyes) are present [5]. Due to its many favourable properties, TiO<sub>2</sub> has many applications and it is one of the most commonly used photocatalysts in processes connected with environmental protection [1]. The catalyst is chemically and biologically inert, stable under a wide range of con-

ditions, noncorrosive, nontoxic and it has high activity [6]. Titania can be prepared by conventional sol-gel method, the process, which is relatively fast and cost-effective, and simultaneously it produces a catalyst characterized with favourable properties [7].

It has been reported that doping of titania with a variety of transition metals and/or their oxides results in surface modification and formation of crystal defects, which can lead to significant improvement in its photocatalytic properties. Zirconia has been successfully used for titania doping, which can be ascribed to the fact that both original elements belong to the same group of elements [8], therefore, their tetravalent cations have comparable atomic radii. In addition, relevant oxides of both original elements (TiO<sub>2</sub> and ZrO<sub>2</sub>) are *n*-type semiconductors with similar physico-chemical properties, which probably lead to their interaction during catalyst preparation [9].

To the best of our knowledge, there are no studies reporting the identical synthesis of titania doped with zirconium/zirconia *via* somewhat modified sol-gel method using zirconium(IV) oxychloride octahydrate as a precursor. There are very few studies [7,8,10,11] investigating an influence of zirconia/zirconium doping on physicochemical properties and catalyst activity of titania, and only a small number of papers [7,8,11,12] investigating photocatalytic reactions of degradation/decolorization of the organic dyes. The authors did not find any earlier study of crystal violet degradation over zirconia-doped-titania. The investigations conducted within this study have demonstrated that doping pro-

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cedure of prepared support/titania has a significant influence on the photocatalytic properties of the final material. Therefore, the obtained results can be significantly different than those published in earlier studies [4,7,9,10].

The present study reports economical and environmentally friendly method for obtaining TiO<sub>2</sub>-based powders by using modified sol-gel method. Additionally, the influence of surface doping with zirconia on physicochemical properties (and activity) of bare titania was observed. Decolorization of cationic dye crystal violet under UV-A light irradiation was used as a test reaction for the purpose of investigating the activity of catalysts. In addition, impacts of several process parameters on the photocatalytic performance of the bare TiO<sub>2</sub> and TiO<sub>2</sub> doped with zirconia were studied, including catalyst dosage, duration of irradiation treatment and initial dye concentrations, as well as number of reaction cycles.

It is important to note that no earlier identical study was conducted concerning the precursor of titania, zirconia precursor, molar ratio of titania to zirconia used as dopant, calcinations temperatures, preparation methods, and tested organic pollutants in model watery solutions. Therefore, there are no completely identical reported and discussed results on physicochemical properties of these photocatalysts and their resulted catalytic performances in the scientific literature [4,7–12].

## EXPERIMENTAL

### Catalyst preparation

#### *Synthesis of TiO<sub>2</sub> nanopowder*

TiO<sub>2</sub>-based catalyst was synthesized *via* modified sol-gel technique using titanium isopropoxide (Aldrich Co.) as a precursor. Two solutions were made as described: the first solution was made by dissolving the measured amount/volume of titanium isopropoxide in 2-propanol according to stoichiometry under inert conditions. The second solution was made by mixing water and 2-propanol in volume ratio 1:3, and was added to the first solution drop by drop under vigorous stirring in nitrogen atmosphere for one hour. The amount of water was calculated so the mole ratio Ti:H<sub>2</sub>O was 1:6. pH of the resulting suspension was adjusted to 10 by use of NaOH. The obtained precipitate was filtered, washed with distilled water and finally with the mixture of isopropanol and water. After that, powder sample was dried at 105–110 °C for 3 h, and then calcined for additional 3 h at the temperature of 450 °C. Catalytic sample was heated to the desired temperature at a heating rate of 10 °C/min.

#### *Preparation of doped Zr<sub>x</sub>O<sub>y</sub>-TiO<sub>2</sub> catalyst*

Sample was doped with zirconium/zirconia by using ZrOCl<sub>2</sub>·8H<sub>2</sub>O (Sigma Aldrich, Co.) diluted in distilled water and impregnated onto the prepared TiO<sub>2</sub> powder in order to achieve nominal mole ratio TiO<sub>2</sub>:ZrOCl<sub>2</sub>·8H<sub>2</sub>O = 1:0.5 mol%. This nominal mole ratio was chosen in order to obtain (final) doped catalyst with acceptable amount of zirconium cations incorporated into titania crystal lattice that would positively affect crystal structure of bare titania, then reduce titania band gap, and thus improve total photocatalytic efficiency of bare titania. In such a way, the authors have tried to gain the improvements in terms of better photocatalytic performances by using relatively small dopant amounts simultaneously providing (more) environmental friendly and cost-effective process in comparison with other authors [7–9]. After drying for 3 h at 105 °C, doped sample was calcined at temperature 800 °C for 3 h, using the heating rate 10 °C/min.

### Catalyst characterization

In order to determine the specific surface area and pore system of the catalysts, Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used, respectively. X-Ray diffraction (XRD) method was used for characterization of the catalysts structure, and the surface morphology was estimated by scanning electron microscopy (SEM). Fourier transformed Infrared spectroscopy (FTIR) method was used for evaluation of catalysts surface properties, namely, the determination of Lewis (LAS) and Brønsted acid sites (BAS) as catalytically active sites.

BET surface area measurements were performed on a Micromeritics ASAP 2010 based on adsorption/desorption of liquid nitrogen at appropriate temperature and pressure (LTN<sub>2</sub>AD), with use of He as carrier gas, in order to determine specific surface area, pore volume and pore size/diameter of catalysts (TiO<sub>2</sub> and doped-TiO<sub>2</sub>). Average pore diameters and pore volumes were observed by using BJH method. Prior to measurements, all powder samples were degassed at temperature 250 °C, and pressure of 3×10<sup>-5</sup> mbar, for 4 h.

Crystallographic analysis was carried out on a Philips APD-1700 diffractometer using Cu-anticathode and monochromator in operating mode of 40 kV and 55 mA. Data were collected in the scan range of 2θ angles between 10 and 80° with the purpose of establishing crystalline phase of the samples. The average crystallite sizes were calculated by using the Scherrer equation [13]:

$$d = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where  $\lambda$  is the X-ray wavelength,  $K$  is constant 0.9,  $\beta$  is the peak width at half maximum, and  $\theta$  is the Bragg

angle. The weight fraction of anatase ( $W_A$ ) in the powder was calculated by the following equation developed by Spurr *et al.* [14,15]:

$$W_A = \frac{100}{1 + 1.265 \left( \frac{I_R}{I_A} \right)} \quad (2)$$

where  $I_A$  and  $I_R$  are the integrated peak intensities of the most intense peaks for anatase (101) and rutile (110), respectively.

The surface morphology and agglomeration level of the catalysts were investigated by the SEM JOEL JSM-6460LV scanning electron microscope. Sample preparation for imaging was carried out by coating with layer of gold, in order to achieve their conductivity. Operating conditions in the SEM imaging were: acceleration voltage 25 kV, 30 mA current at a working distance of 50 mm during 180 s. Magnifications were applied in the range from 10 to 200.000 $\times$ .

FTIR analysis was done after adsorption of pyridine. KBr pellet technique was used to prepare samples for FTIR spectra measurements before and after pyridine adsorption, which were recorded on a Win Bomem Easy spectrometer with 2 cm<sup>-1</sup> resolution. The scanning range was between 4000 and 400 cm<sup>-1</sup>.

#### Photocatalytic activity/reaction

In order to test photoactivity of the catalysts, decomposition of crystal violet dye was tested under irradiation of UV lamp (Roth Co., 16 W, 2.5 mW/cm<sup>2</sup>, 1.71 $\times 10^4$  Lux) (with maximum emission at wavelength 366 nm). The UV lamp was located at a distance of 10 cm from the reaction solution, which was magnetically stirred during the experiments with a constant speed. Dye solution volume was 10 ml placed in quartz reaction tube of 30 mm diameter covered with 0.5 mm thick quartz disk-cover, and then irradiated with UV light.

Prior to the UV illumination, catalysts were mixed with crystal violet test-solution at constant stirring during 24 h in dark in order to establish adsorption-desorption equilibrium of the dye molecules onto the catalysts surface. This was performed with the purpose to avoid adsorption of dye on the catalysts surfaces during the photocatalytic reaction. After the mentioned period, additional fresh CV solution was added onto/over catalysts samples, and placed in dark for next 12 h; the adsorption process was completed when the dye concentration was not changed or it was slightly higher than in the test solution. This indicated that the catalysts surfaces were saturated with crystal violet dye prior to photocatalytic experiments, and consequently, the adsorption process was stopped.

The decolorization/decomposition process was monitored by measuring the absorption spectrum of the CV solution after phase separation using UV/Vis

spectrofotometer (Schimadzu Co.) and following maximum absorbance at  $\lambda_{\max} = 590$  nm. At specified time-intervals, aliquots were withdrawn from the solution, then centrifuged and filtrated prior to measuring.

## RESULTS AND DISCUSSION

### Catalyst characterization

#### Textural properties

The estimated BET surface area of titania catalyst sample was 34.3 m<sup>2</sup>/g (Table 1), which is slightly smaller than previously reported [16]. Doping of bare titania with zirconium-based compound (*i.e.*, zirconia) results in (somewhat) lower pore volume and smaller specific surface area. Considering the thermal treatment of doped catalyst at 800 °C, the decrease in specific surface area may be the result of particles sintering during calcination at elevated temperature(s). The other explanation can be in insufficient dispersion of zirconia, which can be incorporated as oxide (Zr<sub>x</sub>O<sub>y</sub>) or in ionic/atomic form. Zirconia grafting into bare titania has also resulted in the increase of mean pore diameter (Table 1).

Table 1. Textural properties of titania-based catalysts samples

| Sample   | Surface area<br>$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$ | Mean pore<br>diameter, nm | Pore volume<br>$\text{cm}^3 \text{g}^{-1}$ |
|--|---|---------------------------|--|
| TiO <sub>2</sub>                                 | 34.3  | 8.3                       | 0.075                                      |
| TiO <sub>2</sub> -Zr <sub>x</sub> O <sub>y</sub> | 10.1  | 28.9                      | 0.057                                      |

The nitrogen adsorption/desorption isotherm curves of titania and doped titania (TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub>) are shown in Figure 1a and b, respectively. Bare titania sample has exhibited typical s-shape behaviour of type IV sorption isotherm with a type H1 hysteresis loop, while doped titania sample has been characterized with the type IV sorption isotherm with a type H3 hysteresis loop according to IUPAC classification (Figure 1) [17,18].

These observations are typical for mesoporous materials. The observed hysteresis loop also indicates the presence of mostly cylindrical shapes of pores in the bare titania, while doped titania has cracks-like or conical pores. The differences in textural properties (specific surface area, pore volume, pore shape) affect the catalyst activity in the test reaction. The isotherm of the doped catalytic sample calcined at 800 °C has been shifted downward, and the hysteresis loop has been shifted to higher relative pressure. Both of these changes result in a decrease of BET surface area from 34.3 m<sup>2</sup>/g for TiO<sub>2</sub> to 10.1 m<sup>2</sup>/g for TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub>.

Figure 2 shows the pore size distribution of titania-based catalytic samples. The bimodal distribution of pore sizes in the case of bare titania sample shows that

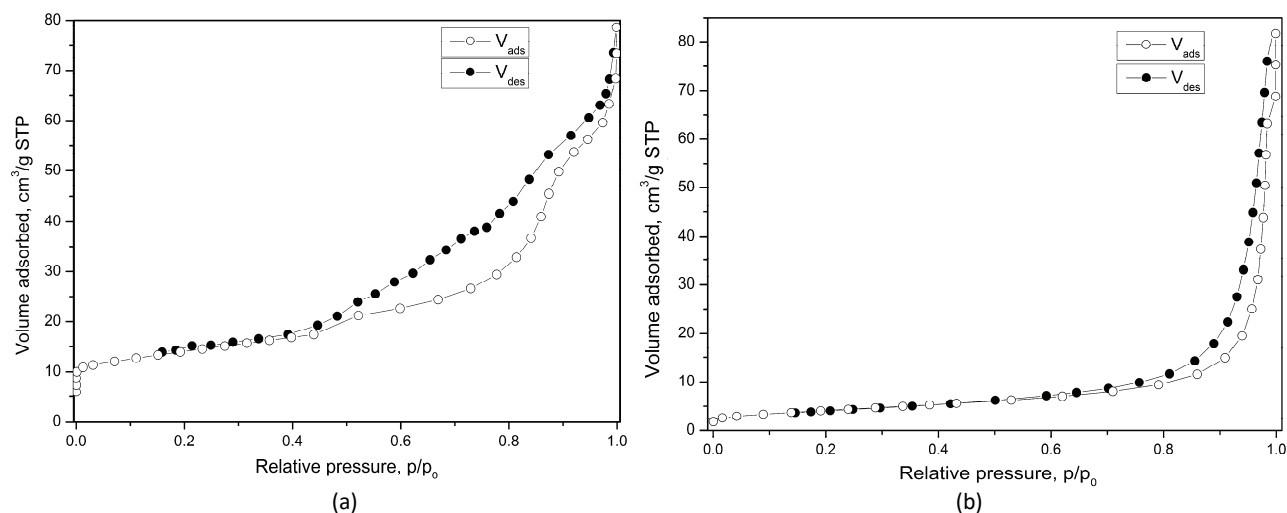


Figure 1. N<sub>2</sub> adsorption–desorption isotherm for: a) TiO<sub>2</sub>, b) TiO<sub>2</sub>–Zr<sub>x</sub>O<sub>y</sub>.

TiO<sub>2</sub> sample possesses two types of pores: micropores or pores at (near-edge) micro–meso pore boundary, and typical mesopores characterized with average/mean pore diameter of about 8 nm (Figure 2a). The doped titania catalytic sample is characterized with atypical bimodal or multi-modal distribution of pore sizes. Consequently, the catalytic sample TiO<sub>2</sub>–Zr<sub>x</sub>O<sub>y</sub> has at least two different pore sizes: micropores probably presented as interstices among titania primary crystallites, and mesopores characterized with mean pore diameter of 45 nm probably associated with interstices among secondary crystallites and poorly dispersed dopant (Figure 2b). It is important to note that somewhat higher volume of mesopores characterized with greater average pore size has been observed in the case of the doped titania.

#### Structural properties

Figure 3 shows XRD patterns of the bare titania and titania doped with zirconia and the effect of the doping and calcination temperatures applied on the crystal phase structure of prepared catalytic materials. The all diffraction peaks of bare titania are characteristic of anatase crystal phase (Figure 3a). However, the XRD pattern of doped titania sample (calcined at 800 °C) shows peaks characteristic of both anatase and rutile phases, and for a fraction of probably brookite titania phase and/or monoclinic zirconia phase (Fig. 3b). The authors were not able to identify few peaks of relatively small intensities appearing after doping of titania powder sample. The increase of calcination temperature and incorporation of dopant improve the crystalline structure of the photocatalyst (stronger and sharper peaks in doped titania sample) (Fig. 3). This indicates anatase-to-rutile phase transformation and formation of larger crystallites sizes (Table 2).

Doping procedure and application of increased calcination temperature decreases the volume fraction

of anatase crystal phase from 100% (in bare TiO<sub>2</sub>) to about 41.2% (in TiO<sub>2</sub>–Zr<sub>x</sub>O<sub>y</sub>), while increasing the size of the anatase phase crystallite from 25.06 nm (TiO<sub>2</sub>) to 40.66 nm (TiO<sub>2</sub>–Zr<sub>x</sub>O<sub>y</sub>, Table 2).

Table 2. XRD results of titania-based catalysts samples

| Sample   | $d_A$ / nm | $d_R$ / nm | $W_A$ / % | $W_R$ / % |
|--|------------|------------|-----------|-----------|
| TiO <sub>2</sub>                                 | 25.06      | –          | 100       | –         |
| TiO <sub>2</sub> –Zr <sub>x</sub> O <sub>y</sub> | 40.66      | 44.94      | 41.2      | 58.8      |

Early research into the subject indicated that photocatalytic activity was related to the existence of the single anatase titania crystal phase [19], but following studies point out to the importance of both anatase and rutile crystal phase for photocatalytic activity of the titania-based materials [20–22]. A group of authors reported that a mixture of anatase, rutile and brookite crystal phases exhibits higher photocatalytic activity than single anatase phase [23].

In this study, the registered presence of titania mixed crystal phases and higher crystallization degree after doping together with other improved physico-chemical properties is expected to ensure high/higher photocatalytic activity when used in the reaction of CV dye degradation.

Taking in mind that ionic radius of Zr<sup>4+</sup> (72 pm) is larger than the same one of Ti<sup>4+</sup> (53 pm) [24], it is expected that doping Zr<sup>4+</sup> would replace the lattice Ti<sup>4+</sup> in substitutional mode. This results in a shift of XRD peaks to somewhat lower diffraction angles in comparison to bare titania (Figure 3).

#### Morphological properties

Figure 4 shows the SEM images of the catalysts samples. The SEM image of bare titania catalytic sample shows typical spherical morphology consisting of primary particles of up to 100 nm in size. Porosity of

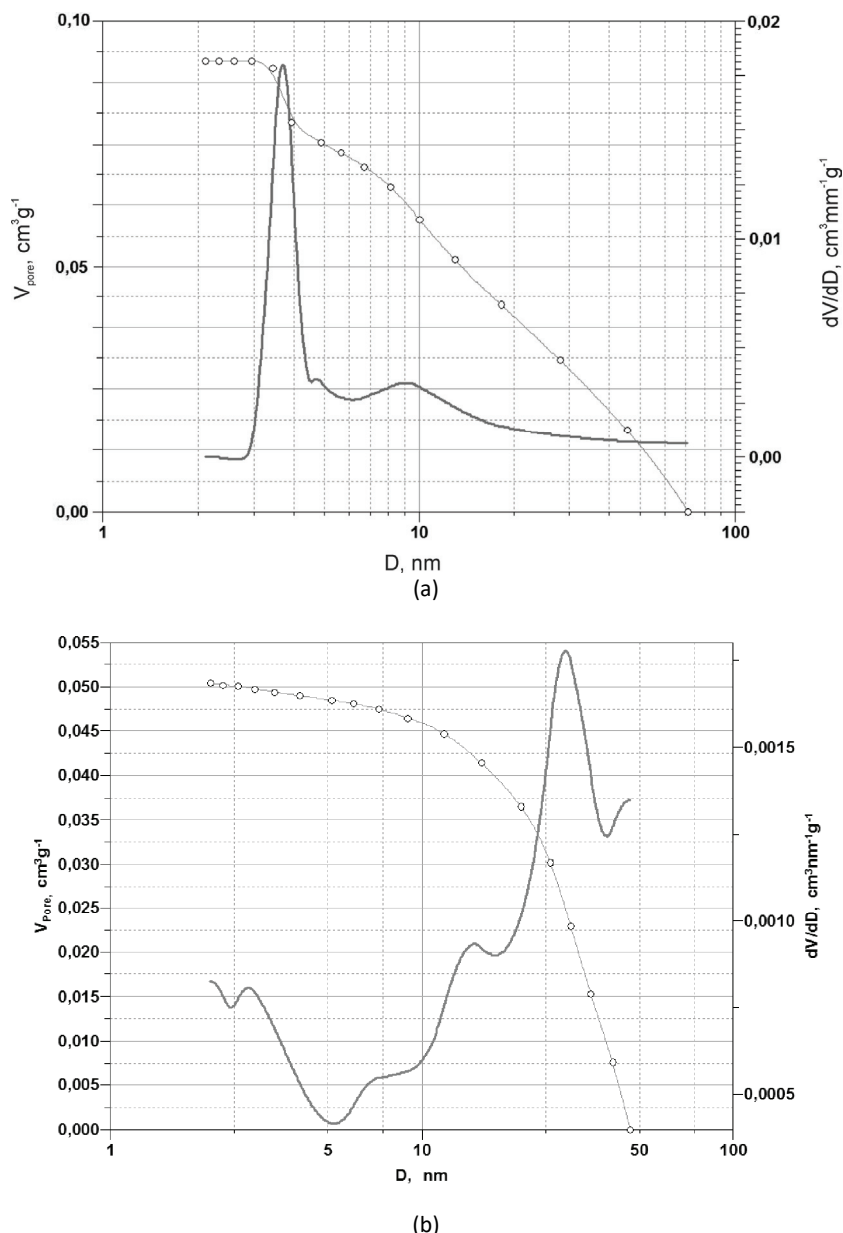


Figure 2. Pore size distribution for: a)  $\text{TiO}_2$ , b)  $\text{TiO}_2\text{-Zr}_x\text{O}_y$ .

bare titania is easily observed (Figure 4a). After doping of bare titania and calcination at 800 °C, the morphology of the (nano)particles is changed. Morphology of doped titania ( $\text{TiO}_2\text{-Zr}_x\text{O}_y$ ) is similar to rhombic structure with porosity, which is difficult to observe (Figure 4b). This phenomenon can be related with a noticeable growth of probably both titania and titania doped with zirconia/zirconium crystallites after calcination at 800 °C.

#### Surface properties

In Figure 5, FTIR spectra of bare titania and doped titania after pyridine adsorption/physorption are presented. The peaks for Lewis acid sites at around 1624, 1587 and 1438  $\text{cm}^{-1}$  are present, along with peaks for Brønsted acid sites at around 1540  $\text{cm}^{-1}$ . The band at

1540  $\text{cm}^{-1}$ , which is the characteristic band of pyridinium cation is formed as a result of pyridine interaction with Brønsted acid sites (Figure 5a).

According to FTIR spectra the surface of the catalytic sample of doped titania is characterized with (somewhat) increased intensity of the LAS at 1438, 1587 and 1626  $\text{cm}^{-1}$  compared with counterpart bands of the bare titania, which point out to a slightly greater number(s) of the Lewis acid sites on the surface of doped titania (Figure 5b).

Bands around 1540  $\text{cm}^{-1}$  in both catalytic samples have similar intensity, so both catalyst samples probably possess similar/comparable number of Brønsted acid sites. Broad adsorption band around 3423  $\text{cm}^{-1}$  is

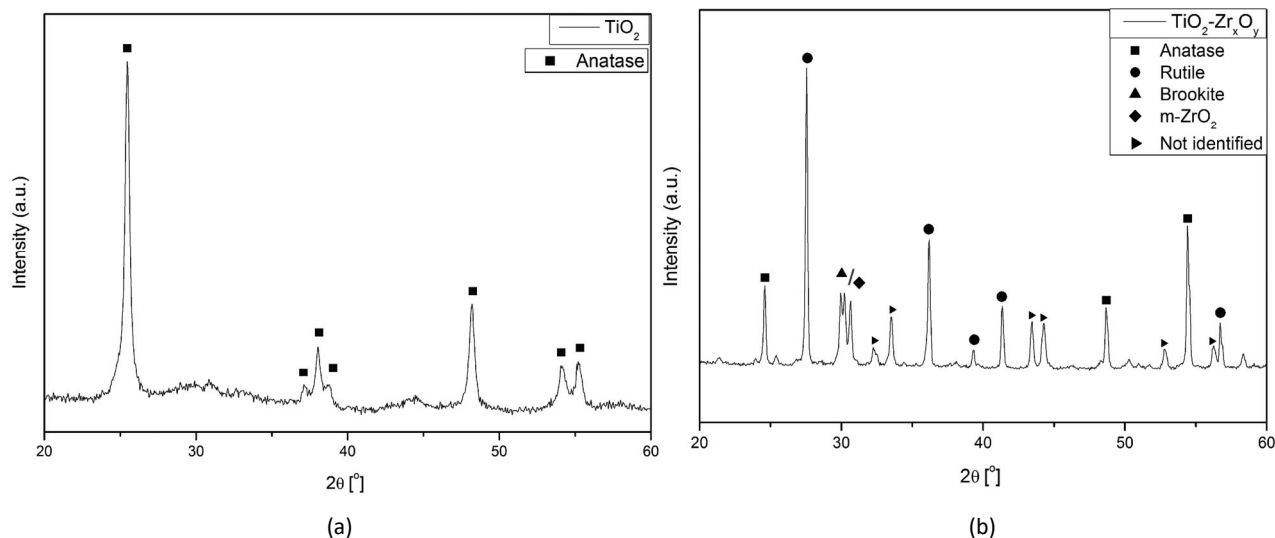
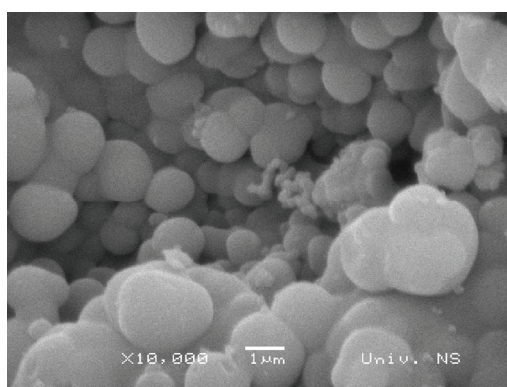
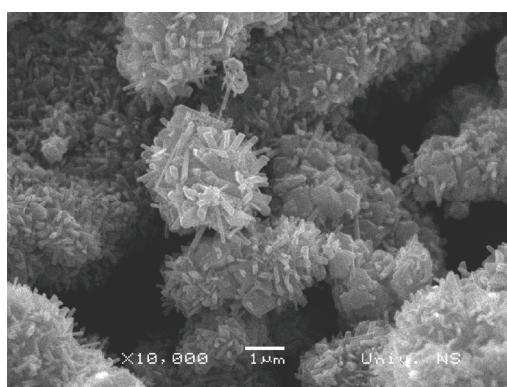


Figure 3. XRD patterns of the a) TiO<sub>2</sub> and b) TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub> samples.



(a)



(b)

Figure 4. SEM micrographs of catalyst samples: a) TiO<sub>2</sub> and b) TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub>.

present in both samples. This band originates from the stretching vibration of titania surface hydroxide groups and molecularly adsorbed water and can also act as a weak surface catalytically active site. A band characteristic of pyridine hydration at around 1120 cm<sup>-1</sup> specific for the hydrated titania anatase crystal phase is present

in both samples, but has a higher intensity in the case of doped titania.

### The photocatalysts activity

#### Dopant impact

Bare titania catalyst has shown a high activity after CV degradation time of around 20 h under relatively mild conditions (low UV radiation energy, unmodified/natural pH) (Figure 6).

Favourable titania photocatalytic activity can be ascribed to acceptable BET specific surface area and pore volume, the presence of highly catalytically active titania anatase crystal phase, and total surface acidity. The photocatalytic degradation of the CV is increased over zirconia-doped titania because of the improved physicochemical properties, and enriched mechanism of CV decolorization/degradation process compared to bare titania. Namely, the doped titania is characterized with bimodal/multimodal distribution of pore sizes in comparison to (bi)modal-pore size distribution in the case of the bare titania. Bimodal/multimodal pore size distribution can enable the reactants to more easily reach the catalytically active sites. In addition, sufficiently large pore volume facilitates an easier transport of reactants to the catalytically active sites, and diffusion of the products back to the reaction mixture.

The authors additionally predict similarly to other authors that better crystallinity of the doped titania [25], and presence of titania mixed crystal phases [20–23] should positively affect catalytic efficiency of the doped titania. Moreover, greater total acidity of the surface of the doped titania TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub> can improve catalytic ability of the catalytic material [26–29] in the process of the photocatalytic degradation/decolorization of CV.

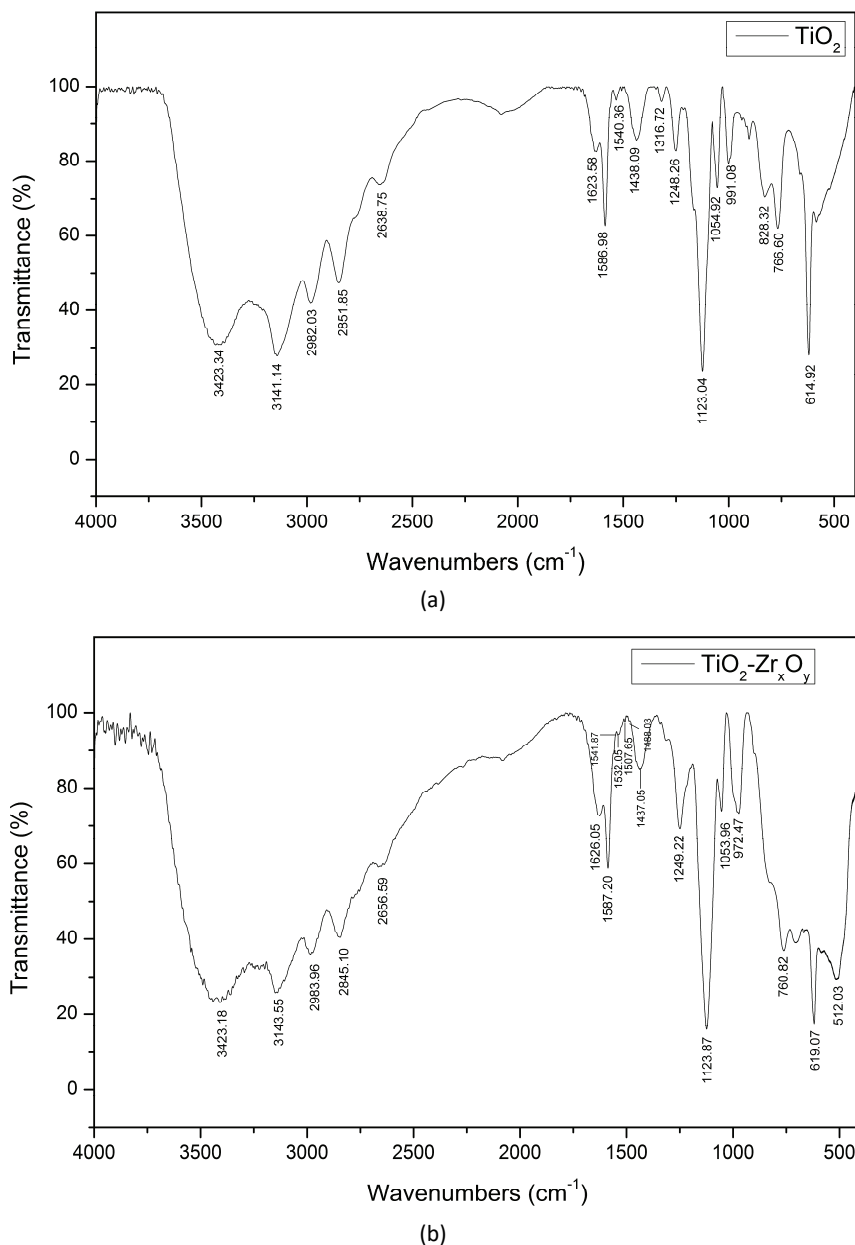


Figure 5. FTIR spectra of catalyst samples: a) TiO<sub>2</sub> and b) TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub>.

Moreover, photocatalytic decolorization of CV over doped titania photocatalysts undergoes to improved process mechanism. The incorporation of doping Zr<sup>4+</sup> in bare titania can generate (additional) formation of O<sub>2</sub><sup>-•</sup> and <sup>•</sup>OH that can take part in the successive photocatalytic (sub)reactions in the effective CV decolorization. The introduction of sufficient amount of doping Zr<sup>4+</sup> in titania lattice can restrict the recombination rate of photogenerated electrons and holes thus enhancing the photocatalytic efficiency of bare titania.

#### *Influence of the catalysts dosage(s)*

The influence of catalysts dosage(s) (amounts from 0.030 to 0.075 g) on the CV degradation process is shown in Figure 7. It is noticed that concentrations of

the selected dye have decreased with the increase of the catalysts amounts when both bare and doped TiO<sub>2</sub> catalysts were used (Figures 7a and b). Greater amounts of catalysts in the case of both catalysts mean that there are greater numbers of catalytically active sites as well as greater numbers of adsorbed photons that may result in the enhanced photocatalytic activity.

#### *Influence of initial concentrations of the selected dye*

The effect of initial concentrations of the selected dye was investigated by varying the initial concentrations of the CV from 0.0075 to 0.0100 mmol/dm<sup>3</sup> with the constant catalyst loading of 0.05 g and at pH between 6.7 and 7.0. As shown in Figure 8a and b, the photocatalytic efficiencies have increased with decreases

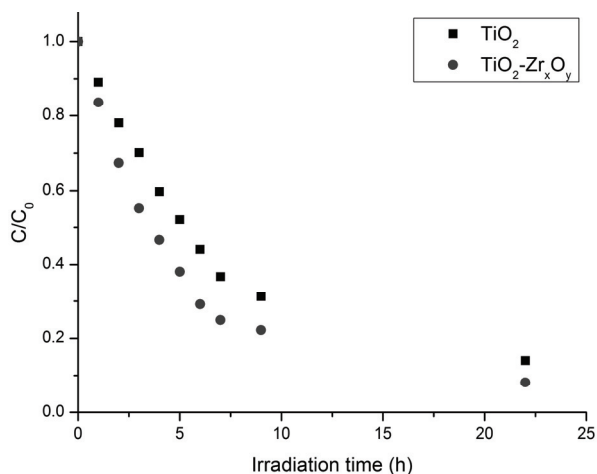


Figure 6. Comparison of degradation rate for the decomposition of crystal violet dye under bare TiO<sub>2</sub> and doped TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub> (experimental conditions: catalyst amounts 0.05 g, initial dye concentration 0.01 mmol/dm<sup>3</sup>, pH 6.7–7.0).

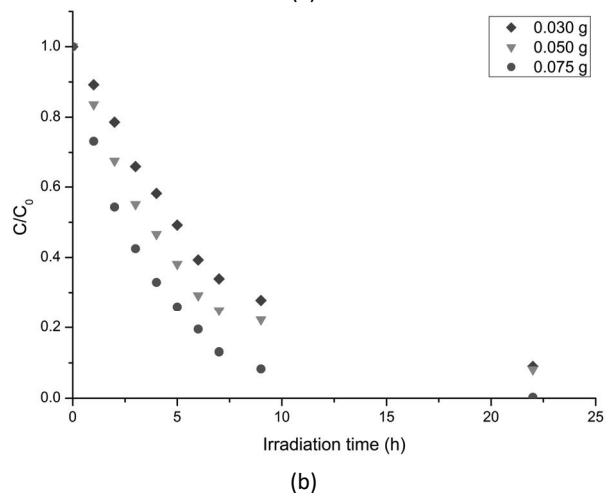
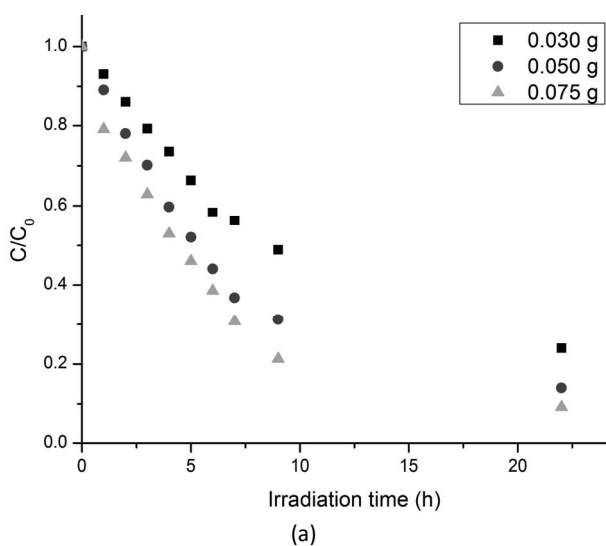


Figure 7. Influence of the catalyst amount: a) bare TiO<sub>2</sub> and b) doped titania, TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub>, on the photodegradation rate/level for the decomposition of crystal violet dye (experimental condition: initial dye concentration 0.01 mmol/dm<sup>3</sup>, pH 6.7–7.0).

of dye concentrations in the tested solutions for both bare and doped TiO<sub>2</sub> powders-catalysts. When the initial concentration of the model pollutant was sufficiently low (the lowest initial concentration of the CV, 0.005 mmol/dm<sup>3</sup>), the CV was completely degraded after photocatalytic run of 16 h at relatively mild conditions of the UV irradiation when bare TiO<sub>2</sub> catalyst was used (Figure 8a); the organic CV dye was degraded during shorter photocatalytic reaction-run when doped catalytic sample TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub> was applied (Figure 8b). With the increase of initial CV concentrations, the levels of photocatalytic degradations over both titania and doped titania decreased (Figure 8a and b).

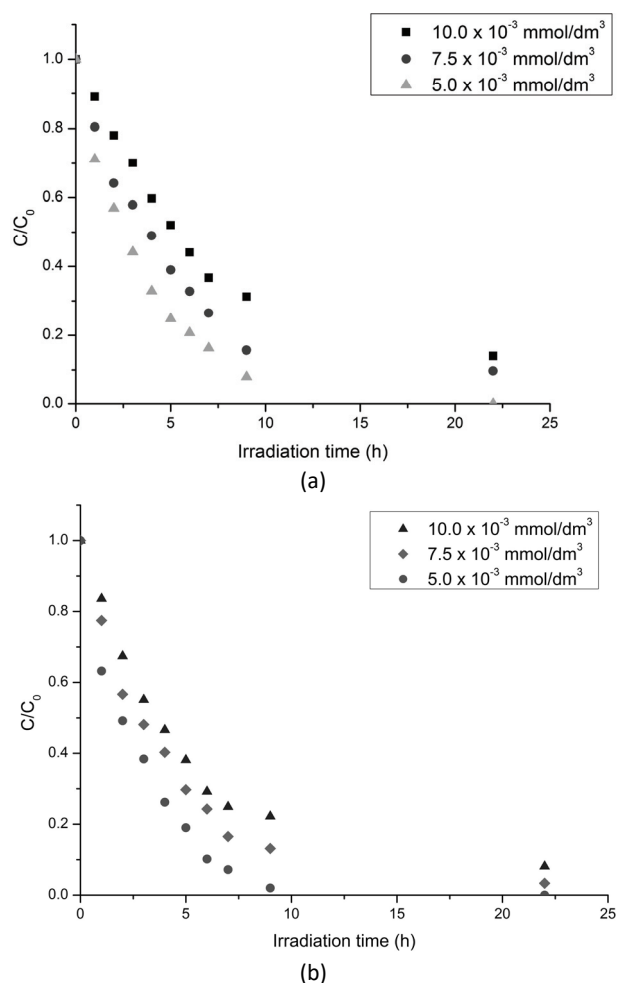


Figure 8. Influence of initial dye concentration on the photodegradation rate/level for the decomposition of crystal violet: a) bare TiO<sub>2</sub> and b) doped titania, TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub> (experimental conditions: catalyst amounts 0.05 g, pH 6.7–7.0).

These observations can be related to: the increases in optical densities of the CV dye solutions with the increases of the dye concentrations, and potential restricts for/to UV irradiation penetrations to the catalysts surfaces (bare and doped titania catalysts) and



throughout the test-solutions that consequently may decrease photocatalytic efficiencies [30,31].

In all the performed photocatalytic runs, the pH of the solutions was between 6.7 and 7.0. Considering that titania is amphoteric and that its zero point charge is at 5.9 [32], the authors predict that the electrostatic attractions between cationic CV dye and negatively charged catalyst surfaces under the applied experimental conditions were driving forces to support the adsorption process of the organic dye and to facilitate further photocatalytic process.

#### Catalyst(s) reuse(s)

In order to test the photocatalytic efficiencies of both catalysts bare and doped titania under long run working conditions, the decolorizations/degradations of CV were studied in repeated cycles without cleaning (pre)treatments of the used catalysts. The relevant kinetic curves of CV decolorizations are shown in Figure 9a and b. It is noticeable, by comparing the first and the third kinetic cycle, that photocatalytic efficiency of bare titania is not significantly reduced under long run working conditions. This phenomenon is especially pronounced in the case of the application of the titania doped with zirconia (Figure 9b), which can be used as promising cost-effective and environmental friendly catalyst.

dosages and original pH value). The obtained results have indicated that physico-chemical properties of pure titania were significantly influenced by doping with zirconia. As a result, doped catalyst had significantly higher photocatalytic activity in decomposition of crystal violet.

It can be concluded that the achieved bimodal/multimodal distribution of pore sizes as well as higher amount of greater mesopores in size in the case of the doped titania (TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub>) resulted in greater photocatalytic activity in the reaction(s) of the selected organic dye (CV) degradation and/or decolorization. In addition, the presence of mixed crystal phases (anatase, rutile and/or brookite) and improved crystalline structure, as well as (somewhat) greater total surface acidity in the case of doped titania can also be related to more effective photocatalytic activity compared with bare titania sample.

The results of process parameters variations showed higher degrees of dye decolorizations with the increases of catalysts dosages and decreases of initial CV concentrations for both bare and doped catalysts samples. Longer reaction-runs of photocatalytic processes provided higher levels of CV decolorizations/degradations over both bare and titania doped with zirconia catalysts. The studied bare titania and titania

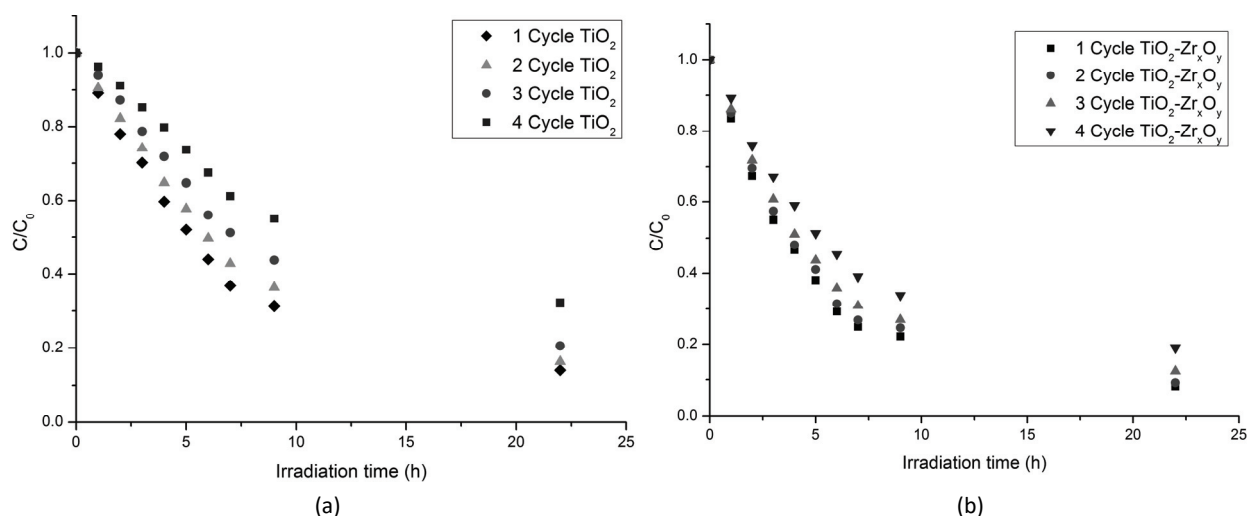


Figure 9. Reuse(s) of catalysts: a) bare TiO<sub>2</sub> and b) doped titania, TiO<sub>2</sub>-Zr<sub>x</sub>O<sub>y</sub> (experimental conditions: catalyst amounts 0.05 g, initial dye concentration 0.01 mmol/dm<sup>3</sup>, pH 6.7–7.0).

## CONCLUSIONS

Modified sol-gel method was used as relatively simple procedure for preparing titania and titania doped with zirconia nanostructured materials as promising photocatalysts. The photocatalytic efficiencies of both catalysts were tested for degradation/decolorization of CV dye, under relatively mild operational conditions (low UV irradiation energy, small catalysts

doped with zirconia can be (re)used in long run working conditions as promising cost-effective and environmental friendly catalysts.

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## IZVOD

### DEKOLORIZACIJA KRISTAL VIOLET BOJE NA TiO<sub>2</sub> I CIRKONIJUM(IV)-OKSIDOM DOPIRANOM TiO<sub>2</sub> FOTOKATALIZATORU

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(Naučni rad)

Katalizatori na bazi TiO<sub>2</sub> i TiO<sub>2</sub> dopiran cirkonijum(IV)-oksidom pripremljeni/sintetisani su modifikovanom sol–gel metodom. Karakterizacija sintetisanih katalizatora izvršena je BET, XRD, SEM i FTIR tehnikama. Fotokatalitička aktivnost katalizatora testirana je u reakciji dekolozacije/degradacije kristal violet (KV) boje pod dejstvom UV zračenja. Ispitivani su efekti procesnih parametara, kao što su uticaj količine katalizatora, inicijalne koncentracije boje, dužine trajanja UV tretmana i broj reakcionih ciklusa. Dobijeni rezultati ukazuju na to da se sa povećanjem količine katalizatora i smanjenjem inicijalne koncentracije KV boje povećava i brzina dekolozacije/razgradnje boje. Pored toga, proučavan je i uticaj dopiranja na fizičko–hemijske osobine titan(IV)-oksida. Dopiranje je imalo uticaj(a) na fotokatalitičke karakteristike finalno dobijenog materijala, kao i na poboljšanje fotokatalitičkih osobina dopiranog katalizatora u reakciji dekolozacije/ degradacije kristal violet boje u poređenju sa nedopiranim TiO<sub>2</sub>.

*Ključne reči:* Kristal violet • Dekolorizacija/degradacija • Dopiranje • Heterogeni katalizatori • Procesni parametri • Titan(IV)-oksid